Micro-Raman Spectroscopy Investigation of Hard Coatings

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Abstract: Micro-Raman Spectroscopy Investigation of Hard Coatings

Diamond, silicon carbide, and boron nitride have attracted great interest in the last years, due to their excellent material properties. Especially the extreme hardness and the high thermal conductivity of these materials favour them as protective layers. The very large hardness gave these materials, deposited as films on various substrates, their name: hard coatings. In contrast to diamond, silicon carbide and boron nitride can be n- as well as p-doped, making them promising candidates for high speed and high temperature electronic applications. Contrarily to the materials mentioned above, carbon nitride was obtained in crystalline form just very recently. Up to now the deposited films mainly consist of amorphous or nanocrystalline, carbon-rich material. For all these material systems inelastic light scattering (Raman spectroscopy) has been already applied for the material properties investigation. However, these investigations usually were restricted to only one of the various Raman spectroscopy tools, described in this work: Incident laser light energy variation, temperature variation, utilizing the selection rules, measurements at varying sample positions, two-dimensional mappings and one-dimensional scans in the conventional plane-view and the additional cross-sectional sample geometry. In contrast to this, this work demonstrates the improvement of the information about the investigated material and/or the sample heterostructure obtained by using the combination of all the above mentioned techniques. In the case of the diamond material system, films deposited on silicon substrates were investigated and an interfacial graphitic layer of 2nm thickness was found by scanning across the interface, which was obscured in the conventional plane-view sample geometry. Similar to this an ultra-thin top layer and buried intermixed regions were identified in the silicon carbide material system utilizing the cross-sectional sample geometry. In addition to this, the temperature and the incident laser light energy dependences for 5 SiC polytypes (3C, 4H, 6H, 15R, and 21R) were measured. A resonance enhancement for the 3C and the 21R polytype was found corresponding to their fundamental bandgaps at 2.46eV and ≈2.8eV, respectively. For the other polytypes no resonance enhancement was found, due to their larger fundamental bandgap. In the boron nitride material system the spatial correlation model for Raman lineshape analysis was applied for the first time and the values of the asymmetric broadening and the frequency downshift for decreasing crystal sizes were evaluated. This was measured for single crystals of different size and for films deposited on silicon substrates. The correlation lengths in the ten nanometer region found for the deposited films corroborate the nanocrystalline nature of these films. Additionally incident laser light energy was measured, revealing the 488.0nm (Ar⁺) and 482.5nm (Kr⁺) laser lines as the optimum laser lines for the boron nitride investigation. Furthermore the dependence of the phonon feature parameters was investigated depending on the incident laser light power. A maximum power of 5-10mW for the micro-Raman spectroscopy setup was found to avoid any laser light induced heating of the investigated material. Two-dimensional mappings of the deposited boron nitride films were performed to improve the information about the material system. In the case of carbon nitride for the first time distinct phonon features were measured in a wide spectral range contrarily to most of the other investigations, which usually show only broad bands.

keywords: Raman spectroscopy, two-dimensional mapping, cross-sectional scans, interface investigations, characterisation, wide-gap semiconductor, diamond, silicon carbide, boron nitride, carbon nitride
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Chapter 1

Introduction

"The universality of the phenomenon, the convenience of the experimental technique, and the simplicity of the spectra obtained enable the [Raman] effect to be used as an experimental aid to the solution of a wide range of problems in physics and chemistry. Indeed, it may be said that it is this fact which constitutes the principal significance of the effect. The frequency-differences determined from the spectra, the width and character of the lines appearing in them, and the intensity and state of polarization of the scattered radiations enable us to obtain an insight into the ultimate structure of the scattering substance.” C. Raman (1930)

These words of the effect discoverer [Ram28, Ram30] lost nothing of their significance until today. But still in the seventies they were considered quite sceptically since infrared absorption experiments were easier to perform and more useful for most of the measurements to be done. But with the propagation of improved lasers the Raman scattering gained an enormous popularity which resulted in a large number of experimental and theoretical works and persists until today.

This Raman effect means the inelastic scattering of light generally in the visible spectral range by elementary excitations in the material. These excitations are for example lattice oscillations (phonons), oscillations of a free electron plasma (plasmons), etc. The inelastic scattering is caused by the incident light, which excites electrons of the material electronic system and induces thus electron-hole pairs. The interaction of these electron-hole pairs with the elementary excitations generates a change in the energy state of the electron-hole pair, which results in a different energy of the light emitted by the recombining electron-hole pair. As a result, in the measured spectrum additional peaks (Raman features) appear in the vicinity of the elastically scattered light (typically in the hundred meV energy range). However, these additional Raman features in the spectra are very weak compared to the elastically scattered light and demand thus high incident light intensities, provided for example by lasers, and sophisticated spectrometer systems for distinguishing these features from the elastically scattered light. Due to the influence of varying material properties, i.e. crystal structure, elements forming the material, and crystalline quality, etc., on the phonon fea-
ture parameters, like intensity, full width at half maximum, and frequency position, Raman spectroscopy has a very high chemical sensitivity.

Apart from the chemical characterization of materials Raman spectroscopy opens several new fields of investigation. They arise due to the drastic decrease of the dimensions in modern electronic devices. Their properties strongly depend on the interface and surface characteristics between adjacent layers, since the formation of additional layers may occur due to intermixing and/or chemical reactivity, and the resulting interface structure can severely influence the growth mode of subsequent layers. As Raman spectroscopy generally utilizes incident light in the visible spectral range optical microscopes can be used to focus the light to the micrometer region (micro-Raman spectroscopy = μ-RS). This makes Raman spectroscopy a suitable method for the spatially resolved investigation of materials with micrometer dimensions. In combination with the high chemical sensitivity this enables the detection of additional layers formed in the layered heterosystem. Furthermore an additionally adapted moveable xy-stage, which allows 100nm steps in both directions, mounted under the microscope can be utilized to evaluate the homogeneity of the investigated material. Due to the influence of stress, temperature, crystallite size, stoichiometry, crystal modification, and others on the phonon frequencies these influences can be determined. If the sample holder is as well rotatable and the selection rules are taken into account the crystallite orientation can be investigated. As mentioned in the citation of C. Raman thus Raman spectroscopy is a versatile tool, for the investigation of the material properties. Because of the plane sample position under the microscope in most of the Raman spectroscopy investigations the used sample geometry is called the conventional plane-view sample geometry.

However, Raman spectroscopy as an optical spectroscopy method is not limited to the material surface. In contrary the whole range given by the light penetration depth at the incident light energy in the material contributes to the Raman spectrum. On the one hand, changing the excitation energy enables the investigation of the material with varying light penetration depths and thus information from different depths is revealed. On the other hand, this does not work if the penetration depth of the deposited material is much higher than the desired depth resolution for the incident light energy. In this case the entire material thickness is illuminated and thus the information is integrated over the full thickness. This prevents a depth-resolved discussion of the material. For that reason, an additional sample geometry was developed, for which the sample was turned onto its side. This permits the investigation of the layered sample heterostructure, if the xy-stage is used for one-dimensional scans across the heterostructure and the obtained phonon feature parameter variations (intensity, full width at half maximum, and energetic position) are discussed depending on the incident light beam position. A deconvolution of the obtained variations is demonstrated to confirm the existence of additional and buried layers in the nanometer region. This sample geometry is called cross-sectional Raman spectroscopy.

In this work several hard coating materials, like diamond, silicon carbide, boron nitride, and carbon nitride, are investigated using Raman spectroscopy. These materials have attracted great interest in the last few years due to their excellent material properties for high speed
and high temperature electronic applications: The hardness and the thermal conductivity are the highest known up to now and apart from diamond they can be n- as well as p-doped. The very high hardness of the materials additionally enables their application as protective coatings for, e.g. cutting tools. In the case of diamond, silicon carbide, and carbon nitride Raman spectroscopy is the most widely used optical characterization method. Nevertheless the Raman spectroscopy investigation of the silicon carbide material system mainly deals with only two, i.e. 3C-SiC and 6H-SiC, of over two hundred reported crystalline modifications. Since for carbon nitride only very recently crystalline deposits were produced only two publications up to now discuss the corresponding phonon features and thus Raman spectra in most publications only corroborate the amorphous or nanocrystalline, carbon rich nature of the deposits. In contrast to this for boron nitride Raman spectroscopy is rarely used, due to the very low scattering efficiency of this material system.

In comparison to most other publications, which utilize generally only one of the possible Raman spectroscopy tools described above, this work demonstrates the improvement of the information obtained about the deposit, if **all** possible Raman spectroscopy tools are combined for the investigation of the sample. For that purpose this work is divided into 6 chapters. The second chapter following this introduction describes the basics of Raman spectroscopy, the experimental and the different optical setups, and the theory for the simulation of the cross-sectional scans across the layered sample heterostructure. The third chapter describes the material systems investigated and the fourth chapter explains in a short overview the production of the investigated samples. In the fifth chapter the results are presented and discussed. The sixth chapter concludes the results.
Chapter 2

Raman Spectroscopy (RS)

This chapter gives an introduction to the theoretical basics of the phonon feature origins in the RS and the possibilities RS provides to determine several material properties like temperature, crystallinity, stress, etc. After the theoretical basics the experimental realization, the optical setups, and the sample geometries are discussed. Finally a short introduction to the confocal optical setup is given.

2.1 Theoretical Basics

The Raman effect is an inelastic light scattering process in which the incident light with momentum $h\mathbf{k}$ and energy $h\omega_i$ (i $\Delta$ incident) is modified by an interaction with elementary excitations of the matter leading to either an increase or a decrease of the scattered photon energy $(h\omega_s)$ as well as a momentum transfer to the matter. In this work the lattice vibrations (phonons) are the elementary excitation of interest described by their quasi-momentum $h\mathbf{q}$ and energies $h\Omega$. A Raman spectroscopy experiment yields the energies of the elementary excitations like phonons by analyzing the frequency positions of the scattered light. Taking the energy conservation into account one obtains

$$h\omega_s = h\omega_i \pm h\Omega$$

(2.1)

where the "−" sign stands for the generation of an elementary excitation and the annihilation of an elementary excitation is given by "+". The scattering processes are called Stokes and anti-Stokes process, respectively. Since in most Raman spectroscopy experiments the Stokes process is measured the positive frequency difference $\Delta\omega = \omega_i - \omega_s$ called Raman shift is used.

Similar to the energy conservation the quasi-momentum conservation rule gives a relation between the incident $\mathbf{k}_s$ and the scattered light momentum $\mathbf{k}_s$ and the quasi-momentum of the elementary excitations $\mathbf{q}$:

$$\mathbf{k}_s = \mathbf{k} \pm \mathbf{q}$$

(2.2)
A backscattering geometry is utilized for all measurements resulting in momenta of the incident and the scattered light with opposite directions and thus the maximum momentum transfer to the system is given by $|q_{\text{max}}| \approx 2|k_i|$. However, in most Raman spectroscopy investigations the excitation light is in the visible spectral range for which the wavevector is approximately some 100 times smaller than the Brillouin zone edge ($\frac{2\pi}{a}$ with $a$ the lattice constant of the material) determining the maximum transferable momentum:

$$
\lambda_i = 5000\text{Å} \Rightarrow |k_i| = n\frac{2\pi}{\lambda_i} \approx 4 \cdot 10^5\text{cm}^{-1}
$$

$$
a = 5\text{Å} \Rightarrow |q_k| = \frac{\pi}{a} \approx 6 \cdot 10^7\text{cm}^{-1}
$$

with $n$ the refractive index of the investigated material (in this work generally between 2 and 4). Due to this the interaction is limited to the Brillouin zone center. The resulting phonon features in the Raman spectra have Lorentzian lineshapes [Bar72] with its natural full width at half maximum (FWHM) $\Gamma_0$, convoluted with the experimental resolution of the spectrometer [Tan80, Tan81]. This is visualized in figure 2.1a). Additionally, the effects of a distorted lattice b) and of a superstructure, e.g. polytypism, c) are shown. In the case of a disturbed lattice (figure 2.1b) the reduced space in the real lattice causes a weakening of the momentum conservation rule (eqn. (2.2)) in the reciprocal lattice, which leads to an asymmetric broadening of the phonon features. For the polytypism (figure 2.1c) the larger

![Figure 2.1](image-url)

Figure 2.1: Lower part of each point: Phonon dispersion relations for different lattices (undisturbed lattice a), disturbed lattice b), and polytypism c)). In the upper part of each point the resulting Raman spectrum is sketched.

of a disturbed lattice (figure 2.1b)) the reduced space in the real lattice causes a weakening of the momentum conservation rule (eqn. (2.2)) in the reciprocal lattice, which leads to an asymmetric broadening of the phonon features. For the polytypism (figure 2.1c)) the larger
periodicity in real space causes a reduction in the reciprocal space and thus of the Brillouin zone. As a result the phonon dispersion relation (PDR) contains more branches at \( q = 0 \). Because the momentum conservation rule is still fulfilled, this gives an increased number of measurable phonon features in the Raman spectrum. These effects on the Raman spectrum are discussed in further detail in the next sections and section 3.2.4.

The interaction of the incident electric field \( \mathbf{E} \) with the phonons as elementary excitations is mediated by the electron system of the investigated material, because the electronic inter- and intraband transitions define the susceptibility \( \chi \) in the visible spectral range. The polarization in the investigated material is given by

\[
\mathbf{P}(\omega_s) = \varepsilon_0 \chi(\omega_s, \omega_l) \mathbf{E}(\omega_l)
\]

with \( \mathbf{P}(\omega_s) \) the oscillating polarization which causes the scattered light wave, \( \varepsilon_0 \) the dielectric constant, and

\[
\mathbf{E}(\omega_l) = \mathbf{E}_0 e^{i(\omega_l t - k \cdot \mathbf{r})}
\]

the oscillating electric field with the amplitude \( \mathbf{E}_0 \) of the incident electromagnetic wave. Since the susceptibility is modulated by the elementary excitations the susceptibility tensor in equation (2.4) exhibits a frequency dependence and thus via the Fourier transformation a time dependence. The time dependence of the incident electrical field in equation (2.5) as well as of the susceptibility leads to a time dependent variation of the polarization, which induces modulated dipoles in the matter. These modulated dipoles emit the scattered light wave with a frequency \( \omega_s \) [Ric76, Pin83]. The time dependent susceptibility tensor can be expressed by a Taylor expansion of the tensor components \( \chi_{\alpha\beta}(\omega_s, \omega_l) \) in terms of the lattice deformation normal coordinates \( Q_j \) for the \( j \)th phonon mode. \( \alpha, \beta \) are the polarization vector directions of the scattered and the incident electric field, respectively. Using plane waves for the phonon modes

\[
Q_j = Q_{0j} e^{i\Omega_j t - 2\pi x \cdot q_j / \lambda}
\]

with \( \Omega_j \) the phonon frequency, \( Q_{0j} \) the amplitude, and \( q_j \) the quasi-momentum of the \( j \)th phonon mode, the susceptibility tensor components are given by:

\[
\chi_{\alpha\beta}(\omega_s, \omega_l) = \chi_{\alpha\beta}^0(\omega_l) + \sum_j Q_j \cdot \left( \frac{\partial \chi_{\alpha\beta}(\omega_l)}{\partial Q_j} \right) + \sum_{j,k} Q_j \cdot Q_k \cdot \frac{1}{2} \left( \frac{\partial^2 \chi_{\alpha\beta}(\omega_l)}{\partial Q_j \partial Q_k} \right) + \ldots .
\]

(2.7)

Additionally to the static susceptibility \( \chi_{\alpha\beta}^0(\omega_l) \) there are two terms given in equation (2.7) describing one- (first term) and two-phonon (second term) processes. In the case of the one-phonon process the energy of the scattered light photons is shifted by \( \Omega_j \). The two-phonon process leads to scattered photons with frequencies of \( \omega_s = \omega_l \pm (\Omega_j \pm \Omega_k) \). There are several additional phonon processes concerning influences by electric fields and deformation gradients, which are not listed here. For further details see [Ric76, Gue93, Ess96].
For a more detailed description of the Raman scattering process the microscopic quantum mechanical perturbation theory has to be used \cite{Pin83}. The Raman scattering process by phonons then can be described by three interactions \cite{Lou63, Bar72, Pin83}, which are visualized in figure 2.2. It should be mentioned, that the interaction of the phonons in the lattice

Figure 2.2: On the left hand side the Feynman graph of a Stokes and on the right hand side the Feynman graph of an anti-Stokes Raman process is given.

with the induced electron-hole pair can be performed for the electron as well as for the hole. Figure 2.2 only displays the electron-lattice interaction.

1. Photon-electronic system interaction: The incident photon induces an electronic transition from the ground state \( |0\rangle \) to an excited state \( |e_1\rangle \) inducing an electron-hole pair.

2. Electron-lattice or hole-lattice interaction: Due to the creation or annihilation of a phonon in the lattice with an energy of \( \hbar \Omega \) the excited state \( |e_1\rangle \) changes to \( |e_2\rangle \) with the energy of the excited state \( |e_2\rangle \) lower (Stokes process) or higher (anti-Stokes process) than that of the state \( |e_1\rangle \).

3. Electronic system-photon interaction: The electron-hole pair in the excited state \( |e_2\rangle \) recombines by emitting a photon with the energy \( \hbar \omega_s \).

The combination of these three interactions leads in third-order perturbation theory to \cite{Pin83}

\[
\chi_{\alpha\beta}(\omega_s, \omega_i) = \frac{e^2}{m_0^2 \omega_s^2 V} \sum_{e,f} \frac{\langle 0 | \hat{\rho}_\alpha | e_2 \rangle \langle e_2 | \hat{H}_{E-L} | e_1 \rangle \langle e_1 | \hat{\rho}_\beta | 0 \rangle}{(E_{e2} - \hbar \omega_s)(E_{e1} - \hbar \omega_i)} \tag{2.8}
\]

with \( m_0 \) the electron mass, \( V \) the scattering volume, \( \hat{\rho}_\alpha \) and \( \hat{\rho}_\beta \) the vector components of the dipole operators of the scattered and the incident light, respectively, and \( \hat{H}_{E-L} \) the Hamilton operator for the electron-lattice interaction. \( E_{e1} \) and \( E_{e2} \) in the denominator of equation (2.8) are the energies of the excited electron states. For higher order scattering as given by the second term in equation (2.7) additional terms of \( E_{e1} - \hbar \omega_i \) appear in the denominator \cite{Lou64, Car83, Pin83}. 
The Hamiltonian $\hat{H}_{E-L}$ in equation (2.8) describes the electron-lattice (hole-lattice) interactions given in equation (2.7). Since these interactions are caused by lattice deformations the corresponding scattering process is called deformation potential (DP) scattering. It can be applied for the longitudinal optical (LO) as well as the transversal optical (TO) phonon modes, in which longitudinal and transversal optical means an oscillating of the phonons parallel and perpendicular to the phonon quasi-momentum (see figure 2.3 [Bru82]). In contrast to materials like silicon or diamond, which are built only by one element, for binary materials, e.g. IV-IV-, III-V-compound semiconductors, polar bonding participates which induces an additional macroscopic electrical field $E_m$ for the LO phonon (see the right hand side of figure 2.3). Because of this field the degeneration of the LO and the TO phonons at $q=0$ is lifted and thus the LO phonon mode frequency at $q=0$ is higher than that of the TO phonons [Ana80, Bru82, Geu93]. This splitting of the LO and the TO phonon mode can be calculated by the Lyddane-Sachs-Teller relation [Bor66]. In addition, this macroscopic electrical field gives rise to light scattering, since it influences the electronic bandstructure. This leads to an additional scattering process via Fröhlich interaction giving rise to additional terms in equation (2.7) [Ric76, Geu93, Ess96].

Since the energy conservation rule (equation (2.1)) is valid only for the total scattering process in equation (2.8) the excited states $|e_1\rangle$ and $|e_2\rangle$ can be virtual and must not necessarily correspond to states in the real electronic band structure. If, on the other hand, the energies of the excited states ($E_{e1}$ and $E_{e2}$) corresponds to real states of the electronic bandstructure with the energy $\hbar\omega_0$, the oscillator strength of the dipole operators $p_\alpha$ and $p_\beta$ and thus the modulation of susceptibility increases drastically [Bar72, Car82] (see figure 2.4). This can be applied by using incident or scattered light energies in the vicinity of $E_{e1}$ or $E_{e2}$, respectively [Dre94], leading to an efficiency enhancement of the Raman scattering process.

![Figure 2.3: On the left hand side the polarization pattern for a TO and on the right hand side for a LO phonon mode is given [Bru82].](image-url)
2.1. THEORETICAL BASICS

Figure 2.4: The modulation $\Delta \chi$ for an incident light frequency ($\omega_1$) well away from an electronic transition and ($\omega_2$) in the vicinity of an electronic transition $\omega_{el}$.

by several orders of magnitude [Bar72, Ric76, Car82]. This effect is called resonant Raman scattering.

2.1.1 Raman Scattering Intensity

In equation (2.4) the interaction of the incident light with an elementary excitation was described inducing a dipole moment in the material. The power $dW$ emitted by a dipole into the solid angle $d\Omega$ is given by [Hee87]

$$dW = \frac{<\frac{d^2P}{dt^2}> \sin^2 \Theta}{16\pi \varepsilon_0 c^3} d\Omega$$

(2.9)

where the brackets stand for the time average, $\Theta$ for the angle between the dipole axis and the direction of emission, $\varepsilon_0$ for the permittivity ($\varepsilon_0 = 8.859 \times 10^{-12} \frac{F}{m}$), and $c$ for the speed of light ($c=2.998 \times 10^8 \frac{m}{s}$). Using equation (2.4) in its cosine form (see for example [Iba81]) and the time average of the cosine functions ($<\cos^2(\omega t)> = \frac{1}{2}$) the power $dW$ emitted by all dipoles in the illuminated volume $V$ can be calculated as given below [Car82, Ric76]

$$dW = \frac{|\chi|^2 V^2 \omega_0^4 P_i}{(4\pi \varepsilon_0)^2 c^4 A} d\Omega$$

(2.10)

with $P_i$ the incident power and $A$ the illuminated area on the sample surface. By replacing $\frac{V}{A}$ with the light penetration depth $d_{pen}$ using $V=d_{pen}A$ and transforming the equation (2.10) the Raman cross section

$$S = \frac{dW}{d_{pen} P_i d\Omega} = \frac{1}{(4\pi \varepsilon_0)^2 c^4 \omega_0^4 V} |\chi|^2$$

(2.11)
can be calculated. With this Raman cross section $S$ the scattering process in the sample is described and the relation

$$I \propto \omega_i^4 V |\mathbf{e}_s \cdot \mathbf{e}_i|^2$$

(2.12)

can be used to estimate the scattering intensity since the measured phonon feature intensity in a Raman spectroscopy experiment and the scattering intensity in the material differ only due to the monochromator transmittance and the chosen polarization configuration. $\mathbf{e}_s$ and $\mathbf{e}_i$ are the unit vectors of the scattered and the incident polarization, respectively, defining the polarization configuration. Equation (2.12) demonstrates the three significant dependencies in the measured Raman spectrum:

1. **The scattered light frequency $\omega_s$:** Since the scattered and the incident light frequency are correlated to each other by equation (2.1) in the case of one-phonon processes, the scattering intensity can be increased by increasing the laser light frequency. In the case of very weak scattered light intensities no longer analogous signals can be measured and thus photon counting has to be performed. Utilizing photon counting detection the scattering intensity is given by $N \omega_s$ with $N$ the number of detected photons. For that reason the scattering intensity follows a third power dependence on the incident light frequency. In addition, the susceptibility tensor $\chi$ depends dramatically on the chosen laser light frequency as demonstrated in the section above (see equation (2.8) and figure 2.4). By varying the incident light frequency this dependence can be used to investigate the inter- and intraband critical points of the electronic bandstructure [Ric76, Car82].

2. **The scattering volume $V$:** The light penetration depth in the material is determined by the absorption coefficient $\kappa$ and the wavelength of the incident light $\lambda_i$ [Iba81]

$$d_{\text{pen}} = \frac{\lambda_i}{2\kappa}$$  \hspace{1cm} (2.13)

This can be utilized to increase the scattering volume, as the light penetration depth generally increases with increasing $\lambda$. On the other hand, the dependence on the incident light energy discussed in point 1 is contrarily. With increasing $\lambda$, $\omega_i^4$ decreases drastically and thus no advantage can be gained. Moreover, in this work mainly materials are investigated with a large light penetration depth, which generally exceeds the deposited film thickness, thus limiting the increase of the light penetration depth. For that reason the sample was turned onto its side and the deposited material was investigated perpendicular to the layered structure. This results on the one hand in a scattering volume enhancement, which is sketched in figure 2.5 for a 5\,\mu m thick transparent film with a width of 5\,x\,5 mm$^2$. With an incident laser light beam focussed to a diameter of 1\,\mu m the scattering volume can be increased by a factor of 1000. Due to the large light penetration depth the whole width of the sample contributes to the spectrum and thus the scattering intensity is increased. Considering the left side of figure 2.5 the sample position is plane and thus this sample position is called **conventional plane-view sample geometry**. The right side displays the additional sample geometry used
in this work. This sample geometry is called **cross-sectional sample geometry**, due to the upright position of the sample. On the other hand the cross-sectional sample geometry enables a depth-resolved investigation of the layered sample heterostructure which cannot be performed with the plane-view sample geometry due to the large light penetration depth and thus the integral depth information of the sample. Moving the sample in the cross-sectional geometry under the focus enables the deconvolution of the position dependent variations and thus the depth-resolved investigation of the material [Zah96, Sch97, Got97].

3. **The chosen polarization configuration and the crystal symmetry e**$_{e}$$_{i}$$_{e}$: The susceptibility tensor $\chi$ in equation (2.12) is also called **Raman tensor**. Which components of these Raman tensors are non zero depends on the crystal system (tricline, monocline, trigonal, tetragonal, orthorhombic, hexagonal, and cubic) and the population of the crystal sites. Basing on this population the allowed vibrations in the crystal lattice and their symmetries can be determined. The corresponding Raman tensors are listed elsewhere for the different 32 point groups [Kuz89, Lou64]. Using the character tables for the different point groups (see for example [Dea72, Pou76, Kuz89]) the **irreducible representation** can be calculated with a group theoretical analysis [Kuz89]. Depending on their symmetry the phonon modes can be Raman and infrared active, either Raman or infrared active, or optically inactive. The optically inactive phonon modes only can be measured by inelastic neutron scattering [Kuz89]. The appearance of the Raman active phonon modes depends on the chosen polarization configuration. For the description of the polarization configuration and thus the relation between the sample and the laboratory coordinate system an easy notation was introduced by *S.P.S. Porto,*
the Porto notation [Dam66]:

$$\mathbf{k}(\mathbf{e}_i, \mathbf{e}_s) \mathbf{k}_s.$$ \hspace{1cm} (2.14)

The symbols inside the brackets describe, left to right, the polarization of the incident and the scattered light, while the ones to the left and right of the brackets are the propagation directions of the incident and of the scattered light, respectively. Due to the nature of the Raman tensor the occurrence of the LO and the TO depends on the choice of the incident and the scattered light polarization and the measurement geometry. The polarization selection rules are listed elsewhere in further detail [Lou64, Fel68a, Fel68b, Bar72, Geu93]. In this work a backscattering measurement geometry is used with the incident and the scattered light beam propagating parallel but with opposite direction in the crystal. Thus the observable TO and LO phonon modes oscillate perpendicular and parallel to the light propagation directions, respectively.

Due to these three points the experimental setup can be chosen in this way, that the scattering intensity of the interesting phonon features are of maximum intensity.

### 2.1.2 Phonon Peak Lineshape

In perfect crystalline samples with long-range periodicity of the lattice the distance a phonon can travel in the lattice is only limited by its lifetime (typical 10-100ps), since the optical phonons can be annihilated by a decay into two acoustical phonons with opposite quasi-momenta. With a velocity in the range of $10^3$-$10^4$ m/s the maximum distance varies between 10 and 1000nm. Due to the momentum selection rule (equation (2.2)) the Raman scattering process is limited to optical phonon modes near the Brillouin zone center ($q=0$) (see figure 2.1(a)). In this case the Raman lineshape for a phonon mode is given by a Lorentzian lineshape [Bar72]

$$I(\omega) \propto \frac{1}{(\omega - \Omega_0)^2 + \left(\frac{\Gamma_0(T)}{2}\right)^2}$$ \hspace{1cm} (2.15)

where $\Gamma_0(T)$ is the natural linewidth at temperature T and $\Omega_0$ the phonon mode frequency of the optical phonon at the Brillouin zone center. The natural linewidth is given by the reciprocal value of the lifetime $\tau$ of the phonon ($\Gamma_0 \propto \frac{1}{\tau}$).

When distortions are introduced into the material the size of the undisturbed regions decrease. This is shown in the figures 2.6 and 2.7, which give an array of atoms (open circles) in which 1%, 5%, and 10% of the atoms are randomly replaced by another sort of atoms (closed circles). Clearly the decreasing size of the undisturbed regions with increasing distortion percentage can be seen. Figure 2.7 shows the evaluation of similar distorted lattices as in figure 2.6. In contrast to figure 2.6 an array of 400x400 atoms was taken to improve the statistics. The x-axis gives the probability $P$ to find the next distortion in a distance $d$. This distance $d$ is given on the x-axis. The lines represent Gaussian fits to the obtained distributions. For clarification the calculated distribution itself are not plotted. The Gaussian fits are calculated
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Figure 2.6: The lattice of one sort of atoms (25x25 open circles) is disturbed by the randomly replacement by another sort of atoms (closed circles).

Figure 2.7: The probability $P$ to find the next distortion at a distance $d$ (in units of the lattice constant $a$). The lines give Gaussian fits to distributions calculated for different percentages of distortions in the lattice.
using the formula
\[ f(x) = A e^{-4\ln^2\left(\frac{x-c}{w}\right)} \]
with \( A \) the amplitude, \( c \) the center, and \( w \) the width of the distribution. The centers of the Gaussian fits give the average diameters of the undisturbed regions between two distortions in the distorted lattice. Clearly the decreasing distance and thus the decreasing diameter of the undisturbed regions with increasing percentage of distortions can be observed. This describes the confinement of the phonons in these regions, as they can travel only in the undisturbed lattice. The size of these regions can be understood as a "mean free path" or as a correlation length for the phonons. Additionally the FWHMs of the Gaussian fits are given. They represent the distribution of the undisturbed region sizes and thus the distribution of the correlation lengths in the lattice.

Since the phonon propagation is influenced by any disturbance like alloying [Jus81, Par84], defects (stacking faults, vacancies, foreign atoms, interstitials, etc.) [Shu70, Ric81, Cam86], and implantation [Tio84, Bra89, Yu89, Hua95] this phonon confinement was observed experimentally in many cases. The theoretical description of this phonon confinement is still under discussion [Age91, Hua95, Zi96, Wer97a]. In this work the so-called spatial correlation model will be discussed in more detail. At the end of this section the results of a recently introduced model given by Zi et al. [Zi96] are compared with the results of the spatial correlation model.

In an ideal crystal the wave function of a phonon with quasi momentum \( q_0 \) can be described by [Ric81, Cam86]
\[ \Phi(q_0, \mathbf{r}) = u(q_0, \mathbf{r}) e^{-i q_0 \cdot \mathbf{r}} \]  
where \( u(q_0, \mathbf{r}) \) are functions built by the Bloch functions, thus exhibiting the periodicity of the lattice \( u(q_0, \mathbf{r}) = u(q_0, \mathbf{r} + \mathbf{R}) \) [Wei89]. \( \mathbf{R} \) gives the real space lattice vector. After distortions are introduced, the phonon propagation is restricted to an undisturbed region (see figures 2.6 and 2.7). Although different geometries for this undisturbed region are proposed (spheres, columns, and sheets [Cam86]) in this work the sphere was chosen, because the distortions are randomly distributed in the 3-dimensional crystal and thus the average form of the remaining undisturbed spaces is a sphere.

The confinement changes the phonon wave function to [Shu70]
\[ \Psi(S, q_0, \mathbf{r}) = W(\mathbf{r}, S) \Phi(q_0, \mathbf{r}) \]
\[ = W(\mathbf{r}, S) u(q_0, \mathbf{r}) e^{-i q_0 \cdot \mathbf{r}} \]
\[ W(\mathbf{r}, S) = \Psi(S, q_0, \mathbf{r}) u(q_0, \mathbf{r}) \]
where \( W(\mathbf{r}, S) \) is the phonon weighting function in the real space with \( S \) the correlation length. The functional expression utilized as weighting function \( W(\mathbf{r}, S) \) has to fulfill the limit \( W(\mathbf{r}, S) = \text{const.} \) for \( S \rightarrow \infty \) [Cam86]. In this work a Gaussian function
\[ W(\mathbf{r}, S) = e^{-\alpha(\mathbf{r})^2} \]
for the weighting function \( W(\mathbf{r}, S) \) has been used, as proposed by Richter et al. [Ric81]. Up to now no theoretical calculations for the value \( \alpha \) were performed. Since it determines the
lineshape of the Gaussian function different empirical estimations were used. In the first paper about the spatial correlation model Richter et al. [Ric81] made the choice $\alpha = 2$, since it is the easiest form of a Gaussian distribution for the weighting function. This gives an amplitude of $\frac{1}{\sqrt{2}}$ at the boundary of the sphere. In contrast to this, Campbell and Fauchet [Cam86] and Huang et al. [Hua95] took $\alpha = 8\pi^2$, since for this choice the boundary condition changes to $\exp(-4\pi^2)$, which agrees better with their experimental data. A possible third choice would be $\alpha = 4\ln 2$, as demonstrated in figure 2.7. For this $\alpha$ value the boundary amplitude is 0.5, and thus the value of the correlation length $S$ coincides to the diameter of the undisturbed region in the real space. On the other hand, for the former two choices $S$ is either smaller ($\alpha = 2$) or larger than the diameter ($\alpha = 8\pi^2$). As a result, the correlation length $S$ obtained from the simulation of a measured Raman spectrum differs drastic. This

\begin{equation}
W(q, S) = e^{-8\pi^2 q^2 S^2}
\end{equation}

To calculate the effect on the Raman spectrum the $\Psi'(S, q, \ell)$ in equation (2.18) has to be
expanded in a Fourier series

\[ \Psi'(S, q_0, \mathbf{R}) = \int C(q_0, q) e^{-i\mathbf{q} \cdot \mathbf{r}} d^3q \]  

(2.21)

To obtain a relation between the phonon wavevector \( q \) and the entire Brillouin zone \((q)\), \( C(q_0, q) \) gives the Fourier coefficients determined by

\[ C(q_0, q) = \frac{1}{(2\pi)^3} \int \Psi'(S, q_0, \mathbf{R}) e^{i\mathbf{q} \cdot \mathbf{r}} d^3r \]  

(2.18)

\[ = \frac{1}{(2\pi)^3} \int W(S) e^{-i\mathbf{q} \cdot \mathbf{r}} e^{i\mathbf{q}_0 \cdot \mathbf{r}} d^3r \]  

(2.22)

Thus the wave function of a confined phonon is a superposition of plane waves with a wavevector \( q \) around \( q_0 \). Since RS in crystalline samples measures only the zone center phonons, \( q_0 \) is set to zero \((q_0=0)\). For the utilized Gaussian real space weighting function (equation (2.20)) the Fourier coefficients in equation (2.22) are

\[ |C(0, q)|^2 = e^{-\frac{q^2}{4r^2}} \]  

(2.23)

The Fourier coefficients describe the weighting function in the reciprocal space. When phonon confinement operates, the Lorentzian lineshapes of equation (2.17) weighted with equation (2.23) has to be integrated for all possible \( q \) in the Brillouin zone giving the lineshape of the Raman phonon mode

\[ I(\omega) \propto \int \frac{e^{-\frac{q^2}{4r^2}} \omega}{\left(\Omega(q) - \Omega(0)\right)^2 + \left(\frac{\Gamma_0(\Omega)}{2}\right)^2} dq \]  

(2.24)

where \( \Omega(q) \) is the one-dimensional PDR, which was demonstrated to provide a suitable approximation for the three-dimensional Brillouin zone integration [Age91], since the PDR can be assumed to behave similar in all three dimensions for cubic materials. This is a simplification which generally only holds for the Brillouin zone center and thus for larger correlation lengths. For smaller correlation lengths the differences in the phonon dispersion branches for the different crystal directions increase, which results in a modification of the obtained Raman lineshape. Nevertheless, it was demonstrated that the assumption of a one-dimensional phonon dispersion relation is able to simulate the measured Raman spectra very well also for nanocrystalline material [Wer97b]. The wavevector \( q \) and the correlation length \( S \) are expressed in units of \( \frac{2\pi}{a} \) and \( a \), respectively, with \( a \) being the lattice constant of the material. \( \Omega(q) \) is usually given as a polynomial regression of neutron scattering or theoretical data [Age91, Hua95, Wer97a]. Figure 2.9 shows in the upper part the PDR of cubic boron nitride calculated by Karch et al. [Kar96] and in the lower part the weighting functions of the reciprocal lattice given by equation (2.23) for five different correlation lengths (S=5, 10, 20, 50, and 100nm). Considering the broadening of the weighting functions in the lower part,
clearly the increasing participation of other regions than the Brillouin zone center can be observed for decreasing correlation lengths. The Raman lineshapes of the LO phonon mode calculated by equation (2.24) with these parameters are given in figure 2.10. Two changes with decreasing correlation lengths are obvious, i.e. the shift of the phonon feature maximum towards lower frequencies and the asymmetric broadening. The downward shift of the frequency position of the phonon feature maximum is caused by the decreasing LO branch given in the upper part of figure 2.9. This decreasing is observed for most of the known materials [Cam86, Age91, Hua95, Kar96, Wer97a]. In addition to the asymmetric broadening, a second maximum arises for very small S values. These changes are caused by the contribution of parts in the PDR with \( q \neq 0 \) to the Raman lineshape as can be judged from the lower part of figure 2.9. The asymmetric broadening thus originates from the superimposition of Lorentzian lineshapes given by equation (2.15), which are weighted with the coefficients of equation (2.23). In the case of \( S < a \) (with a the lattice constant of the material) the material
is amorphous and the coefficients are constant over the entire Brillouin zone

$$\lim_{S \to 0} C(0, q) = e^{-(\frac{\pi q}{S})^2} = 1$$  \hspace{1cm} (2.25)$$

The resulting Raman lineshape calculated by equation (2.24) represents the vibrational density of states of the material [Shu70, Bro83, Kar96]. Since in the Raman lineshape of disordered materials the whole PDR branch participates in the calculations, a critical dependence on the curvature of the PDR branch near the Brillouin zone center (\(|q| = 0\)) and the zone edge (\(|q| = q_{\text{max}}\)) is evident [Age91, Wer97a]. The gradients of the PDR branches at these points are zero (\(\nabla q = 0\)) and thus the phonon density of states has its maxima at these phonon frequencies creating additional features in the Raman spectra of highly disordered materials with \(S \approx a\) [Shu70, Bro83, Che94].

Recently Zi et al. [Zi96] have published, that the spatial correlation model, described above, cannot calculate the correct frequency shift of the phonon feature for nanometer sized material. They used a partial density approach to calculate the force constants up to the fifth neighbours in crystalline material. These force constants were used unchanged for the calculation in the nanometer sized materials consisting of spheres and columns. They give a relation for the frequency shift in their confinement model:

$$\Delta \Omega = \Omega(L) - \Omega_o = -A \left(\frac{a}{L}\right)^\gamma$$  \hspace{1cm} (2.26)$$

where \(\Omega(L)\) is the frequency of the Raman phonon in a nanocrystal with size \(L\), \(\Omega_o\) is the frequency of the optical phonon at the zone center, and \(a\) is the lattice constant of the
crystalline material. The parameters $A$ and $\gamma$ are used to describe the vibrational confinement due to the finite size in the nanocrystal. This relation fits the frequency shift of the phonon mode maximum determined from the Raman spectra very well. In contrast to this, the model does not give any asymmetry for the Raman lineshape of the phonon features, which is usually observed for nanocrystalline material. Since the Raman spectra of nanocrystalline material measured in this work exhibit this asymmetric lineshape the spatial correlation model was used.

The Raman spectra are not only influenced by the scattering volume and the crystallinity of the investigated sample, but the sample temperature and the stress in the sample affect the lineshape and the frequency position as well as induce new features in the spectra [Ess96, Gen93, Her93, Cer72, Ven73, Yam84]. These influences are discussed in the following two sections.

### 2.1.3 Temperature Dependence

The variation of the sample temperature for subsequent Raman measurements modifies the phonon features in Raman spectra, i.e. shifting towards lower frequencies and a symmetric broadening with increasing temperature. The dominating mechanisms for these modifications are (i) thermal expansion, (ii) phonon-phonon coupling, and (iii) the decay of optical phonons into two acoustical phonons with equal but opposite momentum [Kle66]. At elevated temperatures the average atomic distance is increased due to the thermal expansion. This causes a softening of the bonding and shifts the phonon mode frequencies to lower energies. The increase in temperature enables additionally the occupation of higher vibrational states with different overlap integrals. This is caused by the anharmonicity of the electron-phonon or hole-phonon interaction, resulting in a different frequency position of the phonon features in the Raman spectra [Pos68]. The temperature dependent shift of the phonon features in the spectra follows below room temperature quite well a quadratic dependence [Her93]

$$\Delta \Omega(T) = \Omega(0) - A_1 T - A_2 T^2$$

(2.27)

with $\Omega(0)$ the frequency position at $T=0$K and $A_1$ and $A_2$ the temperature coefficient for the linear and the quadratic term, respectively. For temperatures exceeding room temperature equation (2.27) can be approximated by a linear expression, neglecting the quadratic term [Her93]. Finally, anharmonic interactions can lead to the decay of a zone-center optical phonon into two zone-boundary acoustic phonons which gives an additional recombination channel and thus reduces the lifetime of the phonons. This latter effect results mainly in a broadening of the phonon features [Her93, Kle66]

$$\Gamma_0(T) = \Gamma_0 \left[1 + 2n \left(\frac{\Omega(T)}{2}, T\right)\right]$$

(2.28)

with $n$ the phonon occupation number depending on the phonon frequency $\Omega$ and the temperature $T$, $\Omega(T)$ the phonon frequency at temperature $T$, and $\Gamma_0(T)$ the natural linewidth
at temperature T, already used in the section 2.1.2 for the Raman lineshape calculation. The second term in the brackets arises due to the decay of the optical phonon into two acoustical phonons. Both phonons have half the energy and thus half the frequency of the optical phonon. The phonon occupation number is given by

\[ n(\Omega, T) = \frac{1}{e^{\frac{\hbar \omega}{k_B T}} - 1} \]  

(2.29)

with k_B the Boltzmann constant (\( k_B = 1.381 \times 10^{-23} \text{ J/K} \)).

An additional possibility for the sample temperature measurement is the ratio of the Stokes and the anti-Stokes phonon feature intensities [Bal83, Bru86]

\[ \frac{I_{\text{Stokes}}}{I_{\text{anti-Stokes}}} = \left( \frac{\omega_i - \Omega}{\omega_i + \Omega} \right)^4 e^{\frac{\Delta \Omega}{k_B T}} \]  

(2.30)

where \( \omega_i \) gives the frequency of the incident laser light and \( \Omega \) the frequency position of the investigated phonon mode. Because of the production of phonons in the Stokes process and their annihilation in the anti-Stokes process, the anti-Stokes phonon feature intensity increases, while the Stokes phonon feature intensity decreases with increasing sample temperature. It should be noted, that this ratio cannot be utilized if the excitation frequency is in the vicinity of any resonance of the electronic bandstructure and thus the material is not optically thin anymore [Ric76, Her92, Dre94].

2.1.4 Stress Dependence

If a stress \( \epsilon \) is applied in the investigated material the atomic arrangement is deformed, which modifies the crystal volume and the bonding strength and additionally in the case of biaxial stress lowers the symmetry of the crystal [Yam84, Nye93]. In the case of hydrostatic pressure

\[ \epsilon_H = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \]

all crystal directions are deformed in the same manner. This only leads to an increase (compressive stress) or a decrease (tensile stress) of the atomic bonding [Cer72, Ven73, Ana80]. In contrast to this, the biaxial stress

\[ \text{biaxial in (001) plane} \quad \epsilon_B = \epsilon_B \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix} \]

\[ \text{biaxial in (111) plane} \quad \epsilon_B = \epsilon_B \begin{pmatrix} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{pmatrix} \]
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leads to a deformation of the crystal unit cell but maintains its volume, since the deformation is elastic [Wei89, Nye93]. This unit cell deformation leads to a different stress dependence of the LO and the two TO phonon modes [Cer72, Gri78, Ven73, Ana80]. In the case of a cubic crystal these dependencies are given by [Cer72]

\[ \Omega_{\text{LO}} = \Omega_{\text{LO}} + \frac{1}{3} \delta \Omega_{\text{LO}} \epsilon_H \]

\[ \Omega_{\text{TO}} = \begin{cases} \Omega_{\text{TO}} + \frac{1}{3} \delta \Omega_{\text{TO}} \epsilon_H, & \text{for } \epsilon_B = 0 \\ \Omega_{\text{TO}} + \frac{2}{3} \delta \Omega_{\text{TO}} \epsilon_B, & \text{for } \epsilon_H = 0 \end{cases} \]

with \( \Omega_{\text{LO,TO}} \) the phonon frequency positions at room temperature and \( \epsilon = 0 \) of the LO and the TO phonon mode. \( \epsilon_H \) and \( \epsilon_B \) represent the applied hydrostatic or biaxial stress with \( \epsilon_H = \epsilon_{xx} = \epsilon_{yy} = \epsilon_{zz} \) and \( \epsilon_B = \epsilon_{xx} = \epsilon_{yy} = -2\epsilon_{zz} \). \( \delta \Omega_{\text{LO,TO}} / \delta \epsilon_H \) and \( \delta \Omega_{\text{LO,TO}} / \delta \epsilon_B \) give the frequency shift induced by the hydrostatic and the biaxial stress, respectively, with [Cer72]

\[ \frac{\delta \Omega_{\text{LO,TO}}}{\delta \epsilon_H} = \left( \frac{1}{6 \Omega_{\text{LO,TO}}} \right) (p + 2q)(S_{11} + 2S_{12}) \]

\[ \frac{\delta \Omega_{\text{LO,TO}}}{\delta \epsilon_B} = \begin{cases} \left( \frac{1}{2 \Omega_{\text{LO,TO}}} \right) (p - q)(S_{11} - S_{12}), & \epsilon_B \parallel [001] \\ \left( \frac{1}{2 \Omega_{\text{LO,TO}}} \right) rS_{44}, & \epsilon_B \parallel [111] \end{cases} \]

where \( S_{11}, S_{12}, \) and \( S_{44} \) the compliance tensor elements, and \( p, q, \) and \( r \) the phonon deformation potentials [Lan83, Wei89, Nye93]. Obviously one can see in equation (2.31) that a pure hydrostatic stress \( (\delta \Omega_{\text{LO,TO}} / \delta \epsilon_B = 0) \) leads to the same linear shift for all phonon modes [Cer72, Ven73, Ana80]. In contrast to this, the equations (2.31) and (2.32) show that for biaxial stress the degeneration of the TO phonon mode is lifted [Cer72, Ven73, Ana80].

Stress can be introduced in the material by using a diamond anvil cell or can be induced by the deposition conditions. In the diamond anvil cell usually only bulk materials are investigated to evaluate the stress dependence of the material [Cer72, Wei75, Gri78, San83]. The influence of the deposition conditions, especially an additional ion bombardment, can lead to intrinsic stresses in the deposited materials up to the GPa regime [Lif89, Lif90, Lif93, McK93, Rob93, Rob96]. The following paragraphs deal with the biaxial strain induced in sample heterostructures.

If two materials with different bulk lattice constants are grown epitaxially on each other the lattice mismatch causes a biaxial strain at the interface [Mat74, Peo85]. The layer growth starts pseudomorphically which means the layer adapt the lateral lattice constant of the substrate. If the layer thickness exceeds the so-called critical thickness the layer starts to relax to its own lattice constant [Mat74, Peo85]. In this work mainly layered samples with a large lattice mismatch were investigated for which the critical thickness is very small, i.e. much lower than the layer thickness, so that the layers form polycrystalline films. Additionally, the so-called thermal strain is introduced after the deposition process, when the grown heterostructure is cooled down from the deposition temperature to room temperature, since the thermal expansion coefficients of the substrate and the deposited
material are usually different [Rat95]. As a result, the lattice constant can differ much more than during the deposition process inducing a biaxial strain at the interface, due to the increased lattice mismatch, which leads to problems with the adhesion of the deposited films [McK93, Hah96].

Since the stress dependencies for nearly all materials investigated in this work have already been measured, the frequency shifts of the phonon features can be used to determine the strain in the layer and the substrate. The different behaviour of the optical phonon modes in the presence of a biaxial stress at the sample interface can be used to distinguish the compressive and the tensile component of the biaxial stress [Ana80, Bru89, Abs91, Got97]. If, for example, the lattice constant of the film is smaller than that of the substrate the

Figure 2.11: Distinguishing between the in-plane and out-of-plane components of a biaxial strain in a layered sample by Raman spectroscopy using different polarization configurations.

unit cell of the film will be elastically modified. Due to the elasstical modification the lattice constant perpendicular to the interface (a⊥) will be decreased (compressive strain) while the lattice constant in the interface layer (a∥) is increased (tensile strain) compared to the value of the substrate lattice constant. This fact is demonstrated in figure 2.11 for an (001) oriented sample. Caused on the phonon selection rules the LO phonon mode is forbidden in the case of the incident light beam propagating along $\varepsilon = [1\bar{1}0]$ [Geu93]. Considering the second propagation direction $\varepsilon = [00\bar{1}]$ no TO phonon feature is allowed [Geu93]. The respectively forbidden phonon features are crossed in figure 2.11. Depending on the sign of the stress - tensile or compressive - the phonon modes shift differently. Usually a tensile stress shifts the phonons to lower frequencies because the atomic distances are increased and thus the bonding is softened. In the case of compressive stress the atoms are closer and thus the bonding is stronger resulting in a shift towards higher frequencies [Cer72]. These different
stress induced shifts can be used to determine the value of the biaxial stress and the two lattice constants $a_-$ and $a_\parallel$ of the layer.

2.2 Experimental Setup

The aim of this section is to explain the experimental realization of a Raman spectroscopy setup. Since the Raman scattering intensity is very low ($\approx 10$ photons per second) compared to the elastically Rayleigh scattered light intensity ($\approx 10^{12}$ photons per second) Raman spectrometers need a high straylight reduction. Additionally the phonon features in the Raman spectra exhibits full widths at half maximum in the range of $10\text{meV}$ thus demanding a high spectral resolution of the Raman spectrometer. Furthermore the high spectral resolution enables the distinguishing of phonon features in the vicinity of the Rayleigh scattered light.

In figure 2.12 a sketch of the experimental setup is shown. For the investigations of the

![Experimental Setup Diagram](image)

Figure 2.12: Experimental Setup used for the Raman spectroscopy measurements in this work.

samples three different lasers ($\text{Ar}^+$ (Coherent Innova 70), $\text{Kr}^+$ (Coherent Innova 302K), and HeCd (Kimmon IK5651R-G)) provide laser lines from $325\text{nm}$ ($3.81\text{eV}$) to $752.5\text{nm}$ ($1.65\text{eV}$). With these laser lines the near infrared, the visible, and the near ultraviolet spectral regions are covered. The laser light beam is guided via mirrors through several pinholes to the
sample. Firstly these pinholes stop the plasma lines of the laser, which were dispersed by a directvision prism in front of the laser systems and secondly they simplify the alignment if the laser line is changed.

Since the laser light is fully linearly polarized a polarization rotator is used to vary the polarization state of the incident light with respect to the sample crystal axis. The polarization rotator consists of 2 Fresnel rhombbs which have the effect of a $\frac{\lambda}{2}$-plate [Hec87]. For the detection of the scattered light three states are possible: (i) unpolarized, which means the polarization state is not analyzed and only the different reflectivity of the gratings for light polarized parallel or perpendicular to the grooves influences the detection [Kuz89, Dilor1], (ii) horizontal, and (iii) vertical polarized, which means parallel and perpendicular to the entrance slit, respectively. This polarization detection is performed by moving one of two polarization filters, whose transmission axis are perpendicular to each other, into the scattered light beam. The relation between the incident and the scattered polarization state and the sample coordinate system is expressed by the Porto notation (2.14).

The monochromator system (Dilor XY) consists of three monochromators with identical gratings (1800 grooves/mm, f=800mm). The first and the second monochromator are combined usually in a subtractive configuration, while the third monochromator disperses the light onto a CCD (charge coupled device) camera. The subtractive configuration of the two former monochromators provides a sufficient spectral resolution in the range of a few wavenumbers (2.9cm$^{-1}$ at 457.9nm (2.71eV) and 2.1cm$^{-1}$ at 514.5nm (2.41eV) for the usually used 100$\mu$m slits widths) and works as a spectral bandpass with a high straylight reduction [Kuz89, Ess96]. The multi-channel detector measures the whole spectrum in a single shot in contrast to single-channel detectors like photomultipliers. A computer controls the monochromator system as well as the reading of the multi-channel detector.

The monochromator system supports two measurement configurations: (i) macro-Raman spectroscopy and (ii) micro-Raman spectroscopy ($\mu$-RS). These setups are compared in the two following sections. Figure 2.12 shows only the $\mu$-RS setup with the microscope (Olympus BH-6) since this setup is used for nearly all measurements in this work. Under this microscope three different sample stages can be fixed: (i) the normal stage for single $\mu$-RS measurements, (ii) the x-y-stage, which enables sample movements with a minimum step width of 100nm of the sample under the laser beam in both lateral directions, and (iii) a nitrogen cryostate with a heating facility, which is used for temperature dependent measurements from -150°C up to 450°C. Since the incident laser light beam as well as the scattered light passes the microscope this measurement setup realizes a backscattering geometry. The microscope is additionally used for the optical control of the laser beam position on the sample surface. If the incident light intensity is reduced by optical density filters the focus of the incident light on the sample surface can be observed with an adapted camera. For the measurements using the microscope only lines with a wavelength $\geq$ 400nm can be used, because the absorption of the optical lense coatings increases drastically for light with lower wavelengths [Dilor1] and thus the signal to noise ratio decreases.

To investigate the spectral transmittance of the micro- and the macro- Raman spectroscopy
optical setup measurements were performed using a broadband light source under the microscope and in front of the macro-Raman setup. For these measurements a light bulb was used, for which the emission is expected to be featureless in the interesting spectral region (400-800nm). The measured signal intensities are normalized and the reciprocal values of the transmittance were calculated. The reciprocal value give the multiplication factor, which is necessary to remove the Raman spectrometer sensitivity in the measured Raman spectra and is thus called sensitivity factor. In figure 2.13 these sensitivity factors for the micro- 

![Figure 2.13](image-url)  

Figure 2.13: The sensitivity factor for the micro- and the macro-Raman spectroscopy optical setup.

and the macro- Raman spectroscopy optical setup are shown. For clarification the sensitivity factors of the macro-Raman setup are enlarged by factor of 10. The maximum transmittance and thus the sensitivity factor 1 is located at 670.0nm, while for example the sensitivity factor for the blue Ar$^+$ laser line (457.9nm $= 2.71eV$) in the micro-Raman spectroscopy optical setup is $\approx$16.

### 2.3 Macro-Raman Spectroscopy

In the macro-Raman spectroscopy optical setup an achromatic lens (f=200mm) in front of the sample focusses the light onto the sample surface. The focus diameter is about 120$\mu$m [Kog66, Rea71, Rap84]. Due to this large focus diameter the lateral resolution in this configuration is quite low. On the other hand, the possibility of destroying the investigated sample due to huge light power densities is reduced because of the larger focus diameter. Another advantage of this optical setup is the higher elastical straylight reduction than that
of the optical setup using a microscope. This is related to the different beam directions of the incident and the scattered light beam [Dre94]. However, the low lateral resolution reveals no detailed information about the homogeneity of the sample using the macro-Raman spectroscopy optical setup. Furthermore, the very high penetration depth of the visible laser light into the investigated widegap semiconductors reduces the depth resolution of the interesting film, since the information is integrated over the entire light penetration depth. Due to film thicknesses smaller than the light penetration depth for most of the investigated samples the spectra contain additional structures related to the substrate phonon modes. This is demonstrated in figure 2.14, which shows the Raman spectrum of a diamond film deposited on silicon. The dominant feature in the spectrum is the first order LO phonon mode of the silicon substrate, due to the large light penetration depth in the diamond film. A detailed description of the phonon mode assignments in the Raman spectrum is given in chapter 3. The chosen polarization configuration corresponds to the crystal axis of the substrate, since the diamond film is polycrystalline.

This macro-Raman spectroscopy optical setup is only taken for photoluminescence measurements, since the utilized 325.0nm (3.81eV) HeCd laser line cannot be used in the micro-Raman spectroscopy optical setup (see figure 2.13).

**Figure 2.14:** The macro-Raman spectrum of a diamond film on silicon.

2.4 Micro-Raman Spectroscopy (μ-RS)

In the μ-RS optical setup an optical microscope is added in the incident and the scattered light beam. It provides a reduced focus diameter in the micrometer range, depending on the wavelength. If additional pinholes are introduced in the optical setup the confocal optical
setup of the spectrometer can be used. This special case will be discussed in the last section of this chapter. For the μ-RS measurements four objectives are fixed at a turret with different magnifications (x10, x50, x80, and x100) and numerical apertures (NA). The NA is defined by [Hec87]

\[ \text{NA} = n \sin \frac{\Theta}{2} \]  

with \( n \) the refraction index of the surrounding medium (\( n_{\text{air}}=1.0004 \)) and \( \Theta \) the opening angle. Because of different NA and focal lengths the objectives have different focal diameters. The focal diameters are in the micrometer range or higher; for example the mainly used MSPlan100 has a focus diameter of \( \approx1\mu\text{m} \) (\( \Rightarrow \) \text{micro-Raman spectroscopy (μ-RS)}).

The intensity distribution of the incident laser beam is not uniform, but concentrated near the axis of propagation and additionally the phase fronts are slightly curved [Kog66]. This slight curvature is introduced by the mirrors in the resonator of the laser system, which are curved to reduce losses. Nevertheless the incident laser beam is similar to a plane wave. Figure 2.15 illustrates the wavefront curvature, the focusing of a Gaussian beam, and the parameters used in the following equations. To determine the propagation of the Gaussian beam after passing the focusing element one has to solve the scalar wave equation for a field component or potential \( u \):

\[ \nabla^2 u + k^2 u = 0 \]  

with \( k = \frac{2\pi}{\lambda} \) the propagation constant in the medium. For light propagating in the \( z \) direction \( u \) can be expressed by

\[ u = \psi(x, y, z)e^{-ikz} \]  

where \( \psi \) is a slowly varying complex function describing the differences between the real

\[ \text{Figure 2.15: Illustration of the wavefront curvature and the focusing of a Gaussian beam. In the figure D means the illuminated diameter in the focusing lens, F the working distance, } w_0 \text{ the focus radius, } w(z) \text{ the waist radius at point } z, \text{ and } R(z) \text{ the wavefront radius of curvature at point } z. \]
Gaussian light beam and a perfect plane wave [Kog66]. ψ functions of the form

\[
\psi(x, y, z) = H_m \left( \sqrt{\frac{2}{w(z)}} \right) H_n \left( \sqrt{\frac{2}{w(z)}} \right) e^{-i \left[ P(z) + \frac{\lambda}{2w(z)} (x^2 + y^2) \right]} (2.36)
\]

are solutions with \(H_m\) the Hermite polynomials of the mode \(m\), \(P(z)\) a complex phase shift, and \(q(z)\) a complex beam parameter defined by [Kog66]

\[
\frac{1}{q(z)} = \frac{1}{R(z)} - i \frac{\lambda}{\pi w(z)^2} (2.37)
\]

with \(R(z)\) the wavefront radius of curvature at point \(z\) and \(w(z)\) the waist radius at point \(z\). Thus the radius of the waist and the wavefront curvature \(R(z)\) at point \(z\) are given by [Kog66]

\[
w(z) = \sqrt{w_o^2 \left[ 1 + \left( \frac{\lambda z}{\pi w_o^2} \right)^2 \right]} \quad (2.38)
\]

\[
R(z) = z \left[ 1 + \left( \frac{\pi w_o^2}{\lambda z} \right)^2 \right] . \quad (2.39)
\]

Dividing the square of equation (2.39) by equation (2.38) leads to

\[
w_o = \sqrt{\frac{w(z)^2}{1 + (\frac{\pi w(z)^2}{\lambda R(z)})^2}} \quad (2.40)
\]

with

\[
R(z) = \frac{1}{2z} \left( \frac{\pi w(z)^2}{\lambda} \right)^2 \left[ 1 - \sqrt{1 - 4 \left( \frac{z \lambda}{\pi w(z)^2} \right)^2} \right] . \quad (2.41)
\]

Using equation (2.40) the ideal focus diameter of each objective can be calculated, with \(z\) the working distance and \(w(z)\) the incident light radius in the focusing lense of the objective. The calculations are demonstrated for the x100-objective, since it is used for most of the investigations in this work. The working distance \(z\) is 300\(\mu\)m and \(w(300\mu\)m\)\approx0.15mm [Dilor1]. Using a wavelength of \(\lambda=457.9\)nm these values reveal a curvature radius \(R(300\mu\)m\)=300.02\(\mu\)m and an ideal focus diameter of \(2w_o=1.16\mu\)m.

The depth of focus (DOF) is defined as the distance between \(z=0\) and the point \(z\) at which \(w(z)=\sqrt{2}w_o\) [Dilor2]. Solving equation (2.38) for \(z\) yields

\[
\sqrt{2}w_o = \sqrt{w_o^2 \left[ 1 + \left( \frac{\lambda z_{\text{DOF}}}{\pi w_o^2} \right)^2 \right]}
\]

\[
\implies \text{DOF} := z_{\text{DOF}} = \frac{\pi w_o^2}{\lambda} \quad (2.42)
\]

\[
(2.36)
\]
The equations derived in this section are valid for a beam propagation in vacuum or air [Kog66]. Since the focussing of the laser beam tooks place in the surrounding atmosphere (air) these equations are correct. On the other hand, for the last equation one has to remember, that the light is focussed on the sample surface and thus propagates below the focus point in a medium with a refraction index $n$. Due to this the DOF in equation (2.42) has to be modified as follows

$$\text{DOF} = n \frac{\pi}{\lambda} w_0^2.$$  \hspace{1cm} (2.43)

Using the parameters calculated above for the x100-objective, an incident light wavelength of 457.9nm (2.71eV), and for example the refraction index of single crystalline diamond ($n_{\text{dia}}=2.46$ [Phi62]) a DOF=5.68μm can be determined.

### 2.5 Sample Geometries in the μ-RS

Measurements using the μ-RS optical setup were performed using two different sample geometries, (i) the **conventional plane-view geometry** and (ii) the **cross-sectional geometry**. Figure 2.16 sketches the two sample geometries. On the left hand side the conventional plane-view geometry is shown while on the right hand side the cross-sectional geometry is given.

Figure 2.16: The sample geometries used in the μ-RS measurements. The left shows the conventional plane-view geometry while on the right side the cross-sectional geometry is given.

For the plane-view geometry all participating layers and the substrate contribute to the Raman spectrum in the case of transparent films (see section 2.3 and section 2.5.1) and thus no depth-resolved information about the layered sample heterostructure is available. In contrast to this, the cross-sectional geometry enables to distinguish between the layers by moving the sample under the laser beam and taking subsequent spectra at each sample position (see section 2.5.2). The position dependent discussion of the phonon feature parameter variations,
CHAPTER 2. RAMAN SPECTROSCOPY (RS)

i.e. intensity, full width at half maximum, and frequency position provides the depth-resolved investigation of the sample. This makes the cross-sectional sample geometry a suitable tool for the identification and investigation of buried layers and material property variations, like stress, crystallite size, stoichiometry, etc., in the depth of the sample.

2.5.1 Conventional Plane-View Geometry

The conventional plane-view geometry is adapted in most publications using $\mu$-RS. Unfortunately the spectra are dominated by the substrate phonon features due to the large penetration depth in the case of transparent films as described in the macro-Raman spectroscopy section. This is shown in figure 2.17 for the same sample as given in figure 2.14. Similarly to

![Raman Shift vs. Intensity graph]

Figure 2.17: The $\mu$-RS measurements of the diamond film on silicon given in figure 2.3.

the macro-Raman spectrum the dominant feature is the first order phonon mode of the silicon substrate. In contrast to this, the high lateral resolution, due to the focus diameter in the $\mu$m range, enables to distinguish between the different diamond crystallites of the diamond film or to measure between the crystallites. On the other hand, the large light penetration depth can be used to investigate the influence of the film on the substrate. For that purpose the lateral resolution in the $\mu$-RS optical setup and the xy-stage can be used to perform two-dimensional scans (mappings) of the film phonon features as well as the substrate phonon features to investigate the lateral homogeneity.

In this work the conventional plane-view geometry is applied for the first characterization of a film, the investigation of a less known material, or two-dimensional mappings.
2.5.2 Cross-Sectional Geometry

As displayed on the right hand side of figure 2.16 the sample is turned onto its side for the cross-sectional geometry and is fixed with one of its side-faces perpendicular to the incident light wavevector. Utilizing the xy-stage under the microscope the layered heterostructure of the sample is moved under the incident laser light beam focus and for every sample position a full spectrum in the interesting spectral range is taken. This scanning procedure enables a distinguishing of the different layers of the heterostructure, since every layer dominates the spectrum if it is centered under the incident light beam focus. Figure 2.18 shows a typical 3D representation of such a scan across the layered heterostructure of an approximately 10 μm thick diamond film on a silicon substrate, where the diamond film thickness was determined by a transmission electron microscopy (TEM) investigation. The x-axis gives the measured spectral range, the y-axis the measured intensity, and the z-axis the scanned distance in μm. While the first spectrum shows the measurement in the surrounding atmosphere the rear spectrum corresponds to the measurement in the silicon substrate. Clearly the appearance of the phonon features can be observed when the laser focus approaches the respective layer. For comparison figure 2.19 shows the Raman spectrum taken in the conventional plane-view geometry. Due to the diamond film thickness of about 10 μm the silicon phonon feature cannot be observed. This is caused by the large but finite light penetration depth even for crystalline diamond films [Phi62, Gre69]. Since the incident light as well as the scattered light are absorbed in the material, the information depth in a RS measurement is half of
Figure 2.19: The Raman spectrum of the sample given in figure 2.18 measured with the plane-view sample geometry.

the light penetration depth [Iba81]

$$d_{inf} = \frac{d_{pen}}{2}$$  \hspace{1cm} (2.44)

In figure 2.20 the light penetration depth of silicon (solid line) [Asp83], diamond (dashed line) [Phi62], graphite (dotted line) [Gre69], and silicon carbide (dash-dotted line) [Log96] are given. In contrast to the transparency of diamond in the displayed spectral range the value of $\text{Im}(\varepsilon_{\text{dia}}) = 1 \cdot 10^{-11}$ was taken to get a finite but large value in figure 2.20. Taking figure 2.19 into account the light penetration depth in the diamond film is obviously much smaller than for single crystalline diamond. This is caused by the incorporation of graphite in the polycrystalline diamond film, which can be judged by the appearance of the weak graphite band in figure 2.19. The effective dielectric function ($\varepsilon_{\text{eff}}$) of the mixed medium can be calculated using an effective medium approximation, for example Maxwell-Garnett [Max04, Max06]:

$$\varepsilon_{\text{eff}} = \frac{2f \varepsilon_{\text{gra}} - \varepsilon_{\text{dia}}}{\varepsilon_{\text{gra}} + 2f \varepsilon_{\text{dia}}} + 1$$

$$\frac{1}{1 - f \frac{\varepsilon_{\text{gra}} - \varepsilon_{\text{dia}}}{\varepsilon_{\text{gra}} + 2f \varepsilon_{\text{dia}}}}$$ \hspace{1cm} (2.45)

with $\varepsilon_{\text{gra}}$ the dielectric function of graphite [Gre69], $\varepsilon_{\text{dia}}$ the dielectric function of single crystalline diamond [Phi62], and $f$ the filling factor of the inclusion (here $\varepsilon_{\text{gra}}$) in the host material $\varepsilon_{\text{dia}}$. With [Ros93]

$$n^2 = \sqrt{ \left( \frac{\text{Re}(\varepsilon_{\text{eff}})}{2} \right)^2 + \left( \frac{\text{Im}(\varepsilon_{\text{eff}})}{2} \right)^2 + \frac{\text{Re}(\varepsilon_{\text{eff}})}{2} }$$

$$\kappa^2 = \sqrt{ \left( \frac{\text{Re}(\varepsilon_{\text{eff}})}{2} \right)^2 + \left( \frac{\text{Im}(\varepsilon_{\text{eff}})}{2} \right)^2 - \frac{\text{Re}(\varepsilon_{\text{eff}})}{2} }$$ \hspace{1cm} (2.46)
2.5. SAMPLE GEOMETRIES IN THE $\mu$-RS

Figure 2.20: Light penetration depth of silicon (solid line) [Asp83], diamond (dashed line) [Phi62], graphite (dotted line) [Gre69], and cubic silicon carbide (dash-dotted line) [Log96].

the refractive index $n$ and the absorption coefficient $\kappa$ can be calculated for the effective medium. Using the absorption coefficient for $\varepsilon_{\text{eff}}$ the light penetration depth in the effective medium can be calculated. The light penetration depth for a 99% pure diamond film at an incident light energy of 2.71 eV is $\approx 2.6\mu$m and thus the information depth $d_{\text{inf}} \approx 1.3\mu$m. This explains the absence of the silicon phonon feature in figure 2.19. The information depth in diamond films decreases drastically since graphite is a strongly absorbing material. For example a 95% pure diamond film has an information depth of approximately 155nm.

With this conventional plane-view sample geometry no depth-resolved variation of the sample properties, like interfacial reactions, stress, or stoichiometry can be investigated. Moreover, the existence of ultra-thin interfacial or surface layers cannot be discussed [Zah96, Wer97b]. In contrast to this, the cross-sectional sample geometry can be used to investigate the variations of the sample properties depth-resolved with a sensitivity in the submicrometer region [Bru89, Mla90, Abs91, Wer97b]. At this point it should be mentioned that one has to distinguish between the resolution and the sensitivity of a method. The resolution describes the feasibility of a method to distinguish two structures with a defined distance. Figure 2.21 shows as lines the calculated profiles of two Gaussian line shapes with distances of 0.5-FWHM (solid line), 1-FWHM (dashed line), and 2-FWHM (dotted line), respectively. Obviously a distance of approximately the FWHM can be distinguished quite well. Due to this the resolution of the conventional plane-view and the cross-sectional $\mu$-RS is given by the FWHM of the focussed laser beam ($\approx 1\mu$m). Nevertheless, the sensitivity of the RS is much higher, due to its high chemical sensitivity, which reveals distinct phonon features for different chemical species. This enables the detection of ultra-thin layers using the cross-sectional sample geometry.
In the next paragraphs a model is described, which permits the simulation of the measured parameter variations, especially the phonon feature intensity. For this model some important assumptions have to be made for simplification:

- **The focused laser beam and the light inside the sample can be described as plane waves.** Calculating the wavefront curvature radius at the focus point equation (2.41) yields \( R(z=0) = \infty \). In addition, the DOF (equation (2.43)) is generally larger than the information depth of the materials investigated by cross-sectional RS in this work.

- **The wavevector of the incident light beam is perpendicular to the investigated sample surface.** Due to the assumption of plane waves in the first point, the rays of the incident laser beam as well as those of the light inside the material are parallel and no refraction has to be taken into account.

- **The diffraction due to layer thickness smaller than the laser light wavelength as well as the edges will be neglected.** A discussion of the diffraction influence on the measurements will be given at the end of this chapter.

In figure 2.18 the envelope of the phonon feature intensity variation is given by the lines for the distinct phonon features. This intensity variation plotted against the distance of the laser focus movement across the layered sample heterostructure is shown in figure 2.22. The intensity variations of the measured phonon features were obtained by a curve fitting of the measured Raman spectra with Lorentzian and Gaussian lineshapes for the different phonon features. Clearly the appearance of only the carbon related phonon modes of diamond and graphite can be seen when the laser focus approaches the sample surface (light gray region...
2.5. SAMPLE GEOMETRIES IN THE $\mu$-RS

Figure 2.22: The envelope of the phonon feature intensity variation for the distinct phonon features in figure 2.18 are given as open symbols (square for silicon, circle for diamond, up triangle for the graphite G-band, and down triangle for the graphite D-band). In addition, the simulation for these intensity variations are given as straight lines.

in the center of the figure 2.22) from the surrounding atmosphere (white region on the left hand side of the figure). On the right hand side of the figure the dark region represents the silicon substrate. When the laser focus approaches the diamond/silicon interface the layer phonon features disappear while the silicon substrate phonon features emerge.

These variations can be simulated by calculating the convolution of a Gaussian lineshape and several distinct box functions [Wer96, Zah96, Got97, Wer97b, Wer97c, Wer97d]. While the Gaussian lineshape represents the radial intensity distribution of the focused laser beam inside the sample, the box functions stand for the different layers of the sample heterostructure.

The Gaussian lineshape is given by

$$G(x - x_c) = I_o e^{-4\ln 2 \left(\frac{x - x_c}{w}\right)^2}$$  \hspace{1cm} (2.47)

with $I_o$ the maximum intensity, $x_c$ the maximum position, and $w$ the FWHM. The box function can be written as

$$B(x) = \begin{cases} 
1 & \text{for } x \in [x_a, x_b] \\
0 & \text{else}
\end{cases}$$ \hspace{1cm} (2.48)

which is only unequal to zero in a defined distance range. The scattering intensity $I(x_s)$ at
point $x_s$ can be calculated using the convolution

$$I(x_s) = \int_{-\infty}^{\infty} G(\bar{x} - x_s) B(\bar{x}) \, d\bar{x}$$

$$= \int_{x_a}^{x_b} G(\bar{x} - x_s) \, d\bar{x}$$

$$= I_0 \int_{x_a}^{x_b} e^{-4\ln 2(\frac{\bar{x}}{w_s})^2} \, d\bar{x}$$  \hspace{1cm} (2.49)$$

with $x_s \in [0, d_{\text{scan}}]$ and $d_{\text{scan}}$ the scanned distance across the layered sample heterostructure. For example in figure 2.22 is $d_{\text{scan}} = 21 \mu m$. The zero value is given in relation to the surface of the sample. Unfortunately the integral of equation (2.49) cannot be solved analytically anymore and thus the algorithm for the calculation of the intensity variation uses the so-called Romberg integration which utilizes the extended trapezoidal rule [Pre92].

In general the maximum intensity $I_0$ cannot be calculated absolutely, since the exact value of the proportionality factor in equation (2.12) is usually unknown [Ric76]. For this reason, the maximum intensities concerning the different layers in a sample heterostructure are given in relation to the maximum intensity of the substrate phonon feature well away from the interface. The maximum intensity $I_{0,i}$ for the $i^{\text{th}}$ layer is given by

$$I_{0,i} = \frac{S_i d_{\text{inf},i}}{S_{\text{sub}} d_{\text{inf},\text{sub}}} I_{0,\text{sub}}$$  \hspace{1cm} (2.50)$$

with $d_{\text{inf},i}$ the information depth of the $i^{\text{th}}$ layer ($i \in [0, N + 1]$ and $N \in [0, \infty]$ the number of layers on the substrate (layer N+1); the surrounding atmosphere corresponds to layer 0), $S_i$ and $S_{\text{sub}}$ the scattering efficiencies of the $i^{\text{th}}$ layer and the substrate material, and $I_{0,\text{sub}}$ the maximum intensity for the substrate phonon feature.

Only in the case of a strongly absorbing substrate material the constant in equation (2.12) can be calculated [MJa90]

$$I_{0,\text{sub}} = \frac{1}{32 \pi^4 c^5} \frac{\omega_s^3 P_1 (1 - R_s) (1 - R_i) \Delta \Omega_s f_s}{w_i n_i n_s} V_{\text{Gauss}}$$  \hspace{1cm} (2.51)$$

with

$$V_{\text{Gauss}} = \pi \int_0^{d_{\text{inf},\text{sub}}} \left(e^{-4\ln 2(\frac{z}{w_s})^2}\right)^2 \, dz$$  \hspace{1cm} (2.52)$$

the volume integral for the Gaussian shaped volume of the laser beam inside the substrate, and $d_{\text{inf},\text{sub}}$ the information depth of the substrate material. $\omega_s$ and $\omega_i$ are the scattered and the incident laser light frequency, respectively, and $n_s$ ($n_i$) and $R_s$ ($R_i$) the refractive index and the reflectivity at the scattered (incident) laser light frequency. $P_1$ is the incident laser light irradiance, $\Delta \Omega_s$ the collection solid angle, and $f_s$ the measurement setup efficiency. This efficiency can be taken from the figure 2.13.

If the constant $C$ in equation (2.12) cannot be calculated due to a low absorbing substrate, the value of $C$ is determined once by scaling the simulated intensity of the substrate phonon to the
measured value. Afterwards all the other maximum intensities can be calculated relatively to the maximum intensity of equation (2.51) using equation (2.50). The scattering efficiencies used in the equations (2.50) and (2.51) are listed elsewhere in detail [Ric76, Wad80, Fen88a]. Generally only a single box function is necessary in equation (2.49) to describe the intensity variation of the respective layer phonon mode. In this work samples will be discussed in which the crystalline quality and thus the information depth varies in the sample depth or layers of the same material are separated in the sample heterostructure. This requires the combination of several box functions to describe the intensity variation of the corresponding phonon mode and thus equation (2.49) has to be modified to

$$I_i(x) = \sum_{j=1}^{M} I_{ij} \int_{x_{ij}}^{x_{ij}} e^{-4\ln 2 \left( \frac{x-x_0}{\sigma} \right)^2} dx$$

(2.53)

with $M \in [1, \infty]$. The index $i$ counts the different materials of the sample heterostructure, while the index $j$ counts the subsequent layers contributing to the intensity variation of the $i^{th}$ material. The maximum intensities $I_{ij}$ have to be calculated using the relation of equation (2.50) for each index $i$ and $j$.

An example for equation (2.53) is the diamond layer in figure 2.22. Since the side face of the diamond layer, due to the polycrystalline nature of the deposited material, shows several facets the intensity variation is modulated. In addition, the deposited diamond film includes an increasing amount of graphite with decreasing distance to the diamond/silicon interface. This can be verified by the overall increasing intensity of the graphite G-band, the decreasing intensity of the diamond phonon feature, and the graphite D-band, indicating a large amount of highly disordered graphite in the vicinity of the diamond/silicon interface. A detailed discussion of this effect will be given in section 5.1.

Figure 2.23 shows the measured silicon intensity variation from figure 2.22 (open squares) and the simulation using the model discussed above (dashed line). In contrast to the measured intensity variation, the simulated variation shows no peak near the interface. This additional peak is caused by the different information depths in the materials when the laser beam focus passes an interface.

As sketched in figure 2.24 the information depths (see also figure 2.20) of a 99% pure diamond film and of silicon are $\approx 1.3 \mu m$ and $\approx 138 nm$, respectively. Due to this difference the illuminated volume in diamond is $\approx 10$ times larger than in silicon. If the laser beam focus passes the diamond/silicon interface the larger information depth in the diamond film causes an additional illumination of the silicon from the diamond/silicon interface. This is possible since the Raman scattered light intensity is of the order of $10^{-15}$ of the incident light intensity and thus most of the light in the illuminated diamond film region is Rayleigh scattered light with the same energy as the incident light. Due to the spherical dipole emission [Hec87] Rayleigh scattered light can reach the diamond/silicon interface, enter the silicon, and cause Raman scattering processes in the silicon substrate. This additional Raman scattered light only can be detected on the diamond layer side again, since the light penetration depth in the
The silicon phonon feature intensity variation of figure 2.22 (open squares) and simulations (straight lines) using two different models.

silicon is too small for the scattered light to propagate on the substrate side of the interface to the surface.

The illuminated plane at the interface \( A_{k,1}(x_s) \) determines the intensity of the additionally Raman scattered light, due to the proportionality of the scattered light and the illuminated volume inside the silicon \( (V_{\text{add}}) \). This plane has a Gaussian shape and can be calculated as follows

\[
V_{\text{add}}(x_s) = d_{\text{inf},a} A_{k,1}(x_s) = d_{\text{inf},a} C_p \left( 1 - f_d \right) \int_{-\infty}^{\infty} G(x_k - x_s) G(y) \, dy
\]

\[
= d_{\text{inf},a} C_p \left( 1 - f_d \right) \int_{-\infty}^{\infty} d_{\text{inf},b} e^{-4 \ln 2 \left( \frac{x_k - x_s}{w} \right)^2} e^{-4 \ln 2 \frac{x}{^2}} \, dy
\]

\[
= C_p \left( 1 - f_d \right) d_{\text{inf},a} d_{\text{inf},b} \int_{-\infty}^{\infty} \frac{\pi}{4 \ln 2} e^{-4 \ln 2 \left( \frac{x_k - x_s}{w} \right)^2} \, dy
\]

with

\[
f_d = \begin{cases} 
\frac{d_{\text{inf},k+1}}{d_{\text{inf},k}} & \text{if } d_{\text{inf},k} \geq d_{\text{inf},k+1} \\
\frac{d_{\text{inf},k}}{d_{\text{inf},k+1}} & \text{if } d_{\text{inf},k} < d_{\text{inf},k+1} 
\end{cases}
\]

\[
d_{\text{inf},a,b} = \begin{cases} 
d_{\text{inf},a} = d_{\text{inf},k+1}; & d_{\text{inf},b} = d_{\text{inf},k} \text{ if } d_{\text{inf},k} \geq d_{\text{inf},k+1} \\
d_{\text{inf},a} = d_{\text{inf},k}; & d_{\text{inf},b} = d_{\text{inf},k+1} \text{ if } d_{\text{inf},k} < d_{\text{inf},k+1} 
\end{cases}
\]

\( x_k \) (\( k \in [0,N] \)) the position of the interface between layer \( k \) and layer \( k+1 \), and \( C_p \) a scaling constant considering differences between the simulation and the measurement caused by a
2.5. SAMPLE GEOMETRIES IN THE $\mu$-RS

Figure 2.24: A sketch of the illuminated volumes in a 99% pure diamond film (left hand side) and silicon (right hand side).

polycrystalline layer. This effect is difficult to calculate, due to the random orientation of the crystals in a polycrystalline layer. This modifies the light propagation in the material and thus reduces the information depth and the size of the illuminated plane at the interface.

Although figure 2.24 displays only the case of $d_{inf,k} > d_{inf,k+1}$ two cases, as in equations (2.55) and (2.56), has to be considered to determine the material, which scattering volume (equation (2.52)) has to be enlarged with $V_{add,1}$:

- $d_{inf,k} \geq d_{inf,k+1}$: $V_{add}$ has to be added to the scattering volume of the material in layer $k+1$.

- $d_{inf,k} < d_{inf,k+1}$: $V_{add}$ has to be added to the scattering volume of the material in layer $k$.

With this additional term the resulting calculated phonon feature intensity variation fits the measured phonon feature variation very well, as can be seen as solid line in figure 2.23. Similarly to this peak a peak can be observed for the diamond and the graphite at the surface of the sample in figure 2.22. This is caused by the large but finite light information depth inside the diamond film in comparison to the hardly influenced light propagation in the surrounding atmosphere. As a result, an additional term concerning equation (2.54) has to be included in the simulation of the diamond and the graphite phonon feature intensity variation at the surface.

In the following paragraphs a discussion of the diffraction influence is given. The diffraction of the light can be caused by edges and by layers with $d \leq \lambda$ [Bou50a, Bou50b, Som78, Bor85]:

1. Diffraction of the light at an edge of the sample. This edge can be the surface if the
top most layer is high absorbing and/or an interface in the layer stack if a high and a low absorbing material are in contact at this interface.

2. Diffraction of the light due to a transparent layer with a thickness of \( d \ll \lambda \). If a low absorbing layer is embedded in two high absorbing layers the diffraction of a single slit has to be calculated.

3. Diffraction of the light due to an opaque layer with a thickness of \( d \ll \lambda \). If a high absorbing layer is embedded in two low absorbing layers the diffraction of a wire has to be calculated.

Concerning the first point, the exact formalism given by A. Sommerfeld for the Fresnel diffraction at an edge yields an equation which describes the light intensity behind an edge [Bor85]

\[
I_e(x) = \frac{1}{2} \left\{ \left( C(x) + \frac{1}{2} \right)^2 + \left( S(x) + \frac{1}{2} \right)^2 \right\}
\]  
(2.57)

with

\[
C(x) = \int_0^x \cos \left( \frac{\pi}{2} \frac{x^2}{\lambda^2} \right) \, d\tilde{x}
\]  
(2.58)

\[
S(x) = \int_0^x \sin \left( \frac{\pi}{2} \frac{x^2}{\lambda^2} \right) \, d\tilde{x}
\]  
(2.59)

\[
x = 2 \sqrt{\frac{2r}{\lambda}} \sin \frac{\varphi}{2}
\]  
(2.60)

\( r \) the distance to the observation point, and \( \varphi \) the angle between the incident wavevector and a line from the edge to the observation point. The two integrals \( C(x) \) and \( S(x) \) of the equations (2.58) and (2.59) are the so-called Fresnel integrals. Their values are listed in detail elsewhere [Bro85]. Figure 2.25 shows the light intensity \( I_e(x) \) behind an edge. The shaded region of the figure stands for the opaque edge. The values of \( x \) are determined using equation (2.60). These values were used to evaluate the integrals, which were inserted afterwards in equation (2.57). In the transparent region the light intensity oscillates with decreasing amplitude and narrowing maxima for increasing distance to the edge. \( I_e(x) \) approaches \( I_i \) for \( x \to \infty \). Due to the requirements for equation (2.57) this diffraction effect averages to \( I_e=I_i \) for all \( x \) because of an illumination by a round beam [Som78, Bor85, Ber87] and thus the diffraction at edges in the heterostructure can be neglected.

Considering point two with \( d \approx \lambda \), the well known formula for the diffraction by a single slit has to be discussed [Bor85, Ber87]:

\[
I_s = \frac{w}{\lambda_i} \left( \frac{\sin \left( \frac{\pi d}{\lambda} \sin \varphi \right)}{\frac{\pi d}{\lambda} \sin \varphi} \right)^2
\]  
(2.61)

with \( \varphi \) the angle of the diffracted ray to the incident wavevector, \( d \) the width of the slit, and \( w \) the width of illumination (FWHM of the Gaussian shaped laser intensity profile).
2.5. SAMPLE GEOMETRIES IN THE $\mu$-RS

Figure 2.25: The light intensity $I_0(x)$ behind an edge using equation (2.57). The top axis gives the value of $x$, while the bottom axis gives the distance at an observation point with a distance $r=1.3\mu$m (information depth of 99% pure diamond).

Figure 2.26 shows the intensity $I_s$. In order to demonstrate the influence of the slit width (layer thickness) $d$ the intensity was normalized. Clearly the increasing FWHM of the first maximum with decreasing slit width can be observed. Due to this the minima and the next maxima shift to higher angles. The increase of the first maximum FWHM causes an illumination of the interface inside the layer and thus an additional term has to be included in the calculations, similar to equation (2.54), since the Gaussian laser light beam profile is valid for the diffraction, too. On the other hand, the size of the volume is not determined by the light penetration depth relation (1-$I_d$) but by the integrated intensity of $I_s$:

$$\int_{\varphi_{\text{min}}}^{\hat{\varphi}} I_s \, d\varphi = \int_{\varphi_{\text{min}}}^{\hat{\varphi}} \frac{w}{\lambda_I} \left( \sin \left( \frac{\pi d}{\lambda_I \sin \varphi} \right) \right)^2 d\varphi$$

With $\varphi_{\text{min}}$ the minimum angle for which the additional scattering inside the absorbing material can be detected, due to the diffracted light in the transparent medium. The minimum angle is determined by the information depth in the transparent material and half of the layer thickness $d$. Utilizing the substitutions

$$s = \frac{\pi d}{\lambda_I} \quad \text{and} \quad x = s \sin \varphi$$

one obtains for $d\varphi$ and the integration borders:

$$d\varphi = \frac{dx}{\sqrt{\left(\frac{\pi d}{\lambda_I}\right)^2 - x^2}}$$
Figure 2.26: The light intensity $I_s$ transmitted through a single slit depending on the slit width. For clarification the intensity was normalized.

$$\varphi_{\text{min}} \rightarrow s \left( \frac{d}{d_{\text{pen}}} \right)$$

$$\frac{\pi}{2} \rightarrow s$$

With the equations (2.63) - (2.66) the right hand side integral in equation (2.62) transform to

$$\frac{w}{\lambda l} \int_{s}^{s} \left( \frac{\sin x}{x} \right)^2 \frac{dx}{\sqrt{s^2 - x^2}}$$

This integral cannot be solved analytical anymore and thus the sinus function is expanded into a power series. The terms converge quite fast and thus the error is beyond 1% if only the first four terms are concerned [Bro85]:

$$\sin x = \sum_{n=0}^{4} (-1)^n \frac{x^{2n+1}}{(2n + 1)!} \approx x - \frac{x^3}{3!} + \frac{x^5}{5!} - \frac{x^7}{7!}$$

$$\Rightarrow \frac{\sin x}{x} \approx 1 - \frac{x^2}{3!} + \frac{x^4}{5!} - \frac{x^6}{7!}$$

Inserting (2.68) into (2.67) solvable integrals were obtained:

$$\frac{w}{\lambda l} \int_{s}^{s} \left( \frac{\sin x}{x} \right)^2 \frac{dx}{\sqrt{s^2 - x^2}} \approx$$
For equation (2.69) again terms with a higher power than 6 were skipped. The integration of equation (2.69) yields [Bro85]:

\[
D_s = \int_{\varphi_{\text{min}}}^{\pi} I_s d\varphi = \frac{w}{\lambda_l} \left[ \frac{1}{\sqrt{s^2 - x^2}} \int_{s}^{e} dx - \frac{1}{3} \frac{x^2}{\sqrt{s^2 - x^2}} \int_{s}^{e} dx + \frac{1}{90} \frac{x^4}{\sqrt{s^2 - x^2}} \int_{s}^{e} dx - \frac{5}{8064} \frac{x^2}{\sqrt{s^2 - x^2}} \int_{s}^{e} dx \right] 
\]

For equation (2.69) again terms with a higher power than 6 were skipped. The integration of equation (2.69) yields [Bro85]:

\[
D_s = \int_{\varphi_{\text{min}}}^{\pi} I_s d\varphi = \frac{w}{\lambda_l} \left[ \frac{1}{\sqrt{s^2 - x^2}} \int_{s}^{e} dx - \frac{1}{3} \frac{x^2}{\sqrt{s^2 - x^2}} \int_{s}^{e} dx + \frac{1}{90} \frac{x^4}{\sqrt{s^2 - x^2}} \int_{s}^{e} dx - \frac{5}{8064} \frac{x^2}{\sqrt{s^2 - x^2}} \int_{s}^{e} dx \right] 
\]

This can be further simplified for light penetration depths larger than the layer thickness (d_{\text{pen}} >> d):

\[
D_s = \int_{\varphi_{\text{min}}}^{\pi} I_s d\varphi 
\approx \frac{w}{\lambda_l} \left( \frac{\pi}{2} - s^2 \left[ \frac{\pi}{12} + \left\{ \frac{1}{90} - \frac{5}{8064} s^2 \right\} \arctan s \right] \right) 
\]

Up to now only layer thicknesses (slit widths) d ≈ \lambda_l were considered in the discussion. For d << \lambda_l a different formalism given by A. Sommerfeld [Som78] and C.J. Bouwkamp [Bou50a, Bou50b] has to be used. The diffracted intensity I_{ss} inside the small layer can be
calculated as follows

\[
I_{ss} = \left(\frac{\pi d}{2}\right)^4 \frac{1}{\lambda r} \cos^2 \varphi
\]  

(2.72)

with \( r \) the distance of the observation point. Figure 2.27 shows the intensity \( I_{ss} \) depend-

Figure 2.27: The light intensity \( I_{ss} \) transmitted through a small single slit depending on the slit width. In the insert the scaling of the maximum intensity for the angle \( \varphi=0^\circ \) is given.

- For the discussion of its influence the integrated intensity of equation (2.72) in the same borders of the above discussion has to be calculated

\[
D_{ss} = \int_{\varphi_{\text{min}}}^{\bar{\varphi}} I_{ss} \, d\varphi
\]

\[
= \int_{\varphi_{\text{min}}}^{\bar{\varphi}} \frac{s^3 \pi d}{2d_{\text{inf}}} \cos^2 \varphi \, d\varphi
\]

\[
= \frac{s^3 \pi d}{d_{\text{pen}}} \left( \pi - \frac{s \, d}{2d_{\text{pen}}} - \frac{1}{3} \sin \left( 2s \frac{d}{d_{\text{pen}}} \right) \right)
\]  

(2.73)
Equation (2.73) and either equation (2.70) or equation (2.71) has to be inserted in equation (2.54) in the brackets of the term \(1-f_d\) resulting in the new interface supplement equation

\[
V_{\text{add}}(x_s) = C_p \left(1 - f_d + D_N + D_{ss}\right) d_{\text{inf,a}} d_{\text{inf,b}} w \sqrt{4 \ln 2} e^{-4 \ln 2 \left(\frac{w_{s}-w_m}{w_m}\right)^2}
\]  

Concerning point three of the list the argumentation is the same as for point one, but one have to use the equation (2.57) twice, one for each side of the layer. Similar to the discussion for the edge no additional influence on the scattered intensity is expected. For that reason this point is neglected in the calculations. It should be mentioned, that a special treatment for the diffraction by several layers, for example in a superlattice, can also be neglected, since the large sample width (usually several millimeters) prevents the interaction in this case and thus each layer can be treated as a single slit.

With the simulation of the phonon feature intensity variation depending on the laser beam focus position the layer thicknesses in the sample heterostructure are determined. On the other hand, the curve fitting of the subsequent spectra for each laser beam focus position reveals all phonon feature parameters, i.e. intensity, FWHM, and frequency position. The known layer thicknesses in the sample heterostructure can thus be used to deconvolute the variations of the phonon feature FWHM and frequency position. For the deconvolution the algorithm given by Kirillov and Reynolds [Kir94] was used. Dividing the Fourier transformed (FT) convoluted parameter variation \(P'(x_s)\) by the FT of the Gaussian function the FT of the deconvoluted data set \(P(x)\) can be calculated:

\[
\mathcal{F}(P(x)) = \int_{0}^{d_{\text{scan}}} \frac{\mathcal{F}(P'(\tilde{x}))}{\mathcal{F}(G(x-\tilde{x}))} \, d\tilde{x}
\]  

with \(x \in [x_a, x_b]\) and \(\mathcal{F}(f)\) the FT of the function \(f\). A retransformation gives the deconvoluted data set. This procedure yields no solution if one has to divide by zero in the integral. Since the FT of the Gaussian function is again a Gaussian function this cannot happen. For the calculation of the FT computer algorithms given by Press et al. [Pre92] were used.

### 2.6 The Confocal Optical Setup

In this section the third optical setup of the Raman spectrometer is discussed - the confocal optical setup. The technique of the confocal setup was first developed by M. Minsky [Min88]. It utilizes an usual optical microscope with some modifications, which allows the measurement of different depths in a sample with a high sharpness (for examples see [Lic89, Wil90a, Lic94]). The modifications are very simple and consist of two additional pinholes, one in the incident and one in the scattered light beam. Figure 2.28 shows a sketch of this optical setup. The pinholes CF1 and CF2 are pinholes in the scattered and the incident light beam, respectively. These pinholes enable a spatial filtering of the illuminated sample volume. This is visualized in figure 2.28 with the solid and the dashed rays. The solid rays represent the optimum way
for the light beam and the dashed rays demonstrate the spatial filtering for light originating from points above or below the optimum point. They are blocked out at the confocal pinhole CF1 in the scattered light beam. The confocal pinhole CF2 in the incident light beam mainly reduces the illuminated volume in the sample, which leads to an additional increase of the signal to noise ratio.

The influence of the confocal optical setup in the Raman spectrometer was investigated with two experiments. Firstly one-dimensional scans utilizing the xy-stage across the cleaved edge of a GaAs(100) sample in the conventional plane-view sample geometry were taken with different CF1 diameters. The polarization configuration (-100(011,011)100) was chosen to obtain only the deformation potential allowed scattering from the LO phonon mode. In the second experiment the CF2 diameter was fixed at 200\(\mu\)m, but the focus plane of the objective was moved into the depth of a sample with an approximately 2\(\mu\)m thick diamond film on a Si(100) substrate. The same polarization configuration was utilized. For both experiments the pinhole in the incident light beam was not introduced. Since this pinhole is mainly responsible for the signal to noise reduction and not for the spatial filtering, the influence can be neglected.

Considering the first experiment, figure 2.29 shows the intensity variation of the LO phonon
2.6. **THE CONFOCAL OPTICAL SETUP**

![Graph](image)

Figure 2.29: Scans utilizing the plane-view sample geometry and different CF1 diameters across the cleaved edge of a GaAs(100) sample (open symbols).

mode feature. The open symbols give the measurements, while the solid lines represent the simulated intensity variation using equation (2.49). On the right hand side of the figure the CF1 diameters as well as the determined FWHM are given. Two changes with decreasing CF1 diameter are obvious. At first the maximum intensity of the variation decreases and secondly the increase at the edge becomes steeper. Figure 2.30 displays as open circles the measured maximum intensity and as crosses the calculated FWHM depending on the pinhole diameter. For comparison the dependences given in the manual are shown as solid lines [Dilor2]. Considering the maximum intensity dependence no variations between pinhole diameters of 200 μm and 700 μm are expected. Although the measured maximum intensity increases between CF1=200 μm and CF1=700 μm this increase is very small and thus the solid curve corresponds quite well to the measured dependence. For the FWHM dependence on the pinhole diameter a linear dependence is given in the manual [Dilor2]. This linear dependence is reproduced by the measured FWHM dependence giving a good correspondence to the solid curve.

The chosen polarization configuration in these experiments forbids an additional scattering from the side face, since no deformation potential scattering of the LO phonon mode is allowed for the (011) plane [Geu93]. In contrast to this, the deformation potential scattering of the TO phonon mode is allowed and figure 2.31 shows the measured phonon feature intensity of the GaAs TO phonon mode as symbols. Obviously the maximum is obtained if the laser focus is centered above the edge. The solid lines represent the simulations using equation (2.54) and the FWHM values obtained from the simulation of the LO phonon feature variation in figure 2.29. No diffraction influences were considered in these calculations. The simulations
Figure 2.30: The measured maximum intensity (open circles) and the FWHM (crosses) dependence on the pinhole diameter. In addition, the corresponding curves of the manual ([Dilor2]) are given.

fit the measured variations very well, which is a good validation of the derived equation (2.54).

Considering the second experiment the CF1 pinhole was fixed at a diameter of 200\,\mu m. Figure 2.32 shows as open symbols the measured variation of the phonon feature intensity for the silicon and the diamond phonon feature depending on the microscope stage z movement. The increase of the diamond phonon feature intensity is simulated using only equation (2.49) with a FWHM of 1\,\mu m and is given as the solid line in figure 2.32. Since the diamond film on the silicon already absorbs, the silicon phonon feature intensity increase cannot be simulated. On the other hand, the difference in the stage z positions for the diamond and the silicon phonon feature intensity maximum can be used to estimate the layer thickness (\approx 2\,\mu m). The dashed lines in figure 2.32 gives the exponential decay of the phonon feature intensity due to absorption in the material [Hec87]:

\[ I(z) \propto e^{-2n\alpha z} \]  \hspace{1cm} (2.76)

with \( n \) the refraction index of the material, \( \alpha \) the absorption coefficient, and \( z \) the depth in the sample. The factor 2 is caused by the absorption of the incident as well as the scattered light, similar to the formulation of the information depth in equation (2.44). For the decay of the diamond phonon feature an absorption coefficient of \( \alpha_{\text{dia}}=3610\pm50\,\text{cm}^{-1} \) and for the silicon an absorption coefficient of \( \alpha_{\text{sil}}=29050\pm50\,\text{cm}^{-1} \) was obtained. The determined absorption coefficient of silicon corresponds quite good with the literature (36689\pm1\,\text{cm}^{-1} [Asp83]).

In the cross-sectional \( \mu \)-RS scans in this work the diameter of the confocal pinhole CF1 was chosen, considering figure 2.30, between 200\,\mu m and 400\,\mu m. This results in detected sample volumes with diameters in the range of 0.9\,\mu m to 1.5\,\mu m.
Figure 2.31: The measured TO phonon feature intensity (open symbols) due to scattering at the side face. The solid lines represent the simulations using the parameters of figure 2.29 and the equation (2.54).

Figure 2.32: The measured phonon feature intensity variations for the diamond (open circle) and the silicon (open square) phonon feature depending on the microscope stage z movement. The straight lines represent calculations of the intensity variations.
Chapter 3

Material Systems Investigated

In this work a large variety of materials was investigated containing the elements carbon, nitrogen, boron, and silicon, i.e. amorphous carbon, graphite, diamond, cubic boron nitride, hexagonal boron nitride, carbon nitride, and different silicon carbide polytypes. They were investigated as deposited films on silicon substrates as well as single crystals or implanted bulk material.

In this chapter an introduction in these materials and their properties, in particular their Raman features is given. Before the different materials are discussed in detail, the parameters of interest are introduced.

3.1 Introduction

For all materials detailed reviews are published elsewhere (diamond [Sol70, Tui70, Spe89], graphite [Nem79], amorphous and diamond-like carbon [Rob86, Tsa87], silicon carbide [Fel68a, Fel68b, Bul87], carbon nitride [Rie94, Li95] and boron nitride [Hal90, McK90]). For that reason only a short overview on the properties is given.

Table 3.1 lists the values for the fundamental bandgap energy $E_g$, the phonon frequencies at room temperature and atmospheric pressure, the hydrostatic pressure dependence $\frac{\delta \Omega}{\delta P}$, and the linear term of the temperature dependence $A_1$ of the optical phonons. Data of the crystal structure for the materials in table 3.1 are given in the respective sections following this introduction. For silicon carbide (SiC) only the cubic (3C) and a hexagonal (6H) polytype are listed in table 3.1, since these two polytypes are the polytypes discussed in section 5.2. A detailed description of the notation will be given in section 3.2.4. It should be mentioned that the phonon mode assignment (TO,LO) in the case of the 6H-SiC polytype is related to incident light entering the sample along the (0001) crystal direction [Fel68a, Fel68b]. The TO phonon mode for the 6H-SiC, listed in table 3.1, is the strongest of three phonon modes, which will be discussed in more detail in section 3.2.4 [Fel68a, Fel68b, Mea77]. In the case of the
Table 3.1: The fundamental bandgap energy $E_g$ at room temperature (the abbreviations ind. and dir. in the brackets describe whether the gap is indirect or direct, respectively), the phonon frequency position $\Omega_{\text{RT}}$ at room temperature and atmospheric pressure, and the phonon frequency position dependence on hydrostatic pressure $\frac{\partial \Omega}{\partial \rho_{\text{H}}} \text{ at } \text{RT}$ and temperature variation $A_1$ (only the linear term) for the materials investigated in this work. Any data on the crystal structure are given in the respectively section.

<table>
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<tr>
<th>material</th>
<th>$E_g, \text{RT}$ eV</th>
<th>$\Omega_{\text{RT}}$ cm$^{-1}$</th>
<th>$\frac{\partial \Omega}{\partial \rho_{\text{H}}} \text{ cm}^{-1} \text{GPa}$</th>
<th>$A_1 \times 10^{-2} \text{cm}^{-1} \text{K}^{-1}$</th>
<th>reference</th>
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<td>1.12 (ind.)</td>
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<td>5.20</td>
<td>- 2.12</td>
<td>[Wei75, Fen88a, Har70]</td>
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<td>5.50 (ind.)</td>
<td>1332.5</td>
<td>3.20</td>
<td>- 0.67</td>
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<td>graphite</td>
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<td></td>
<td></td>
<td></td>
<td>[Taf65, Han89, Sav86]</td>
</tr>
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<td>3C-SiC</td>
<td>2.41 (ind.)</td>
<td>TO 796.2</td>
<td>3.88</td>
<td>- 2.18</td>
<td>[Bim81, Ole82a, Ole82b]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>LO 972.7</td>
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<td>- 2.90</td>
<td>[Fen88a, Fen88b, Ole82c]</td>
</tr>
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<td>E$_1$(TO) 788</td>
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<td>- 3.00</td>
<td>[Fel68a, Fel68a, Mea77]</td>
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<td></td>
<td>A$_1$(LO) 964</td>
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<td>- 3.10</td>
<td>[Sal91, Liu94]</td>
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<td>cub. BN</td>
<td>6.45 (ind.)</td>
<td>TO 1054.7</td>
<td>3.39</td>
<td>- 1.00</td>
<td>[Gie67, Chr74, San83]</td>
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<td>- 0.92</td>
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<td></td>
<td>E$_{2u}$ 1366.0</td>
<td>4.00</td>
<td>- 1.20</td>
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<td>$\Gamma$</td>
<td>$\Gamma$</td>
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<td></td>
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<td>$\Gamma$</td>
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[Wei75, Fen88a, Har70] [Gri78, Age93, Her93] [Taf65, Han89, Sav86] [Age90, Nem79, Dil84] [Bim81, Ole82a, Ole82b] [Fen88a, Fen88b, Ole82c] [Fel68a, Fel68a, Mea77] [Sal91, Liu94] [Gie67, Chr74, San83] [Alv92, Her93] [Gei66, McK90, Nem81] [Kuz78, Hof84, Exa91] [Liu89, Cor93, Che95] [Yen95, Wad81a, Wer97e] [Li95, Liu90]
C$_3$N$_4$ the different values for the lowest indirect bandgap are obtained from different theories applied for the calculation [Lin90, Cor93]. For the phonon frequency positions the frequency range in which the phonon features should appear for the two listed crystal modifications is given, since up to now only two publications about Raman spectroscopy at crystalline C$_3$N$_4$ are published [Che95, Yen95] (see section 3.2.3). Due to this fact no information about the temperature and the pressure dependence of phonon modes is obtainable. Since in most optical spectroscopy investigations of carbon nitride (see for example [Li95]) only two broad bands at $\approx$1300cm$^{-1}$ and $\approx$1600cm$^{-1}$ are observed (see section 5.5) these band positions are listed, too.

3.2 Material Systems

3.2.1 Carbon

Diamond and graphite are the widest spread pure carbon modifications with well-known crystalline forms. They are the cubic (diamond) and the hexagonal arrangement with planar rings (graphite) of the carbon atoms. However, there exist different additional carbon polytypes e.g. lonsdaleite, which are not as common [Ber81, Kni89, Spe89, Spe90]. The lonsdaleite exhibits a structure close to that of diamond with similar properties and thus is often called hexagonal diamond. Figure 3.1 shows the crystal structures of cubic and hexagonal diamond (lonsdaleite) and graphite [Spe89, Kni89]. In contrast to the planar hexagonal rings in the graphite modification the hexagonal rings in the cubic and the lonsdaleite diamond polytype are non-planar but puckered [Spe89, Spe90]. In the cubic polytype they have the so-called chair form while the lonsdaleite polytype is build of the chair as well as the so-called boat form rings (see the atom arrangement in figure 3.1). Table 3.2 lists the crystal structure data for the diamond polytypes and the graphite [Spe89, Kni89]. Each of these

<table>
<thead>
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<th>property</th>
<th>diamond</th>
<th>lonsdaleite</th>
<th>graphite</th>
</tr>
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<td>symmetry</td>
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</tr>
<tr>
<td>space group</td>
<td>O$_h$</td>
<td>D$_{6h}$</td>
<td>D$_{6h}$</td>
</tr>
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<td>atoms per unit cell</td>
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<td></td>
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</tbody>
</table>

modifications and polytypes of carbon is formed from carbon hybridized in a $sp^3$, $sp^2$, or $sp$ state. The $sp$ states form the so-called carbynes which are cross-linked linear carbon chains. The crystal structures of the diamond polytypes are completely formed from tetrahedrally bonded $sp^3$ carbons. In contrast to this the graphite modification is completely formed by $sp^2$ bonded carbon atoms. These $sp^2$ bondings form the planar benzene-like rings, while
3.2. MATERIAL SYSTEMS

Figure 3.1: Schematic diagrams of the unit cells of the cubic (a) and hexagonal (lonsdaleite) diamond (b) and graphite (c) [Spe89, Kni89]. In the case of the diamond polytypes one tetrahedron is shown and below the unit cells the atom arrangement is added. The shaded regions give the form of the non-planar hexagonal rings in these polytypes [Spe89].

The bonds between the planar rings are formed by weak van-der-Waals-bondings. The short carbon-carbon distance in the rings reflects the aromatic character and is responsible for the high frequency of the crystalline graphite band in the Raman spectrum (see figure 3.2). But the very weak van-der-Waals-bonding between these planar rings often leads to a high disorder along the c-axis. The degree of this disorder along the c-axis gives rise to the definition of the four graphite forms [Tui70, Kni89]: (i) If the ordering is very good for nearly the whole sample the graphite is called **highly oriented pyrolytic graphite** (HOPG). It is the synthetic form close to single crystalline graphite [Kni89]. (ii) In **polycrystalline graphite** the region of the ordering along the c-axis is reduced to 1-10μm [Tui70]. (iii) If the ordering is fully disappeared along the c-axis, the planar rings are still parallel but they are randomly rotated. This form is called **turbostratic graphite** [Kni89]. (iv) If the parallel ordering of the planar rings is as well removed the graphite is **amorphous** [Tui70, Kni89]. Due to the weak bonding along the c-axis graphite can very easily be cleaved parallel to the planar rings. Figure 3.2 shows the Raman spectra of a cubic diamond single crystal (a), of hexagonal diamond (lonsdaleite) powder [Kni89], of HOPG (c), and of polycrystalline graphite. For single crystal diamond only the triply degenerated zone center phonon (T_{2g}) at 1332.5cm\(^{-1}\) can be observed (spectrum (a)) since diamond is centrosymmetric and non-polar.

In the lonsdaleite the irreducible representation is given by [Kni89, Spe90]:

\[
\Gamma = 1A_{1g} + 1B_{2g} + 1E_{1g} + 1E_{2g} + 1B_{1u} + 1E_{2u}
\]
CHAPTER 3. MATERIAL SYSTEMS INVESTIGATED

Figure 3.2: Raman spectra for a cubic diamond single crystal (a), hexagonal diamond (lonsdaleite) powder (b) [Kni89], a high quality graphite crystal (c), and polycrystalline graphite (d).

Three Raman-active modes exist ($A_{1g}$, $E_{1g}$, and $E_{2g}$) with the $A_{1g}$ and the $E_{2g}$ mode corresponding to the triply degenerated stretching mode of cubic diamond, here splitted into a component vibrating in plane of the hexagonal layers, formed by the puckered rings, and a component vibrating perpendicular to these hexagonal layers, respectively. Since the bonding strength of hexagonal diamond is comparable parallel and perpendicular to the hexagonal layers the wavenumber separation between these two modes is quite small thus forming a single but broad band at $\approx 1310\text{cm}^{-1}$ (spectrum (b)), since in the measured powder the phonon features are broaden [Kni89]. The third Raman phonon mode $E_{1g}$ is a shear mode which appears in the low frequency range, but could not be observed until now, since this mode disappears with any disorder in the stacking sequence [Kni89]. The modes $B_{2g}$, $B_{1u}$, and $E_{2u}$ are optically inactive and can only be observed by neutron scattering. For that reason lonsdaleite, like cubic diamond, has no first order infrared absorption.
For graphite the irreducible representation gives 6 phonon modes [Kni89, Nem79]:

$$\Gamma = 2E_{2g} + 1A_{2u} + 1E_{1u} + 2B_{2g}$$

The two $E_{2g}$ modes are Raman active and have been observed at 42 cm$^{-1}$ and 1581 cm$^{-1}$, respectively. They correspond to the interplanar "rigid-layer shear" mode and the "in-plane" C-C stretching mode in the hexagonal layers, respectively. In the spectrum (c) in figure 3.2 only the higher frequency phonon mode is shown. The $A_{2u}$ and the $E_{1u}$ phonon modes are infrared active while the two $B_{2g}$ are optically inactive. Similar to the lonsdaleite shear phonon mode at low frequencies the graphite shear layer mode is hardly observable if any disorder occurs in the stacking sequence. The two bands observable in the polycrystalline graphite (see spectrum (d)) correspond to the crystalline graphite band of spectrum (c) which is called G-band (1580.3 cm$^{-1}$). In addition a weak shoulder on the high frequency side of the G-band is observable. It is correlated to disorder induced Raman scattering, as described in section 2.1.2, at the maximum between $\Gamma$- and $\text{M}$-point of the phonon dispersion relation of graphite [Nem79]. The frequency position of this maximum is about 1620 cm$^{-1}$ which correlates very well with the measured value of 1619.1 cm$^{-1}$. Additionally this disorder induced Raman scattering over the whole Brillouin zone is responsible for the appearance of the second distinct band visible in figure 3.2d. It is thus called disorder band $\Delta$ D-band (1365.9 cm$^{-1}$). This band is correlated to highly disordered graphite which only shows the correct coordination to its next neighbours and is correlated to maxima in the phonon density of states around 1350 cm$^{-1}$[Nem79].

### 3.2.2 Boron Nitride

Boron nitride (BN) in the crystalline form has four modifications, with the hexagonal (h-BN) and the zincblende or cubic (c-BN) [Mck90] structure being the most important ones. BN also crystallizes in a wurtzite structure (w-BN) [Mck90, Kes87]. The formation enthalpy of this modification is rather low and thus w-BN up to now only was observed in ion beam assisted depositions of BN films [Mck90]. In addition, a rhombohedral modification is observed (r-BN) [Ish81]. Since very little information is available and no rhombohedral BN was observed in this work this modification will not be discussed in further detail. Figure 3.3 sketches the crystalline structure of c-BN, h-BN, and w-BN [Gei66, Mck90]. Similar to the carbon modifications the layers in the BN modification are formed either by puckered rings completely in the chair form (cubic), by puckered rings in the chair form as well as in the boat form (wurtzite), or by planar rings (hexagonal). In figure 3.3 the wurtzite crystal structure (c) corresponds to the lonsdaleite structure of figure 3.1. For clearance another viewpoint was chosen. The planar rings in the case of the hexagonal modification are again formed by the $sp^2$ hybridized bonds while the $sp^3$ hybridized bonds are responsible for the formation of the c-BN as well as the w-BN. Table 3.3 lists the crystal structure data for c-BN, h-BN, and w-BN [Paa52, Bun63, Gie67, Her93]. The summation in the line "atoms per unit cell" means the two different sorts of atoms in the sublattices. Comparing the lattice constants of table 3.2 and 3.3 the values for the BN modifications are slightly smaller than those of
Figure 3.3: Sketch of the crystal structures of c-BN (a), h-BN (b), and w-BN (c) [Gei66, McK90].

Table 3.3: Crystal structure data for the boron nitride modifications [Pea52, Bun63, Gie67, Her93].

<table>
<thead>
<tr>
<th>property</th>
<th>c-BN</th>
<th>h-BN</th>
<th>w-BN</th>
</tr>
</thead>
<tbody>
<tr>
<td>symmetry</td>
<td>cubic</td>
<td>hexagonal</td>
<td>hexagonal</td>
</tr>
<tr>
<td>space group</td>
<td>Td</td>
<td>Dhh</td>
<td>C4v</td>
</tr>
<tr>
<td>atoms per unit cell</td>
<td>4+4</td>
<td>2+2</td>
<td>2+2</td>
</tr>
<tr>
<td>lattice constant (Å)</td>
<td>3.615</td>
<td>a=2.504</td>
<td>a=2.55</td>
</tr>
<tr>
<td></td>
<td></td>
<td>c=6.661</td>
<td>c=4.20</td>
</tr>
</tbody>
</table>

The carbon modifications. These differences are induced by the mixed covalent-ionic bonding while the bonding in the carbon modifications is completely covalent. For that reason the BN modifications have lower mechanical strength and thermal conductivity than carbon. But due to the small differences the properties of BN are close to carbon [Ric95].

In contrast to the carbon modifications the BN modifications are polar due to the boron and nitrogen atoms on the lattice sites. As a result the triple degeneration of the optical phonons in the cubic modification is lifted leading to a splitting of the LO and TO phonon modes with the frequency position of the LO mode at higher energies than the TO mode [Ana80, Bru82]. Figure 3.4 shows the Raman spectra of a c-BN single crystal of 1mm size (a), a polycrystalline h-BN sputter target (b), and a polycrystalline and randomly orientated w-BN powder of submicrometer size, taken from [McN94] (c). Clearly the splitting of the LO and the TO phonon in the c-BN (a) can be observed. Only two phonon modes are visible
in the spectrum since the TO phonon mode is still doubly degenerated [Lou64, Bru82]. The frequency positions of the TO and the LO phonon modes with $F_{2g}$ symmetry are $1056.4\text{cm}^{-1}$ and $1305.5\text{cm}^{-1}$, respectively [Her93].

H-BN has the irreducible representation [Nem81]:

$$\Gamma = 2E_{2g} + 1A_{2u} + 1E_{1u} + 2B_{1g}$$

Of these, the two $E_{2g}$ modes are Raman active, the $A_{2u}$ and the $E_{1u}$ are infrared active, while the two $B_{1g}$ are optically inactive. The Raman spectrum obtained from polycrystalline h-BN material is given in figure 3.4b. The investigated material was taken from a magnetron sputter target of high crystalline quality and purity. As in the case of graphite the high frequency position of the $E_{2g}$ ”in-plane” mode ($1366.2\text{cm}^{-1}$) reflects the very strong bonding in the plane of the planar hexagonal rings. The low frequency ($51.8\text{cm}^{-1}$) of the $E_{2g}$ ”rigid layer shear” phonon mode is again due to the weak van-der-Waals bonding between the

Figure 3.4: Raman spectra for a c-BN single crystal of 1mm size (a), a polycrystalline h-BN sputter target (b), and a w-BN powder of submicrometer size [McN94] (c).
hexagonal rings [Kuz78, Nem81]. In figure 3.4b only the high frequency phonon mode is shown.

For the w-BN only one publication deals with Raman measurements of a submicrometer and randomly orientated powder of which the spectrum given in figure 3.4c was taken from [McN94]. The irreducible representation is [McN94]:

$$\Gamma = 2E_2 + 1A_1 + 1E_1 + 2B_1$$

The two $E_2$, the $A_1$, and the $E_1$ phonon modes are Raman active, the $A_1$ and the $E_1$ phonon modes are also infrared active, while the $B_1$ phonon mode is optically inactive. Although three distinct peaks with frequency positions of about $950.7\text{cm}^{-1}$, $1012.1\text{cm}^{-1}$, and $1294.5\text{cm}^{-1}$ and an additional shoulder on the high frequency side of the most intense peak at $1045.6\text{cm}^{-1}$ can be observed, no symmetry assignments were made, due to the random orientation of the crystallites [McN94].

### 3.2.3 Carbon Nitride

The existence of carbon nitride was predicted theoretically before any experimental effort was done to produce such a material [Liu89, Liu90, Che95]. Since the carbon sits in a 4-fold and nitrogen in a 3-fold coordinated site the chemical formation is given by $C_3N_4$ [Liu90]. Thus the $C_3N_4$ crystallizes in two structures similar to $Si_3N_4$ [Liu89, Liu90]. These structures, called $\alpha$-$C_3N_4$ and $\beta$-$C_3N_4$ are formed by CN tetrahedra linked with threefold coordinated nitrogens NC$_3$. The structure for $\beta$-$C_3N_4$ is given in figure 3.5 [Cor93, Rie94]. Carbon atoms are shown as filled spheres. Each carbon atom has four nearest-neighbor nitrogen atoms forming an almost regular tetrahedron while each nitrogen has three nearest-neighbour carbon atoms forming $120^\circ$ bond angles. X-ray diffraction measurements reveal the hexagonal beryllium silicate (Be$_2$SiO$_4$) crystal structure [Rie94].

![Figure 3.5: Crystal structure of $\beta$-$C_3N_4$. The filled spheres give the carbon atoms [Cor93, Rie94]. In the case of the $\alpha$-$C_3N_4$ an intermediate double layer is introduced rotated by $60^\circ$ [Wad81a].](image)
with their three neighbouring carbon atoms form a layer, which is linked to a second layer formed by the carbon-nitrogen tetrahedra. These double layers give the structure of the $\beta$-C$_3$N$_4$ in an ABAB... sequence [Wad81a]. In the case of the $\alpha$-C$_3$N$_4$ an additional double layer rotated by 60° is introduced between these layers leading to a stacking sequence of ABCDABCD... [Wad81a]. Since the crystal structure of the $\beta$-C$_3$N$_4$ in figure 3.5 is already quite complicated, the crystal structure of $\alpha$-C$_3$N$_4$ is not shown. For details see references [Har57, Wyc66]. Table 3.4 lists the structure data for the $\alpha$- and the $\beta$-modification of C$_3$N$_4$.

Table 3.4: Crystal structure data for the C$_3$N$_4$ modifications [Cor93, Rie94].

<table>
<thead>
<tr>
<th>property</th>
<th>$\alpha$-C$_3$N$_4$</th>
<th>$\beta$-C$_3$N$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>symmetry</td>
<td>hexagonal</td>
<td>hexagonal</td>
</tr>
<tr>
<td>space group</td>
<td>C$_{3v}$</td>
<td>C$_{6h}$</td>
</tr>
<tr>
<td>atoms per unit cell</td>
<td>12+16</td>
<td>6+8</td>
</tr>
<tr>
<td>lattice constant (Å)</td>
<td>a=6.56</td>
<td>a=6.44</td>
</tr>
<tr>
<td></td>
<td>c=2.51</td>
<td>c=2.46</td>
</tr>
</tbody>
</table>

[Cor93, Rie94]. Due to its much more complicated crystal structure C$_3$N$_4$ exhibits a large variety of possible phonon modes. N. Wada et al. [Wad81a] reports a group theoretical analysis for the irreducible representation:

$\alpha$-C$_3$N$_4$: $\Gamma = 14A_1 + 14A_2 + 28E$

$\beta$-C$_3$N$_4$: $\Gamma = 4A_g + 3B_g + 2E_{1g} + 5E_{2g} + 3A_u + 4B_u + 5E_{1u} + 2E_{2u}$

Surprisingly these irreducible representations do not follow the rule, that 3N phonon modes are possible with N the number of atoms in the elementary cell, since $\alpha$-C$_3$N$_4$ has N=14 atoms and $\beta$-C$_3$N$_4$ N=7 atoms resulting in 42 and 21 phonon modes, respectively. However, since no own group theoretical analysis was performed, here the results of Wada et al. [Wad81a] are given. Considering the $\alpha$-C$_3$N$_4$ the $A_1$ and the $E$ modes are Raman as well as infrared active. One of each phonon modes is an acoustical phonon mode and thus generally not detectable in a Raman experiment. The $A_2$ phonon modes are silent. For that reason 40 Raman active phonon modes are expected [Wad81a]. In the case of the $\beta$-C$_3$N$_4$ the $A_g$, the $E_{1g}$, and the $E_{2g}$ phonon modes are Raman active yielding 11 Raman active modes. The $A_u$ and the $E_{1u}$ are infrared active giving 6 infrared phonon modes since one of the $A_u$ and one the $E_{1u}$ are acoustical phonon modes. The remaining phonon modes are silent [Wad81a].

Figure 3.6 shows the Raman spectrum of a nominal $\beta$-C$_3$N$_4$ deposit on a silicon substrate taken from Chen et al. [Che95]. Up to 21 Raman modes can be observed easily with frequency positions given in Table 3.5. Several very weak structures are also visible but not listed in the table. Obviously most of the observed structures visible in the C$_3$N$_4$ crystals can be correlated either to $\alpha$-Si$_3$N$_4$ or $\beta$-Si$_3$N$_4$, since the silicon substrate reacts with the nitrogen of the deposited C$_3$N$_4$ [Che95]. The remaining phonon features cannot be correlated with phonon frequencies of other possible reaction products like silicon carbide (see table 3.7 in section 3.2.4). The arrows in figure 3.6 mark the phonon features which cannot be related
Figure 3.6: The Raman spectrum of nominal C₃N₄ taken from Chen et al. [Che95]. The silicon first order optical phonon feature was truncated since its intensity is several orders of magnitudes higher than the other phonon features.

either to α- or β-Si₃N₄. Although the Si₃N₄ spectra are taken from single crystalline material the very low crystalline quality and the intrinsic stress of the material disables any assignment to group theoretically determined phonon modes [Wad81a]. It should be mentioned, that a lot of the phonon features observable in figure 3.6 correlate to the silicon substrate [Tem73, Zwi93] (first order optical phonon mode - around 520 cm⁻¹ - and second order phonon modes - around 300 cm⁻¹ and between 950 and 1050 cm⁻¹ -). They were not considered in table 3.5. Due to these correlations to silicon and Si₃N₄ the C₃N₄ Raman spectrum of Chen et al. [Che95] has to be used carefully. Up to now only a second publication shows Raman spectra for crystalline C₃N₄ deposits [Yen95]. T.-Y. Yen [Yen95] measured their spectra at films deposited on nickel substrates. They do not observe all the predicted phonon features but only a few features around 300 cm⁻¹. A further discussion of these results will be given in the section 5.5 in comparison to the results obtained in this work.

The main problem for the production of C₃N₄ films is the increase of the nitrogen content to the correct stoichiometry [Li95, Fri97a] and the deposited material is thus usually called CNₓ. The Raman spectroscopy investigations of such samples only exhibit broad features around 1300 cm⁻¹ and 1600 cm⁻¹. In figure 3.6 both bands can be observed, too. The bands are related to the D-band and G-band of amorphous carbon (see section 3.2.1). Nevertheless, investigations by infrared spectroscopy, x-ray photoelectron spectroscopy, and elastic recoil detection analysis shows C-N, C= N, and C≡N bondings in the films [Kau89, Che95, Fri97a].
Table 3.5: Raman frequencies obtained from the Raman spectrum given by Chen et al. [Che95].
For comparison the Raman frequencies of $\alpha$-Si$_3$N$_4$ and $\beta$-Si$_3$N$_4$ are given taken from Wada et al. [Wad81a].

<table>
<thead>
<tr>
<th>C$_3$N$_4$</th>
<th>$\alpha$-Si$_3$N$_4$</th>
<th>$\beta$-Si$_3$N$_4$</th>
<th>C$_3$N$_4$</th>
<th>$\alpha$-Si$_3$N$_4$</th>
<th>$\beta$-Si$_3$N$_4$</th>
</tr>
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<tr>
<td>153</td>
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<td>514</td>
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<td>392</td>
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<td>951</td>
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<td>1107</td>
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<td></td>
<td>1142</td>
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<td>487</td>
<td>470</td>
<td></td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>

3.2.4 Silicon Carbide

Similar to the diamond polytypes silicon carbide (SiC) exists in a large variety of polytypes [Spe90, Ver66]. Up to now more than 200 polytypes are reported. The structure of these polytypes has been determined mainly by x-ray diffraction analysis [Fre92]. But in recent years great effort was done to apply Raman spectroscopy to the polytype determination of SiC since the pioneer work of Feldman et al. [Fel68a, Fel68b, Nak86, Nak87, Nak89a, Nak89b, Nak91, Nak94]. In this subsection at first a short introduction to this polytypism is given followed by the discussion of the common polytypes 3C, 4H, 6H, 15R, and 21R.

The structure of SiC polytypes can be viewed as stacking SiC double layers on top on one another along the c-direction (0001). There are several notations to describe polytypes [Fre92, Nak94]. Atomic position of the Si-C pairs, the Si or C atoms in a double layer, is indicated by A, B, and C. The 6H polytype is represented by ABCACB and the 15R polytype by ABACBCACBABCBCBAC. Although the ABC notation gives a complete description of the structure, it is too difficult for longer period polytypes like 132R. Ramsdell represented a
SiC polytype by the number of layers in the unit cell and added to it the letter H or R to specify the lattice type. Thus a symbol nH represents a structure with an n-layered repeat period along the c-direction and a primitive hexagonal lattice, while 3nR denotes a structure with a 3n-layered periodicity along the c-direction and a primitive rhombohedral cell, with n a natural number. This notation is too simple to describe polytypes which have the same unit cell size but different stacking sequences. This problem occurs in the polytypes with large stacking sequences, for example 51R with seven possible stacking sequences given in the Zhdanov notation by (433222)\(3n\), (433222)\(3\), (423222)\(3\), (443222)\(3\), (432422)\(3\), (424232)\(3\), or (424232)\(3\) [Nak94]. The Zhdanov notation is especially suitable for describing polytypes with known stacking structure. All atoms in SiC polytypes lie in (11\(\overline{2}\)) planes, and on these planes the atoms lie in zigzag patterns characteristic of the stacking, as can be seen for 3C, 4H, 6H, 15R, and 21R in Figure 3.7. In the 6H polytype the sequence moves three positions to the righthand side (A→B→C→A) before reversing and moving three positions to the lefthand side (A→C→B→A). Zhdanov represented the sequence in the zigzag movement by the number of steps to the right- and to the lefthand sides. In this notation the 6H polytype is indicated by 33. Since in this work only shorter period SiC polytypes (3C to 21R) are investigated, the Ramsdell notation will be used.

One of the investigated polytypes is cubic (3C), two (4H and 6H) are hexagonal, and two (15R and 21R) are rhombohedral. Table 3.6 lists the structure data for all the investigated polytypes [Fel68a, Fel68b]. The lattice constants are given in the so-called hexagonal representation in which the lattice constant is calculated by multiplying the distance between the SiC double layers (2.517 Å) with the Ramsdell number. For that reason the lattice constants are proportional to the number in the Ramsdell notation [Sha69]. Additionally the lattice

![Figure 3.7: Zigzag sequences of Si and C atoms in the (11\(\overline{2}\)) plane along the (0001) direction. The atoms are represented by the larger open and the smaller filled spheres, respectively. The notation is referred to the Ramsdell notation used in this work. In addition, the Zhdanov notation is shown in brackets.](image-url)
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Table 3.6: Crystal structure data for the investigated SiC polytypes [Fel86a, Fel86b, Sha69]. The lattice constants are given in the hexagonal representation.

<table>
<thead>
<tr>
<th>property</th>
<th>3C</th>
<th>4H</th>
<th>6H</th>
<th>15R</th>
<th>21R</th>
</tr>
</thead>
<tbody>
<tr>
<td>symmetry</td>
<td>cubic</td>
<td>hexagonal</td>
<td>hexagonal</td>
<td>rhombohedral</td>
<td>rhombohedral</td>
</tr>
<tr>
<td>space group</td>
<td>$T_d^2$</td>
<td>$C_{6v}^4$</td>
<td>$C_{6v}^4$</td>
<td>$C_{3v}^5$</td>
<td>$C_{3v}^5$</td>
</tr>
<tr>
<td>atoms per unit cell</td>
<td>4+4</td>
<td>4+4</td>
<td>6+6</td>
<td>5+5</td>
<td>7+7</td>
</tr>
<tr>
<td>lattice constant (Å)</td>
<td>$a=3.083$</td>
<td>$a=3.076$</td>
<td>$a=3.081$</td>
<td>$a=3.080$</td>
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<td>$c=7.551$</td>
<td>$c=10.053$</td>
<td>$c=15.079$</td>
<td>$c=37.70$</td>
<td>$c=52.78$</td>
</tr>
<tr>
<td></td>
<td>$a_c=4.359$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$a_{\text{rho}}=12.69$</td>
<td>$a_{\text{rho}}=17.683$</td>
</tr>
</tbody>
</table>

Due to the increased periodicity for polytypes with larger stacking sequences the Brillouin zone dimension has to be reduced. This can be represented by a shifting of the next Brillouin zones towards the $\Gamma$-point, which can also be described in the first Brillouin zone as a "folding" into the reduced Brillouin zone [Nak86, Nak89a, Nak89b]. This folding of the Brillouin zone is also applied for the superlattices [Mil89, Jus89]. In the following text the term folding will be used since it is more common than the shifting. Due to this folding the phonon modes of other points in the Brillouin zone are now located in the Brillouin zone center. Since the Raman scattering process in these crystalline materials involves only phonon modes at the $\Gamma$-point (phonon quasi momentum $q_{\Gamma}\approx 0$) these additional phonon branches in the Brillouin

![Figure 3.8](image-url)
zone center result in an increased number of possible phonon features in the Raman spectra. Figure 3.8 shows on the left hand side the large Brillouin zone which means that the reduced Brillouin zone for polytypes with longer stacking sequences was extended to the dimension of the basic Brillouin zone of the 3C-SiC. This is possible since the lattice constant \( c \) of the polytypes is proportional to the number in the Ramsdell notation \( n \) (see Table 3.6). For that reason phonon modes of the \( m^{th} \) folded mode of a long-period polytype correspond to the phonon mode of the basic polytype with a reduced wavevector \( 2m/n \) of the Brillouin zone of the basic polytype. Here \( m \) is an integer between 0 and \( \frac{n}{2} \). For example in the 15R polytype \( n \) is 5 and thus \( m=0, 1, 2 \) resulting in new phonon modes at \( x=q/q_{\text{max}}=0, 0.4, \) and 0.8 [Fel68b]. This is visualized on the right hand side of figure 3.8. The phonon dispersion branches are folded to the reduced Brillouin zone. Due to this, additional phonon modes are obtainable at \( x=0 \). In figure 3.9 and figure 3.10 Raman spectra obtained for the investigated SiC polytypes are given. Clearly the increasing number of folded phonon modes in the TO phonon mode

![Figure 3.9: Raman spectra measured in the frequency range of the TO phonon modes for all investigated SiC polytypes.](Image)

...
range with increasing Ramsdell number is observable. The intensity of the folded phonon modes can be calculated in the bond polarization model described in detail by Nakashima et al. [Nak86, Nak89a, Nak89b]. The Raman scattering intensity depends on the bond Raman polarizability and the relative displacement of neighboring atoms relevant to the bond. In the figures 3.9 and 3.10 the measured Raman spectra in the TO region of the different polytypes and the folded acoustical phonon modes of the 15R-SiC polytype are shown, respectively. The measured phonon frequencies correlate excellently with the measured and calculated phonon mode frequencies of Nakashima et al. [Nak89a] and the measurements of Feldman et al. [Fel68b]. The calculation of the phonon mode frequencies uses a linear chain model for which the eigenvalue problem has to be solved [Nak86]. In the case of the folded modes around 250 cm$^{-1}$ the splitting is only 4 cm$^{-1}$ (meas.) or 2 cm$^{-1}$ (calc.). For that reason these two modes hardly can be separated. The phonon modes in figure 3.9 can be assigned as given in Table 3.7. Since the cubic Brillouin zone is the basic Brillouin zone only one TO phonon is observable. In the case of the other investigated polytypes the irreducible representations are [Fel68a, Fel68b]:

- **4H:** $\Gamma = 4(A_1 + B_1 + E_1 + E_2)$
- **6H:** $\Gamma = 6(A_1 + B_1 + E_1 + E_2)$
- **15R:** $\Gamma = 10(A_1 + E)$
- **21R:** $\Gamma = 14(A_1 + E)$

Due to the reduction of symmetry the axial modes $A_1$ and $B_1$ both reduces to $A_1$ and the planar modes $E_1$ and $E_2$ both reduces to $E$ modes. These phonon mode frequencies for the different $x$ in Table 3.7 are given in figure 3.8 as the open symbols.
Table 3.7: Phonon mode assignments and their frequencies in cm\(^{-1}\) for the investigated polytypes [Fe68a, Fe68b].

<table>
<thead>
<tr>
<th>polytype</th>
<th>(x=q/q_{\text{max}})</th>
<th>planar acoustic</th>
<th>axial acoustic</th>
<th>planar optic</th>
<th>axial optic</th>
</tr>
</thead>
<tbody>
<tr>
<td>3C</td>
<td>0</td>
<td>(F_{2g}) 0</td>
<td>(F_{2g}) 0</td>
<td>(F_{2g}) 796</td>
<td>(F_{2g}) 973</td>
</tr>
<tr>
<td>4H</td>
<td>0</td>
<td>(E_1) 0</td>
<td>(A_1) 0</td>
<td>(E_1) 788</td>
<td>(A_1) 964</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>(E_2) 196</td>
<td>(B_1) forbidden</td>
<td>(E_2) 773</td>
<td>(B_1) forbidden</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>(E_1) 196</td>
<td>(A_1) 610</td>
<td>(E_1) 767</td>
<td>(A_1) 838</td>
</tr>
<tr>
<td>6H</td>
<td>0</td>
<td>(E_1) 0</td>
<td>(A_1) 0</td>
<td>(E_1) 788</td>
<td>(A_1) 964</td>
</tr>
<tr>
<td></td>
<td>0.33</td>
<td>(E_2) 145</td>
<td>(B_1) forbidden</td>
<td>(E_2) 787</td>
<td>(B_1) forbidden</td>
</tr>
<tr>
<td></td>
<td>0.67</td>
<td>(E_1) 236</td>
<td>(A_1) 504</td>
<td>(E_1) 769</td>
<td>(A_1) 889</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>(E_2) 262</td>
<td>(B_1) forbidden</td>
<td>(E_2) 766</td>
<td>(B_1) forbidden</td>
</tr>
<tr>
<td>15R</td>
<td>0</td>
<td>(E) 0</td>
<td>(A_1) 0</td>
<td>(E) 788</td>
<td>(A_1) 964</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>(E) 167</td>
<td>(A_1) 331</td>
<td>(E) 782</td>
<td>(A_1) 932</td>
</tr>
<tr>
<td></td>
<td>0.8</td>
<td>(E) 172</td>
<td>(A_1) 337</td>
<td>(E) 785</td>
<td>(A_1) 938</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>(E) 254</td>
<td>(A_1) 569</td>
<td>(E) 768</td>
<td>(A_1) 858</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>(E) 256</td>
<td>(A_1) 577</td>
<td>(E) 769</td>
<td>(A_1) 860</td>
</tr>
<tr>
<td>21R</td>
<td>0</td>
<td>(E) 0</td>
<td>(A_1) 0</td>
<td>(E) 788</td>
<td>(A_1) 964</td>
</tr>
<tr>
<td></td>
<td>0.29</td>
<td>(E) 126</td>
<td>(A_1) 241</td>
<td>(E) 794</td>
<td>(A_1) 947</td>
</tr>
<tr>
<td></td>
<td>0.57</td>
<td>(E) 132</td>
<td>(A_1) 242</td>
<td>(E) 796</td>
<td>(A_1) 949</td>
</tr>
<tr>
<td></td>
<td>0.86</td>
<td>(E) 217</td>
<td>(A_1) 453</td>
<td>(E) 781</td>
<td>(A_1) 906</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>(E) 219</td>
<td>(A_1) 455</td>
<td>(E) 783</td>
<td>(A_1) 908</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>(E) 258</td>
<td>(A_1) 591</td>
<td>(E) 764</td>
<td>(A_1) 849</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>(E) 260</td>
<td>(A_1) 592</td>
<td>(E) 767</td>
<td>(A_1) 850</td>
</tr>
</tbody>
</table>

Depending on the so-called propagation angle \(\Theta\) the phonon modes of Table 3.7 change their character from longitudinal to transversal [Lou64, Kuz89]. This propagation angle is defined by the angle between the direction of the incident light beam and the c-axis of the investigated polytype. In addition, the phonon modes for \(x=0\) show a dependence in their phonon frequencies on the propagation angle [Lou64, Fe68a]. These dependences of the phonon mode frequency are given in the following formulas originally evaluated by R. Loudon [Lou64]:

\[
\begin{align*}
\Omega_{T}(\Theta) &= \sqrt{\Omega_{T||}^{2} \sin^{2} \Theta + \Omega_{T\perp}^{2} \cos^{2} \Theta} \\
\Omega_{L}(\Theta) &= \sqrt{\Omega_{L||}^{2} \cos^{2} \Theta + \Omega_{L\perp}^{2} \sin^{2} \Theta}
\end{align*}
\]

with \(\Omega_{||}\) the phonon mode frequency for \(\Theta=0^\circ\) and \(\Omega_{\perp}\) the phonon mode frequencies for \(\Theta=90^\circ\) [Lou64, Fe68a]. This frequency variation is caused by the crystal anisotropy and is quite small but detectable. For example in the 6H polytype \(\Omega_{L||}=964\text{cm}^{-1}\), \(\Omega_{L\perp}=973\text{cm}^{-1}\),
\[ \Omega_{T\parallel} = 788 \text{cm}^{-1}, \quad \text{and} \quad \Omega_{T\parallel} = 796 \text{cm}^{-1} \] [Fel68a]. In Table 3.7 the frequency positions for \( \Theta = 0^\circ \) are used at \( x = 0 \) since these values correlate to the phonon mode assignments of the other phonon modes in the table. This optical anisotropy is only measured for the 6H-SiC polytype [Fel68a]. For that reason the frequency positions of the 6H polytype are given in table 3.7. The appearance of the phonon modes in the measured Raman spectra can be controlled by varying the polarization configuration [Kuz89].
Chapter 4

Sample Preparation

In this work mainly samples produced by other groups were investigated. For the deposition of these samples two vapour deposition techniques were applied. There exist different chemical vapour deposition techniques [Kob88, Web92, Kla93, Lau93, Roe95, Ric96], magnetron sputtering [Hah97b], and ion implantation [Rot92, Hee95a]. Since these techniques are described in detail elsewhere, in this chapter only a short overview over the specific problems and the experimental setups is given. For the growth of the bulk single crystals, investigated additionally in the case of the c-BN, the high pressure - high temperature synthesis (HPHT) was used [Wei89].

4.1 High pressure - high temperature (HPHT) synthesis

The HPHT synthesis utilizes pressures in the range of several GPa and temperatures in the range of 1000-3000 K to crystallize single crystalline material, in our case c-BN. As starting material the hexagonal phase in combination with different metallic catalysts is used [Sol94]. This synthesis was established since the first calculations of the p,T-diagram for boron nitride yields that c-BN is for no pressure value the stable phase for all temperatures. For that reason high pressures and high temperatures have to be applied to transform the hexagonal to the cubic phase. Figure 4.1 shows the phase p,T-diagram of the boron nitride system [Bun63, Sol88, Sol94]. Two different predictions are made for the boron nitride system: (i) The original work by Bundy and Wentorf [Bun63] and (ii) a newer investigation by Solozhenko [Sol88]. The theory of Bundy and Wentorf predicts, that the c-BN is never the stable phase for all temperatures at atmospheric pressure. First at a pressure of at least 1.2 GPa c-BN can be produced. For that reason the HPHT synthesis was introduced to produce c-BN single crystals. Due to the extreme environmental conditions necessary in the synthesis only small crystals with a size of at maximum a few millimeters can be produced [Wei89]. They are used
for example as coverage for drills or cutting tools. Newer calculations and experiments by Solozhenko [Sol88] predict the cubic phase to be the thermodynamical stable boron nitride phase at room temperature. Nevertheless the HPHT synthesis is still used to produce single crystalline material since the low pressure deposition of boron nitride by vapour deposition techniques as thin films still results in polycrystalline material.

4.2 Chemical Vapour Deposition (CVD)

In this growth process the reactant materials (precursors) are offered to the substrate in gaseous form from a vapour. The materials start to react chemically in the vicinity of the heated substrate or on its surface. Different CVD processes are known. A short overview of three of them will be given for material systems investigated in this work: Organic CVD for the silicon carbide deposition on silicon and microwave assisted plasma CVD and hollow cathode arc discharge CVD for the diamond deposition on silicon.

4.2.1 Organic CVD

In this CVD process the precursors for samples like silicon carbide layers on silicon are organic materials (hydrides like silan, methane, ethane, acetylene, etc.) and thus the process is called organic CVD. The precursors added to a carrier gas which is mostly hydrogen at an operating pressure of about 1000Pa. The partial pressures of the precursors are at
the order of some hundred Pa and thus the total pressure is dominated by the carrier gas. The precursor ratio SiH$_4$/CH$_4$ is 1:1 and thus the ratio of the precursors to the carrier gas (SiH$_4$+CH$_4$)/H$_2$ is about 1:40. The substrate is heated to the growth temperature ranging from some hundreds °C to more then 1000°C. The growth temperature is chosen depending on the stability of the substrate and the desired deposit material. In the case of cubic silicon carbide growth on silicon the growth temperature lies between 1300°C and 1400°C. Depending on the substrate temperature the growth rate of this material can be manipulated, since the adsorbed molecules and the reaction products can desorb again [Web92, Ric96].

To increase the film quality usually the substrates were pretreated before the film growth starts [Web92]. They were thermally etched by heating them up to 1250°C in a high vacuum. Afterwards the surface of the substrates were converted into silicon carbide by exposing them to the gas flow while heating up from 500°C to the growth temperature.

Considering diamond deposition CVD techniques were shown to be successfull in preparing films of this materials on silicon and other substrate materials [Zhu95, Jof88, Kla93, Alb95]. For the deposition of boron nitride CVD techniques were applied [Alb95] but in comparison to the sputter techniques the cubic phase content in the layers is lower [Hah97b]. Unfortunately these materials require an additional stimulation for the deposition of the interesting cubic phase [Kob88, Spe89, Yar90, Alb95]. Detailed reviews of the "activation" methods like microwave assisted plasma CVD, hot filament CVD, acetylene plasma torch, etc. are given by Klages [Kla93], Bachmann and Lydtin [Bac91], and Albella et al. [Alb95]. In the following two subsections the microwave plasma and the hollow cathode arc discharge as activation methods are discussed since the diamond films on silicon were produced using these CVD techniques.

### 4.2.2 Microwave Assisted Plasma CVD (MWPCVD)

The microwave assisted plasma CVD (MWPCVD) is besides the hot filament CVD the most frequently used deposition technique for diamond films on several substrates [Ang88, Kob88, Spe89, Lee90, Kla93, Alb95]. The "activation" of the precursors is generated by a microwave plasma (usually 2.45GHz [Roe95]) in the vicinity of the heated substrate. Although intensive thermodynamical calculations were performed, the mechanism of diamond formation is not fully understood yet and only a conceptual diagram for diamond formation is discussed [Kob88, Fre91, Yar91, Fra94].

Since the processes in the plasma and at the substrate surface are very complex and the reactor chamber geometries differ strongly no predictions about the optimum growth parameters can be given and the optimum growth parameters for each reactor chamber have to be found by numerous calibration runs. For the samples investigated in this work an optimum growth temperature range of ≈750-800°C was found at a microwave power of 1.1kW, a total gas pressure of 4000Pa, and a CH$_4$/H$_2$ ratio of 1% [Flo95].

As in the case of the organic CVD process the substrate pretreatment plays an essential
role for the quality of the deposited diamond films [Flo94]. It was found that scratching with diamond powder of 1 \( \mu m \) grain size enhances the nucleation and thus the diamond film quality. On the other hand, this method do not lead to epitaxial but to highly textured diamond films. Since these pretreatments were performed before introducing the substrate to the reactor chamber an alternative pretreatment in the reactor chamber was demonstrated to enhance the nucleation density and thus the diamond layer quality, too. The substrate is exposed to an increased CH\(_4\)/H\(_2\) ratio at a reduced total pressure while a negative d.c. bias voltage of up to -300V is applied for several minutes (bias enhanced nucleation = BEN) [Yug92, Jia92, Sto92, Rob93, Jia94, Rob95, McG95, Ger96]. In contrast to scratching, the BEN leads to nearly epitaxial diamond films. This improvement can be understood in the light of the "subplantation model" suggested by Lifshitz et al. [Lif89, Lif90, Lif93] and modified by Robertson [Rob93, Rob95, Ger96]. It describes the diamond nucleation by a subplantation of accelerated ions in the graphitic material of the sample. After the nucleation phase the growth is performed without a bias voltage. During the following growth the nucleated diamond seeds grow leading to a polycrystalline layer [Dri67]. For the samples in this work an increased CH\(_4\)/H\(_2\) ratio of 2\% and a total pressure of 2300Pa were applied with a bias voltage of -200V for 15min to the sample before the parameters were changed to start the growth [Flo95, Sch97].

4.2.3 Hollow Cathode Arc Discharge CVD (HCADCVD)

The plasma CVD utilizing a hollow cathode arc discharge is a less used method for diamond deposition on silicon substrates compared to deposition techniques like hot filament CVD and MWPCVD [Sti92, Sti93, Lau93, Sti94]. As in the case of the MWPCVD the precursors are dissociated and ionized in a plasma. In contrast to the MWPCVD process, this plasma is not initiated by a microwave but in a metal tube of high melting material (W, Ta, Mo) at a temperature of 2000-2800K and a constant potential connected to the front of the hollow cathode. Ions in the gas lead through the cathode - in the case of diamond deposition H\(_2\) - are deflected to the cathode and knock out electrons. These electrons are accelerated to the anode. At a critical density the plasma starts burning [Lau93]. Two growth setups are used: (i) a diode configuration and (ii) a triode configuration. Considering the former the substrate and the anode are identical which causes many problems [Lau93]. To overcome these problems the triode configuration was used for the growth of the samples investigated in this work. The anode and the substrate are divided and an additional d.c. voltage can be used to heat the substrate independently. The anode is shaped as a ring in the middle of the chamber. Above this ring anode the methane inlet is located. The substrates were pretreated by a mechanical polishing using a 1\( \mu m \) diamond powder followed by an ultrasonic cleaning with ethanol. Typical growth parameters are CH\(_4\)/H\(_2\) ratio 0.7\%, substrate current 2.3A, arc current 5A, a substrate temperature of 780\(^\circ\)C at a total pressure of 2500Pa.
4.3 Sputtering

Sputtering techniques, especially the magnetron sputtering, are well established for the deposition of cubic boron nitride. As in the case of the MWPCVD and the HCADCVD the support by a plasma is necessary for the film deposition. Two modifications are used to sputter the solid target materials. In the first case a direct current is applied to the conducting target (d.c. magnetron sputtering) or secondly a high frequency alternating voltage is applied to the target inducing a negative d.c. bias voltage at the target surface (r.f. magnetron sputtering). The negative voltage in both modifications accelerates the ions to the target and causes the sputtering of the target material. The working gas in the growth chamber is normally a mixture of argon and nitrogen with a ratio $N_2/Ar$ of a few percent [Hah96, Hah97a, Hah97b]. The substrate is additionally applied with a negative bias voltage to increase the ion bombardment towards the growing film.

As target for the r.f. magnetron sputtering different boron containing materials were used, like boron, hexagonal boron nitride, and boron carbide [Hah97b]. In the case of the d.c. magnetron sputtering the target must be conducting. For that reason, only boron carbide and heated boron targets were used [Sch95, Sch96, Hah96, Hah97b]. Boron only can be used since it shows a sufficient conductivity for temperatures around 800°C [Hah96, Hah97b]. In contrast to boron nitride or pure boron targets a boron carbide target contains carbon leading to a high carbon incorporation in the films. The films investigated in this work were produced either with r.f. magnetron sputtering using hexagonal boron nitride or boron targets or d.c. magnetron sputtering using a boron and a boron carbide target [Hah97b, Sch95, Sch96].

Before the growth starts, the target as well as the substrate were cleaned by plasma etching [Hah96, Hah97a, Hah97b]. For that purpose a shutter in the growth chamber is closed. Typical growth parameters are 500-1000W r.f. power or 200W d.c. power, a total pressure of 0.2-1Pa, a substrate temperature of 350°C, a $N_2/Ar$ ratio of 3% for the hexagonal boron nitride target and 10% for the boron target.

4.4 Ion Implantation

The ion beam techniques are necessary processes for the fabrication of electronic devices. Since in this work ion implanted 6H silicon carbide (6H-SiC) samples were investigated, in this section the specific problems for this material processing is discussed. There are main applications, i.e. (i) the doping, (ii) the chemical modification, and (iii) the crystallographic modification. Since in this work only unintentionally doped samples were investigated the first point will not be discussed furthermore in this section. Concerning point two the ion implantation can be used to modify surface layers or to fabricate a variety of buried compound layers of the substrate material and the implanted material (for example see [Ste90, Lin94, Lin96]). It is postulated layers could similarly be synthesized in SiC with a good control over their width, composition, and polytype structure, if the ion energy, the ion dose, the implantation
4.4. ION IMPLANTATION

temperature, and the annealing conditions were chosen properly [Hee95a, Hee96, Zah96]. In this work samples were investigated, which were co-implanted with aluminum and nitrogen at different doses and fluences to form a solid solution. Using TRIM calculations the energies and fluences of the aluminum and the nitrogen were chosen to have similar depth profiles in the SiC. Typical values for the energies and the fluences are 100keV Al\(^+\) (1·10\(^{16}\text{cm}^{-2}\)), 160keV Al\(^+\) (2.5·10\(^{16}\text{cm}^{-2}\)), 65keV N\(^+\) (1·10\(^{16}\text{cm}^{-2}\)), and 120keV N\(^+\) (2.5·10\(^{16}\text{cm}^{-2}\)). These values are expected to produce a buried (SiC)\(_x\)(AlN)\(_{1-x}\) mixture layer with a composition of \(x\approx0.20\), which is expected to crystallize in the cubic polytype [Hee96]. Afterwards the samples were annealed between 1300°C and 1700°C. The annealing is necessary, since at temperatures of \(\approx1450°C\) the solid phase epitaxy starts, which removes the damages in the implanted SiC and recrystallizes the amorphized SiC [Boh87, Hee95a, Yag95]. The depth of implantation depends on the fluences, the energies, the ion diameter, and the angle of incidence [Gib80, Bro82, Sze85, Rot92]. Especially the angle of incidence can increase the implantation depth significantly because of the ion channeling. Due to the ion channeling effect the usually Gaussian distribution of the implanted ions in the material is expanded by an exponential tail up to one magnitude in the depth [Gib80, Sze85]. Another idea of using the implantation technique is the crystallographic modification of the implanted substrate (point three of the list above). In a set of samples in this work this implantation technique was used to transform a layer in the 6H-SiC substrate into another polytype. It was demonstrated that this ion implantation with a following annealing step can be used to change the polytype structure from 6H to 3C, while maintaining its single crystallinity [Pez92a, Pez93, Kal94]. On these samples an additional epitaxial 3C-SiC layer was grown to demonstrate the ability of the method to grow polytype superlattices.
Chapter 5

Results

This chapter discusses the Raman spectroscopy measurements of hard coatings in the material systems containing boron, nitrogen, carbon, and silicon. Apart from the single element materials there are a large amount of possible binary and ternary compounds which can be formed. However, only a selection of these large amount of compounds could be measured, i.e. diamond, boron, boron carbide, boron nitride, carbon nitride, and silicon carbide. Most of the investigated materials were deposited as films on different substrate materials, but additional investigations were performed for single crystalline, polycrystalline, or implanted bulk material.

The single element system carbon, especially diamond and graphite, are investigated in the first section. Since Raman spectroscopy is one of the most important characterization tools in this material system all the tools discussed in the chapter 2 are applied to improve the information obtainable for the deposited films. The experience gained in these investigations, especially with the cross-sectional Raman spectroscopy, is used in the second section, which deals with the investigations in the silicon carbide material system.

Similar to the carbon material system for silicon carbide Raman spectroscopy is a widely used characterization method. However, most of the measurements are performed for only two (3C- and 6H-SiC) of the various possible polytypes and thus investigations of five polytypes, namely 3C, 4H, 6H, 15R, and 21R, are performed to get information about the temperature and the incident laser light energy dependence of these polytypes.

The third section describes the investigations of polycrystalline boron and boron carbide bulk material as a survey investigation for the boron nitride material system in the fourth section. For boron nitride Raman spectroscopy is an only less used characterization method. The measurements are mainly performed for single crystalline HPHT synthesized bulk material and thus, similar to the measurements in the silicon carbide material system, the incident laser light energy dependence for the two most important crystal modifications cubic and hexagonal boron nitride was measured. Additionally the dependences on the incident laser light power and the particle size are investigated for the cubic crystal modification before the
boron nitride films are examined. In the last section the carbon nitride material system is discussed. As for the investigation of single crystalline carbon nitride with Raman spectroscopy only two publications was found, these measurements are discussed in comparison to recently published theoretical calculations.

5.1 Diamond Films on Silicon(100)

In this section the investigations in the carbon material system are discussed, for which Raman spectroscopy is one of the standard characterization methods. This is caused by its high chemical sensitivity, which enables RS to distinguish between different crystal modifications, like diamond and graphite [Nem88, Spe90, Tam94]. Nevertheless, the tools described in chapter 2, i.e. investigation of the particle size and/or crystalline quality with the spatial correlation model, of the layered sequence in the sample heterostructure using the additional cross-sectional sample geometry, of the stress in the sample heterostructure utilizing different polarization configurations, and of the deposition homogeneity by two-dimensional mappings in the conventional plane-view sample geometry are only less used to increase the information about the deposited film [Bru89, Abs91, Aji95, Hay95]. Most of the Raman spectra from deposited films were measured with a macro- or a micro-Raman spectroscopy optical setup in the conventional plane-view sample geometry and only in the interesting spectral range of the carbon related phonon features [Cel92, Ghe92, Sil93, Bac94, Haq94, Kae95, Ece96].

To demonstrate the improved information obtainable for example in the carbon material system the following subsections deal with Raman spectroscopy measurements utilizing all tools of chapter 2. Although the subsections describe measurements for different samples, they show the potential of combined Raman spectroscopy investigations of diamond deposits.

In the first subsection the measurements with the micro-Raman spectroscopy optical setup utilizing the conventional plane-view sample geometry are given. These measurements are used to discuss the variations in the Raman spectra for differing growth conditions and the homogeneity and the orientation of the deposited diamond film. The second subsection still utilizes the conventional plane-view sample geometry and additionally the xy-stage under the microscope. This enables two-dimensional mappings of the deposited diamond films. In the third subsection the one-dimensional scans utilizing the cross-sectional sample geometry are demonstrated to enable a depth-resolved investigation of the deposited diamond film and the detection of thin interfacial layers.

5.1.1 Plane-View Geometry Measurements

In this subsection measurements using the micro-Raman spectroscopy optical setup with the conventional plane-view sample geometry of three types of samples are discussed. The
first sample series was deposited by MWPCVD on 3” silicon (100)-oriented wafers by S. Rölke and is used to examine the variation of the Raman spectra depending on the growth conditions. For that purpose single spectra in the center of the wafer were taken. Figure 5.1 shows two measurement series of samples deposited at a substrate temperature of about

![Raman spectra](image)

Figure 5.1: Raman spectra of a sample series grown with different methane concentrations \( \text{CH}_4/\text{H}_2 \) and base pressures [Roe95]. The other growth parameters are \( T_{\text{sub}} \approx 700^\circ \text{C} \) and \( t_g \approx 12 \text{h} \).

\( T_{\text{sub}} = 850^\circ \text{C} \) with a growth time of \( t_g = 12 \text{h} \). The left hand side panel shows a sample series grown with a methane concentration of \( \text{CH}_4/\text{H}_2 = 2\% \) and the right hand side panel displays a sample series grown with a methane concentration of 4%. The label at the different spectra gives the base pressure during the growth. A detailed discussion of the variations and their correlation to scanning electron microscopy (SEM) investigations (see for example figure 5.2) is given in [Roe95]. Considering the left part of figure 5.1 an improved diamond crystal quality with increasing base pressure can be observed. An exception is the highest base pressure (100hPa), for which the diamond phonon feature intensity starts to decrease again and the FWHM is enlarged. This is caused by an increased number of stacking faults and an
enhanced twinning [Roe95]. Moreover, the SEM photographs in figure 5.2 [Roe95] exhibit a variation of the diamond film quality. While the diamond film shows a "ball-like" structure for low pressures, the crystal formation with size of \(\approx 2\mu m\) for the 60hPa sample, and the twinning and crystal size reduction for the 100hPa sample can be seen [Roe95]. A similar pressure dependence was found by K. Kobashi et al. [Kob88], J.F. DeNatale et al. [DeN91], and K. Edamatsu et al. [Eda91]. The sample series deposited with a methane concentration of \(\text{CH}_4/\text{H}_2=4\%\) shown in the right part of figure 5.1 develop in the same manner as the sample series deposited with a lower methane concentration [Roe95]. In contrast to the lower methane concentration the graphite phonon bands at 1350\(\text{cm}^{-1}\) and 1550\(\text{cm}^{-1}\) are still visible in the spectrum of the sample deposited with the highest base pressure. This demonstrates the necessity of using higher pressures at higher methane concentrations for an increase of the diamond crystal quality [Kob88, DeN91]. In both sample series an additional phonon

Figure 5.2: SEM photographs from three of the samples given in the left panel of figure 5.1.
feature at about 1150 cm$^{-1}$ can be observed for the samples deposited at lower base pressures (2\%: 3 kPa and 4 kPa; 4\%: 2 kPa, 4 kPa, and 6 kPa). The origin of this phonon feature was related either to nanocrystalline diamond [Nem88] or the formation of polymeric chains [Bri84] and aromatic rings [Rou83]. Recent investigations seem to corroborate the assignment to nanocrystalline diamond, since the phonon feature only can be observed in polycrystalline diamond films with small crystal sizes [Mar94a, Bha95, Lop96]. This is confirmed by the intensity variation of the phonon feature in figure 5.1. With increasing base pressure and thus with increasing diamond crystal size (except from the highest base pressure in the left part) the phonon feature disappears.

For the sample series deposited with a methane concentration of 4\% the variation of the diamond phonon feature lineshape is shown in figure 5.3. The measured spectra are normalized to equal maximum intensity for a better comparison. The increasing asymmetry in the Raman lineshape with decreasing base pressure is evident, demonstrating the decreasing crystallite size for the decreasing base pressures. The solid lines represent the simulations using equation (2.24) of the spatial correlation model. It should be noted, that an adjustment of the natural linewidth $\Gamma_0$ for very small sizes, as discussed by Yoshikawa et al. [Yos93], may lead to a further improvement of agreement between fit and measurement, in particular on the high frequency side of the LO phonon feature. In these calculations the natural linewidth was increased from 1.9 cm$^{-1}$ [Kir94] to 4.3 cm$^{-1}$. This modification is quite successful.

![Figure 5.3: Measured Raman spectra (open symbols) in the spectral region of the diamond phonon feature for the sample series deposited with a methane concentration of 4\%. The solid lines give the simulations using the spatial correlation model with and without the graphite D-band contribution, respectively.](image-url)
possible explanation is the increase of recombination channels for phonons in very small particles compared to bulk material. This reduces the phonon lifetime $\tau$ and thus increases the natural linewidth ($\Gamma_0 \propto \frac{1}{\tau}$). For the Raman spectrum of the sample grown at a base pressure of 80hPa a very good fitting of the measured and the simulated lineshape is obtained. Nevertheless, an increasing difference between the measurement and the simulation on the high frequency side of the phonon feature with decreasing base pressure can still be observed. This is caused by the increasing participation of the graphite D-band at approximately $1350\text{cm}^{-1}$ in the Raman spectrum with decreasing base pressure (see right hand side panel of figure 5.1). The correlation lengths of up to 100nm illustrate the good quality of the deposited diamond crystals, since the correlation length is usually some orders of magnitude smaller than the crystallite size, due to the incorporation of defects [Gon85, Age91, Wer97a, Wer97c].

In figure 5.4 measurements on three different points of a sample are shown. The spectra cor-

![Figure 5.4: Raman spectra at three different points on a sample: center, half way to the edge, and near the edge.](image)

respond to measurements taken in the center, half way to the edge, and near the edge of the wafer. They are shifted relative to each other for clarification. Obviously the spectra show hardly any difference indicating a quite homogeneous deposition. For comparison samples supplied by M. Presia were investigated, which exhibit in contrast to the samples discussed above a very inhomogeneous deposition. Therefore these samples are used to illustrate the advantages of an one-dimensional scan across to sample its homogeneity is illustrated. Figure 5.5 displays the phonon intensity variation depending on the laser beam focus position. The scan starts in an uncovered region (left light gray region), moves then across the deposition area (dark grey and white regions) and finishes again in an uncovered region (right light gray region).
Figure 5.5: Variation of the phonon feature intensities for the one-dimensional scan across the deposition area. The open symbols represent the phonon features of silicon (squares), diamond (circle), nanocrystalline diamond (up triangle), D-band (down triangle), and G-band (diamond). The lines are shown additionally as guide for the eye.

region). The open symbols represent the measured phonon feature intensity variations. No simulation of these variations was performed, but the lines shown in the figure represent a guide for the eye. Clearly the appearance of the carbon related phonon features (diamond, graphite) can be observed when the laser beam enters the deposition area. In the edges of the deposition area (dark gray regions) the graphite related phonon modes and the nanocrystalline diamond phonon feature dominate the spectra indicating the small diamond crystallite size and the high incorporation of graphite in the deposited diamond. In contrast to this, in the center of the deposition area (white region) the strongest phonon feature visible is the diamond phonon mode. Its intensity is 3-5 times higher than this of all the other phonon features in the scan and dominates the spectra in the central deposition area. The silicon phonon feature exhibits a comparable intensity only outside the deposition area. Obviously these samples are very inhomogeneous exhibiting all the possible Raman spectra of a diamond film deposited on a silicon substrate (pure silicon, graphite rich diamond deposit, nanometer sized diamond, large crystalline diamond) in a single scan. This contrarily deposition homogeneity in comparison to the sample in figure 5.4 is related to the utilized deposition technique (plasma jet), which enables high growth rates but only small deposition areas.

With a third sample set provided by S. Laufer the evolution of the deposited crystal alignment to the substrate crystals with increasing deposition time was determined and is demonstrated in the following paragraphs. For these measurements the so-called alignment modulated Raman spectroscopy = AMORS was used [Wag95], which means the samples are step-
5.1. DIAMOND FILMS ON SILICON(100)

wise rotated and the Raman spectra were taken in the interesting spectral region for each sample orientation in a crossed polarization configuration. Figure 5.6 shows the obtained pole figures for two stages of the diamond growth on a silicon substrate. Pole figure (a) cor-

![Pole figures](image)

Figure 5.6: Pole figures for two different stages of the diamond growth on a silicon substrate. The open symbols gives the measured phonon feature intensity for the silicon (squares) and the diamond (circles) phonon mode, while the straight lines represent simulations of the phonon feature intensity variation: silicon (solid) and diamond (dashed).

responds to half the deposition time of pole figure (b). The measurements were performed with a crossed polarization configuration [Wag95, Wer95]. Due to the (100)-oriented substrate surface the silicon phonon feature (open squares) reaches its maximum for the polarization configuration $\mathbf{100}(010,001)100$ and vanishes for the polarization configuration $\mathbf{100}(001,011)100$ [Wag95, Geu93]. The open circles gives the intensity variation of the diamond phonon feature and the lines represent simulations of the phonon feature intensity variation depending on the azimuthal angle $\Theta$. Using the following equation [Yos90, Wag95, Wer95]

$$I(\Theta) = I_{\text{off}} + A \sin^2(2\Theta + \Theta_{\text{mis}})$$

with $I_{\text{off}}$ the offset and $A$ the amplitude of the modulation the intensity variation was simulated. The azimuthal angle offset $\Theta_{\text{mis}}$ describes the misalignment of the diamond (100) crystals in relation to the silicon substrate crystal orientation. Obviously the diamond seeds present after 30min deposition time are tilted and rotated exhibiting a large distribution of crystal orientations as the pole figure is nearly circular and thus no preferential growth of the (100) surface seems to be existing. However, a weak modulation is observable, indicating an already existing weak dominance of (100)-oriented diamond seeds. Due to the chosen growth conditions these (100) oriented seeds are preferred relatively to seeds with other orientations. This preferential growth leads to a faster growth of the (100) crystals and thus they dominate the diamond deposit in thicker films [Dri67, Wil90b, Wil93, Bar95]. This can be observed after 1h growth, for which the diamond film exhibits several crystals
with sizes of approximately 1\,\mu m and a clear (100) surface (determined by scanning electron microscopy). One of these crystals with a quite good orientation relation to the silicon substrate was chosen to perform the second AMORS measurement. Pole figure (b) displays the measured phonon feature intensity variations. Clearly the enhanced quality and the reduced tilting of the diamond crystals can be observed in the increased modulation. Furthermore, the azimuthal angle offset is very small ($\Theta_{\text{mis}} \approx 4^\circ$), due to the quite good alignment of the chosen diamond crystal in relation to the silicon substrate. Nevertheless, the diamond film includes still other crystalline surfaces than the (100) surface and many of the crystals are tilted and rotated and thus a measurement using a larger focus diameter (for example the macro-Raman spectroscopy optical setup) would show a modulation similar to that of pole figure (a). This demonstrates the feasibility of AMORS to determine the diamond crystal alignment to the substrate for varying growth conditions.

The measurements discussed in this subsection demonstrate the high suitability of Raman spectroscopy for investigations in the carbon material system. However, up to now, apart from the one-dimensional scan in figure 5.5, only single measurements at distinct sample positions were made. On the other hand, the one-dimensional scan verified the usefulness of such scans for the deposition homogeneity investigation and thus the next section deals with two-dimensional scans utilizing the xy-stage under the optical microscope.

### 5.1.2 Mapping

The two-dimensional scans (mappings) were achieved by moving the xy-stage in steps of 100\,nm in a defined array line by line. The computer automatically controls the movement of the xy-stage and starts the measurement of the investigated phonon feature at each position. The spectra were curvefitted using an asymmetric Lorentzian lineshape providing the phonon parameters, i.e. intensity, frequency position shift, FWHM, and asymmetry of the interesting phonon feature. The asymmetric Lorentzian lineshape is defined by

\[
I(\omega) = \frac{1}{1 + e^{\frac{\omega - \Omega}{w_l}}} (\omega - \Omega)^2 + \frac{1}{1 + e^{\frac{\omega - \Omega}{w_r}}} (\omega - \Omega)^2 + \frac{I_0}{1 + e^{\frac{\omega - \Omega}{w}}}
\]

with $I_0$, the maximum intensity of the phonon feature, $\Omega$ the frequency position of the phonon feature, and $w_l$ and $w_r$ the left and right FWHM, respectively. The Fermi distribution

\[
\frac{1}{1 + e^{\frac{\omega - \Omega}{w}}}
\]

was chosen to obtain a participation of only the first term for $\omega < \Omega$ and a participation of only the second term for $\omega > \Omega$. At $\omega = \Omega$ both terms reveal the value 0.5 and thus the lineshape maximum has the value $I_0$. In equation (5.2) a very "cold" temperature of $T \approx 10$\,K (denominator 0.001 of the exponential functions in equation (5.2)) was used to get a steep decrease and increase around $\Omega$. Since $w_l$ and $w_r$ are the full width at half maximum of the
left and the right phonon feature, respectively, the arithmetic average of \( w_l \) and \( w_r \) is used for the calculation of the FWHM of the measured phonon feature. The asymmetry \( \Gamma \) of the phonon feature is then given by the ratio of the left and the right width:

\[
\Gamma = \frac{w_l}{w_r}.
\]  

(5.4)

The fraction in the numerator of the second term provides a smooth lineshape at \( \Omega \). The variation of the phonon feature parameters plotted in an array is then used to investigate the homogeneity of the sample. Samples of two suppliers are examined:

(i) One sample was supplied by Dr. M. Schreck in the group of Prof. B. Stritzker of the University Augsburg. The sample was deposited by MWPCVD on silicon and exhibits in the central deposition area a nearly epitaxial (100) orientation of the diamond film in relation to the silicon substrate.

(ii) Several samples from S. Laufer and G. Schaaarschmidt in the group of Prof. H.-J. Hinneberg of the TU Chemnitz. The samples were deposited by HCADCVD on silicon substrates with varying thicknesses ranging from small diamond seeds up to \( \mu \)m thick films with different degrees of orientation in the thick films.

Considering the first sample set figure 5.7 shows the intensity (a), the frequency position shift (b), the FWHM (c), and the asymmetry of the diamond phonon feature in an array of 10\( \times \)10\( \mu \)m\(^2\) of the central depositon area. For the mapping the corner of four diamond crystals was chosen. These four regions can be observed in the mapped array, marked by the numbers. Surprisingly the sample exhibit an inhomogeneous mapping in the respectively four crystals. The intensity varies only slightly between 4 and 6cts/mWs with some spikes towards lower intensities due to defects in the crystals, like twins, graphitic inclusion, etc. (see for example the upper right corner near number 3). These regions are correlated to increased FWHM and asymmetries. The slight intensity difference between the two crystals 1, 2 and the two crystals 3, 4 is caused by a small height difference of these crystals leading thus to a defocussing of the incident laser light beam on the crystals 3 and 4. Near number 2 the diamond intensity increases to \( \approx \)10cts/mWs. This increase is correlated with a decrease in the FWHM and a positive shift of the diamond phonon and is thus likely caused by a small compressive strained diamond crystal twin with a high crystalline quality located in the diamond film surface.

Considering the second set several samples with different diamond film quality and alignment relation to the silicon substrate were investigated. Diamond films with a nearly epitaxial relation to the silicon substrate exhibit a very similar behaviour as the film described above. In addition, the mappings of just closed polycrystalline diamond films on silicon substrates are discussed in detail in the refs. [Wer95, Wer96] and thus no mappings of diamond films of this second series are shown in this section, which results although will be discussed in comparison to the mappings of the first sample series.
Since the diamond crystal size affects the frequency position as well as the FWHM, the correlation of these two parameters provides a measure for the quality of the deposited diamond film [Age91] (see for example figure 5.3). Figure 5.8 shows this correlation for two diamond films of the second sample set (sample 1,2 - open and closed squares) and for the sample from Augsburg (sample 3 - open and closed diamonds). Considering the former, sample 1 corresponds to a just closed polycrystalline film, while sample 2 is a nearly epitaxially oriented film. Figure 5.8 additionally shows the relation for a natural diamond crystal (closed circle), literature data [Age91] (open circles), and the theoretical dependence due to the spatial correlation model (SCM - solid line). Clearly the increased spreading of the data for the larger mapped arrays (closed symbols) is visible, caused by the increased number of diamond crystals included in the mapping. This demonstrates the still rather high inhomogeneity of the different deposited diamond crystals in the films. In contrast to this, the smaller mappings show a decreased parameter variation, illustrating the quite good
homogeneity inside a diamond crystal. In sample 1 the large FWHMs are related to the polycrystallinity of the just closed film. The FWHM around 12\text{cm}^{-1} is related to an average correlation length of \approx 6nm [Age91]. On the other hand, the solid line in figure 5.8 represent the prediction of the spatial correlation model for the relation between the FWHM and the frequency position. Obviously a decreased correlation length causes a frequency downshift of the phonon feature (see also figures 5.3 and 2.10), while the frequency positions in sample 1 are shifted towards higher frequencies. A similar behaviour can be observed for all investigated films. They follow a dependence, which gives higher frequency positions for higher FWHM’s. This increasing discrepancy with increasing FWHM between the theoretical prediction by the spatial correlation model and the measured values is correlated to an increasing intrinsic stress in the polycrystalline films [Age91]. This stress is reduced for thicker diamond films with a good epitaxial relation to the substrate (sample 2 and 3), but is quite large for the just closed diamond film (sample 1). The difference between the measured frequency positions and the prediction by the spatial correlation model correlates to an average stress in the samples 2 and 3 of about 470MPa and in sample 1 of \approx 900MPa [Wer95, Wer96]. J.W. Ager III et al. [Age91] found a similar behaviour of their diamond films deposited on silicon substrates (see the open circles in figure 5.8).

The measurements described in the subsections up to now utilized the conventional plane-view sample geometry. A lot of information were gained about the crystalline quality, the
crystal size, and the intrinsic stress. Using additionally the xy-stage for one- and two-dimensional scans further information about the deposition homogeneity were determined and AMORS revealed the alignment of the deposited diamond film in relation to the silicon substrate. However, no depth-resolved information about the variation of the material parameters, like crystalline quality, crystallite size, chemical modifications, and stress can be achieved due to the integral measurements in this sample geometry. Furthermore the identification of thin buried layers is not possible, since they are obscured by the strong diamond, graphite, and silicon phonon features in the spectra [Wer95, Wer96]. To overcome these disadvantages of the plane-view sample geometry additional measurements in the cross-sectional sample geometry were performed.

5.1.3 Cross-Sectional Measurements

For the one-dimensional cross-sectional scans across the sample heterostructures in this section two sample sets are discussed. The samples of the first sample series are similar to those discussed in the last subsection, while in the second sample set the deposition took place on patterned silicon substrates. All samples were supplied by S. Laufer and G. Schaarschmidt.

In a first step cross-sectional scans with different laser lines were performed to determine the optimum laser line for these investigations. The laser light energy dependence was measured for several Ar\textsuperscript{+} and Kr\textsuperscript{+} laser lines. Figure 5.9 shows the 3D representations of cross-sectional scans with a stepwidth of 200nm with the 457.9nm, 488.0nm, and the 514.5nm laser line of the Ar\textsuperscript{+} laser. These scans were taken at the same sample position. Thus the changes between the different 3D representations are related to the incident laser light energy. In every 3D representation the x-axis gives the investigated spectral range, the y-axis the intensity of the different measured spectra, and the z-axis the distance the laser light beam moved across the sample heterostructure. The first spectra correspond to a laser beam position well away from the diamond/silicon interface in the silicon substrate. Clearly only the first and the second order phonon features of silicon at \(\approx 520\,\text{cm}^{-1}\) and around \(1000\,\text{cm}^{-1}\) are observable. With increasing distance the laser beam passes the silicon/diamond interface and enters the diamond film. This leads to a decrease of the silicon phonon features, while the phonon features related to the diamond film appears: The diamond phonon feature at about \(1332\,\text{cm}^{-1}\), the two graphite bands at \(\approx 1350\,\text{cm}^{-1}\) and \(\approx 1580\,\text{cm}^{-1}\), respectively.

The most evident change between the 3D representations is the drastical increase of the luminescence background, if the laser beam is centered in the diamond layer. Since luminescence features are constant in their energy position, they shift in the Raman spectrum if the laser light energy is changed. The maxima of the luminescence in diamond films is centered around 2eV [Ber93]. As a result, the luminescence appears stronger in the spectra, the more the incident laser light energy approaches the luminescence maximum. The cross-sectional scan using the 568.2nm (2.18eV) Kr\textsuperscript{+} laser line is not displayed, since only a broad luminescence background and no Raman features are visible in the spectra.
Figure 5.9: 3D representations of the cross-sectional scans at the same sample position to demonstrate the dependence on the laser light energy.

As described in section 2.5.2 the spectra of the cross-sectional scans were curve-fitted using several Lorentzian and several Gaussian lineshapes for the distinct phonon features to obtain the phonon feature parameters. The variations of the intensity depending on the laser beam position is given in figure 5.10 for the silicon, the diamond, the graphite D-band, and the graphite G-band (open symbols) for the three laser light energies shown in figure 5.9. Simulations of these phonon feature intensity variations are represented by the lines.

Clearly the decreasing maximum intensity with increasing incident laser light energy well away from the interface for all phonon feature intensity variations can be observed. They decrease due to the decreasing monochromator sensitivity with increasing energy in the blue-green spectral region (see figure 2.13). However, the silicon phonon feature decreases from \( \approx 48 \text{cts/mWs} \) down to \( \approx 8 \text{cts/mWs} \), while the diamond phonon feature maximum intensity decreases only from about \( 34 \text{cts/mWs} \) down to approximately \( 14 \text{cts/mWs} \) revealing an intensity ratio \( I_{\text{dia}}/I_{\text{si}} \) increase from 0.71 to 1.75. Considering the graphite related phonon
features, the intensity ratio $I_{o}^{\text{dia}}/(I_{o}^{D\text{-band}} + I_{o}^{G\text{-band}})$ increases from 1.28 to 3.68. These effects are caused by the increase of the Raman scattering efficiency difference ($\Delta S$) between silicon and diamond and between graphite and diamond with decreasing incident laser light energy. The Raman scattering efficiency difference between diamond and graphite is already measured for the 514.5nm Ar$^+$ ($\Delta S=50$) and the 632.8nm HeNe laser line ($\Delta S=233$) [Wad81b, Sto93, Sai96]. Using the formula for the diamond quality presented by S.R. Sails et al. [Sai96] the Raman scattering efficiency difference $\Delta S$ for the 457.9nm Ar$^+$ laser line was calculated. The comparison of two Raman spectra measured at the same sample position with two different laser lines reveals a Raman scattering efficiency difference of $\Delta S=41$. This indicates the increased Raman efficiency of diamond and the decreased Raman efficiency of graphite in the blue spectral region. Due to the more pronounced diamond phonon feature
For the simulations shown in figure 5.10 the model described in section 2.5.2 was used with two box functions, representing the silicon and the diamond layer, and a laser beam FWHM of 1.2µm. As a result of the simulation the interface position is known and thus the x-axis is given in relation to the interface position. Obviously an increased intensity of the silicon phonon feature appears at the interface. The height of this peak in the vicinity of the interface indicates that no additional layer has to be assumed at the interface. This corroborates results of Jiang and Klages [Jia93] and L. Chang et al. [Cha96] who found a direct nucleation of the diamond seeds in the silicon. Although an interfacial layer was excluded in the calculations a discrepancy between the measured and the calculated phonon feature intensities of the graphite D- and G-band is visible. Since this difference increases with decreasing laser light energy it is correlated to additional graphite incorporated in the diamond film near the interface. This graphite demonstrates the decreased diamond crystallite size in the vicinity of the interface, due to the origin of the diamond films from small seeds [Dri67, Wil90b, Wil93, Bar95]. Between these diamond crystals amorphous carbon and graphite is accumulated. With the decreased diamond crystal size the surface area and thus the amount of incorporated amorphous carbon or graphite increases. Figure 5.11 shows the FWHM of the silicon and the diamond phonon feature depending on the laser beam position.

![Figure 5.11: The deconvoluted FWHM of the silicon (open squares) and the diamond (open circles) phonon features depending on the laser beam position.](image)

The straight lines represent polynomial regressions of the measured data given as guide for the eyes. The FWHM dependencies are deconvoluted using equation (2.75). Evidently the increasing FWHM of the silicon and the diamond phonon feature in the vicinity of the interface can be observed. In the case of the silicon this is likely caused by the bias enhanced...
nucleation process, which disturbs the single crystallinity of the substrate surface and thus no increased FWHM well away from the interface was measured. The FWHM at the interface of \( \approx 4 \text{cm}^{-1} \) corresponds to a correlation length of approximately 11nm [Ric81]. The FWHM of the diamond phonon feature near the interface increases drastically and is related to a correlation length of about 7nm [Age91], but in contrast to the silicon phonon feature dependence the FWHM decrease with increasing distance to the interface continues. This is related to growing crystal sizes and thus an increasing diamond crystal quality with increasing distance to the interface [Dri67, Wil90b, Wil93, Bar95]. Using the spatial correlation model the FWHMs at the interface are correlated to a frequency position shift to lower frequencies of \( \approx 1.5 \text{cm}^{-1} \) [Ric81] and \( \approx 3.5 \text{cm}^{-1} \) [Age91] for the silicon and the diamond phonon feature, respectively. Figure 5.12 displays the phonon feature frequency position depending on the laser beam position. As in figure 5.11 the measured frequency positions are deconvoluted using equation (2.75). The frequency position of the silicon phonon feature and that of the diamond phonon feature shifts in the vicinity of the interface towards higher and lower frequencies, respectively. This is caused by the direct contact of the diamond crystallites with the silicon substrate, giving a compressive stress in the case of the silicon phonon feature and a tensile stress in the case of the diamond phonon feature [Gri78]. However, the frequency positions are modified by the frequency position shift due to the reduced correlation length in the vicinity of the interface (see figure 5.11), which shifts the frequency positions of the phonon features towards lower frequencies [Ric81, Age91]. Taking the influence of the spatial confinement into account the frequency position shift in the case of the silicon

![Figure 5.12](image-url)
The frequency position shift in the case of the diamond phonon feature is decreased, leading to a compressive stress of approximately 120 MPa, which corresponds very well to the value obtained from the frequency position shift of the silicon phonon feature. Furthermore, a decrease in the frequency position of the diamond phonon feature with increasing distance to the interface can be noticed. This decrease corresponds to a reduced intrinsic stress in polycrystalline diamond films with larger crystal sizes as already discussed in figure 5.8. Considering these depth-resolved variations of the phonon feature frequency position and FWHM the drastically increased FWHM and the frequency position shift towards higher frequencies in figure 5.8 for the just closed diamond film (sample 1) can be interpreted as the measure of the interface induced variations shown in figure 5.11 and 5.12. With increasing diamond film thickness these interface induced variations are obscured in the plane-view sample geometry by the diamond deposit with larger crystallite size above it.

Although results of Jiang and Klages [Jia93] and L. Chang et al. [Cha96] show a direct nucleation of the diamond seeds in the silicon, Robertson and Gerber [Ger94a, Ger94b, Rob95, Ger96] and Kulisch et al. [Kul95] found an interfacial layer of amorphous SiC [Sto92, Kul95] or amorphous carbon [Rob95, Ger96]. A cross-sectional scan across the layered heterostructure of such a sample is shown in figure 5.13 demonstrating the ability of cross-sectional μ-RS to detect these ultra-thin interfacial layers. The measured phonon feature intensity variations
are given as open symbols, while the solid lines represent the simulations. Evidently an additional peak at the interface is observable for the silicon phonon feature variation as well as for the graphite bands. Since the FWHM dependence of this sample is similar to that given in figure 5.11 a similar crystallite size in the diamond layer near the interface can be assumed. To demonstrate the influence of the interfacial layer simulations were performed for three different graphitic interfacial layer thicknesses: (i) 2nm (solid line), (ii) 0nm (dashed line), and (iii) 20nm. Clearly the additional peak of the silicon phonon feature intensity variation is reproduced by all these simulations, but its height is only fitted well by the simulation with a graphitic interfacial layer thickness of 2nm. This is supported by the phonon feature intensity variations of the graphite bands, which are also only reproduced well by the simulation with an interfacial layer thickness of 2nm.

Considering the frequency position dependence of this sample given in figure 5.14 the effect of such a graphitic interface layer is demonstrated. The silicon (open squares) and the diamond (open circles) phonon feature frequency position shows a constant behaviour depending on the laser beam position. This indicates the effect of the graphite interfacial layer as a stress compensating buffer. Moreover the diamond phonon feature frequency position is shifted towards higher frequencies by approximately 0.6cm$^{-1}$. This shift correlates to an intrinsic stress in the diamond layer of about 190MPa.

Comparing the two samples discussed up to now in this subsection the feasibility of cross-sectional Raman spectroscopy for the detection of the depth resolved material parameter variations like stress, crystallite quality and size, and the formation of additional layers in
the sample heterostructure is demonstrated. Although the measurements were performed utilizing a laser beam focus of $\approx 1\ \mu m$ ultra-thin layers in the second sample heterostructure could be determined. On the other hand, it should be mentioned, that this detection was enabled by the large light penetration depth in the diamond film compared to that in the graphitic interface layer (see figure 2.20) and the high Raman scattering efficiency of graphite. As a consequence the existence of any amorphous SiC at the interface cannot be excluded, although no SiC phonon features are visible in the Raman spectra near the interface. This is caused by the very low Raman scattering efficiency of SiC and amorphous SiC [Ino83, Bul87, Fen88a].

Concerning the second sample set, for which the diamond deposition took place on patterned silicon substrates, the cross-sectional scans were applied to get a view inside the trenches, since the diamond film overgrows these trenches during the deposition. A detailed discussion of the substrate preparation, the deposition process, and the cross-sectional $\mu$-RS measurements of these samples is given in refs. [Flo95, Sch97] and thus only an overview of the advantages using cross-sectional $\mu$-RS for these samples is given. Figure 5.15 shows the cross-sectional scans across the sample heterostructure at two points:

1. Across the upper layer on top of the substrate surface.

2. Inside a trench starting in the surrounding atmosphere, passing the closed diamond layer on top of the patterned silicon substrates, the space inside the trench, the diamond layer in the trench bottom, and then entering the silicon substrate.

The transmission electron microscopy (TEM) photograph shown in figure 5.15 displays the dimensions of the trenches at which the scans were performed. The trench was completely overgrown by the diamond film and the diamond film at the bottom of the trench has no contact to the upper diamond layer. Considering the first scan clearly the diamond layer on top of the silicon substrate can be seen. For the simulation of the phonon feature intensity variation no graphitic interfacial layer was assumed. Obviously the simulated intensity variation fits the measured phonon feature intensity variation very well indicating a high quality of the deposited diamond. Due to the high quality of the deposited diamond film the additional peak in the silicon phonon feature variation at the diamond/silicon interface is well pronounced. In contrast to this, the second scan taken inside the trench shows two distinctly separated diamond deposits. The altered contributions of the graphite D- and G-bands to the spectra indicates a poorer diamond quality of the deposit on the trench bottom and on the inner side of the upper layer. It is noteworthy, that the phonon feature intensity variation of all phonon features never reach the zero in the space of the trench, since the width of it was $1.8\ \mu m$ and the FWHM of the laser beam $1.5\ \mu m$. For that reason the tails of the Gaussian laser beam can enter the deposit and the silicon at the trench side walls and thus a contribution to the spectra is obtained. The deposit at the side walls is rather inhomogeneous and of low quality leading to a modification of the phonon feature intensity variation in this region. Due to the simulation procedure, which includes no changes of the
Figure 5.15: Intensity variations of the phonon features for two different positions on the sample heterostructure of a diamond film deposited on patterned silicon substrate. The TEM photograph shows the positions of the scans and the dimensions of the trenches.

Sample heterostructure perpendicular to the scanning direction, these phonon feature intensity variations cannot be simulated correctly. A detailed discussion of the results considering different deposition parameters and technologies are given in ref. [Sch97].

In conclusion can be stated, that on the one hand diamond films can be grown on silicon substrates with a nearly epitaxially relation of the diamond crystals to the silicon substrate with a very high quality of the deposited diamond. On the other hand, these highly epitaxially grown diamond films are usually restricted to quite small areas of the deposited diamond film, while the remaining film exhibit a polycrystalline nature with (100) oriented crystals forming the film, but with randomly distributed azimuthal angles. Furthermore, if the growth process is optimized for a large area deposition the diamond quality can be improved to a quite high level, but do not reach the nearly epitaxially quality of the former diamond films. Although
5.2  Silicon Carbide (SiC)

In contrast to all the other materials investigated in this work, only the silicon carbide (SiC) material system exhibit the large number of approximately 200 different polytypes [Dav91]. Analogous to diamond, the SiC polytypes are wide bandgap semiconductors with fundamental bandgap energies ranging from 2.4eV (3C-SiC) up to 3.33eV (2H-SiC). Since only few measurements using Raman spectroscopy were performed for other polytypes than 3C and 6H, this section introduces two survey investigations for 5 SiC polytypes, namely 3C, 4H, 6H, 15R, and 21R. At first the dependence on the incident laser light energy and secondly the temperature dependence is investigated. For these measurements bulk material of the polytypes 3C, 4H, 6H, 15R, and 21R was used. The third part deals with plane-view and cross-sectional μ-RS measurements at 3C-SiC films deposited by CVD on Si(100) substrates. In the fourth subsection 6H-SiC wafers implanted with aluminum and nitrogen...
Figure 5.16 displays the LO phonon mode frequency range of the 5 investigated polytypes shown in figure 3.9. The frequency position of the cubic $F_{2g}$ mode is $\approx 973\text{cm}^{-1}$. Since the measured crystal face of all higher SiC polytypes was the (0001) face the LO phonon modes have $A_1$ symmetry and should be located around $964\text{cm}^{-1}$ (see table 3.7 and equations (3.1)). It is worthy to note, that the LO phonon feature of the 15R-SiC sample in figure 5.16 is shifted towards higher frequencies, in comparison to the other polytypes. This is caused by the coupling of the LO phonon mode with a plasmon (coupled plasmon-LO phonon mode = PLP mode) induced by free carriers in the material [Col72, Kle72, Yug87, Gen93, Ess96]. Following the formalism given by M.V. Klein et al. [Kle72] with the correction given by H. Yugami et al. [Yug87] the frequency position and the lineshape of the LO phonon mode in the figure correlates to a free carrier concentration of about $2 \times 10^{18}\text{cm}^{-3}$. For these calculations
the parameters given for 6H-SiC has to be used, since most of the necessary parameters for
the 15R-SiC are still unknown.

5.2.1 Incident Laser Light Energy Dependence

Because of the wide bandgaps of the SiC polytypes and the very low Raman scattering effi-
ciency single crystalline material of different polytypes were measured with several laser lines
ranging from 441.6nm (2.81eV) up to 647.1nm (1.92eV) utilizing laser lines of an Ar⁺, a Kr⁺,
and a HeCd laser. Figure 5.17 displays the Raman spectra taken with different laser lines
for the 3C-SiC polytype. Three changes in the spectra are evident. At first the luminescence
shifts with decreasing incident laser light energy towards a lower relative frequency position.
This luminescence originates from near edge transitions of the bandgap and thus its absolute
energy position is constant with varying incident laser light energy. For that reason the lu-
minescence band passes the Raman spectrum, since the incident laser light energy is changed
from 2.81eV - larger than the bandgap energy - to 1.92eV - smaller than the bandgap energy
-. The second change between the Raman spectra is the steep decrease of the luminescence
intensity near 2.46V, which is caused by the transparency of the material for light energies
smaller than the fundamental bandgap. The third change concerns the intensity variations

Figure 5.17: Dependence of the Raman scattering on the incident laser light energy for the 3C-SiC
polytype.
of the phonon features itself. Due to the $E_o$ and the $E_o + \Delta_o$ transition from the highest spin-orbit splitted ($\Delta_o$) valence band to the lowest conduction band resonant Raman scattering can be performed for the 3C-SiC polytype (see page 11) [Ric76, Fen88a, Dre94]. Figure 5.18 displays in the left panel the corrected Raman scattering intensity using the sensitivity factors for the $\mu$-RS setup given in figure 2.13. Clearly the resonant enhancement can be observed. The maximum of the resonant Raman scattering is centered at about 19900cm$^{-1}$ (502.5nm = 2.46eV). This value is somewhat higher than the theoretical values given in the literature (2.41eV [Bim81]) and thus additional room temperature photoluminescence (RT-PL) measurements for the 3C-SiC bulk crystal were performed. In the right panel of figure 5.18 the measured spectrum is shown. The maximum of the photoluminescence is located at 508.4nm (2.44eV) and is thus also higher than the theoretical fundamental bandgap. On the other hand, the difference between the RT-PL measurement and the resonant Raman scattering measurements corresponds quite good to the energy of an exciton (typically 20-30meV), which has to be considered in the PL measurements. Basing on the results of the resonant Raman scattering and the PL measurements the fundamental bandgap energy given by theoretical calculations seems to be too low. This is corroborated by optical transmission measurements from W.J. Choyke [Cho86]. He founds a fundamental bandgap energy of 2.43±0.3eV.

Figure 5.18: Left panel: Corrected Raman scattering intensity using the sensitivity factor of figure 2.13 depending on the incident laser light energy for the TO and the LO phonon of the 3C-SiC polytype (open symbols). The straight line shows a Lorentzian fit to the data. Right panel: RT-PL measurement of the 3C-SiC crystal.
Two additional structures are observable on the higher wavelength side of the RT-PL spectrum in figure 5.18 at 531.8nm and 558.4nm. This gives binding energies of 107.3meV and 218.4meV and are likely to be correlated to different ionized nitrogen impurities [Kuw76, Lan83].

The fundamental bandgaps of all other polytypes are larger than 2.71eV [Cho69] and thus no resonant Raman scattering but the $\omega^3$ dependence can be observed. This is visualized in figure 5.19, which shows the corrected Raman scattering intensities for the remaining SiC polytypes. Obviously the phonons follows the $\omega^3$ dependence very well. Nevertheless, in the case of the 21R SiC polytype (lower right panel) an increasing discrepancy between the corrected phonon feature intensities and the $\omega^3$ dependence with increasing frequency can be observed. This is likely to be caused by the beginning of a resonance enhancement, since the fundamental bandgap of 21R-SiC for room temperature is of about 2.8eV [Cho69]. Due to the structureless dependence of the higher periodicity polytypes and the resonance enhancement of the 3C-SiC at about 503nm for the following investigations the 501.7nm laser line of an Ar$^+$ laser was used.

![Figure 5.19: Corrected Raman scattering intensity (open symbols) depending on the incident laser light energy for the different TO and the LO phonon for the remaining SiC polytypes. The straight lines give the $\omega^3$ dependences.](image-url)
5.2.2 Temperature Dependence

For the temperature dependence investigation the nitrogen cryostate under the optical microscope in the μ-RS optical setup was utilized. The samples were fixed with contacting glue on a copper block for a better thermal contact. Through this copper block liquid nitrogen is pumped and afterwards the meanwhile gaseous nitrogen passes the sample chamber in a second turn. This second turn can cause some problems, since the obtainable liquid nitrogen is not very pure. Due to this an ice layer starts to grow on the samples if temperatures below -50°C were hold for longer than a few minutes. On the other hand, the sample has to be kept at the chosen temperature for one minute to obtain a thermal equilibrium, since the temperature is measured by a thermocouple inside the copper block. For that reason only two measurements were performed at lower temperatures than -50°C. Afterwards the sample was heated to room temperature in order to remove any possible grown layer. Then the sample was cooled down again. Using this procedure the temperature dependencies were measured in the temperature range from -150°C up to 450°C.

Table 5.1 lists the linear and the quadratic term of equation (2.27) obtained from the quadratic polynomial regression of the measured temperature dependent shift of the phonon features for all 5 polytypes (displayed in figure 5.20). The open symbols display the measured temperature dependence of the distinct phonon features for the different SiC polytypes and the solid lines represent quadratic polynomial regressions using equation (2.27). The measured temperature dependence for the 3C-SiC and the 6H-SiC corresponds quite good to the temperatures dependencies given in the literature [Mea77, Ole82c]. For the other polytypes no literature data could be found. In the case of the larger periodicity polytypes the TO phonon corresponds to the strongest E₂(TO) (4H, 6H) and the most intense E₁(TO) (15R, 21R) mode, respectively, while the LO phonon means the A₁(LO) in all cases.
Figure 5.20: Temperature dependence of the phonon features for the 5 polytypes investigated in this work.
5.2.3 3C-SiC Films on Silicon (100)

The 3C-SiC films on 3"-silicon (100) substrates were performed by chemical vapour deposition at cs GmbH, Munich. The deposition process is described in detail elsewhere [Web92]. Due to the single side deposition these wafers exhibit bendings of about 50 µm measured utilizing the bending plate method [Got97]. This bending is caused by the different lattice constants of Si (5.435 Å) and 3C-SiC (4.364 Å) at room temperature, and additionally by the different thermal expansion coefficients (Si: 1.98·10⁻⁵ K⁻¹ and 3C-SiC: 1.57·10⁻⁵ K⁻¹) [Fen88a]. Because of the large differences high bendings of the coated wafer are observable. Figure 5.21 displays the measured bendings of the substrate without any deposit (1), with an 1.9 µm 3C-SiC film on one side (2,3), and an additional TiW coating on top of the SiC film (4-6). This additional TiW metallization was deposited to investigate its influence on the micromechanical and microelectronic applications. The metallization layer reverses the bending from the concave curvature after the SiC deposition (2,3) to a flat convex curvature (4). Bending measurements at 700°C performed after the SiC deposition (3) and after TiW deposition (5) demonstrate the influence of the different thermal expansion coefficients. Additionally the curve 6 in figure 5.21 shows the bending after the temperature cycle with the TiW metallization. A new stable bending is reached even at room temperature leading to an irreversible intrinsic stress in the sample heterostructure [Got97].

For this sample heterostructure several measurement between the subsequent deposition steps were performed. The sample after the deposition of the 3C-SiC film was measured in the
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conventional plane-view and the cross-sectional sample geometry and an additional cross-sectional scan was performed after the deposition of the TiW metallization layer. This second cross-sectional scan was measured after the temperature cycles described before, to clarify the results.

Considering the plane-view sample geometry measurements of the 3C-SiC film figure 5.22 shows two Raman spectra taken with two different polarization configurations. The solid line represents the parallel and the dotted line the crossed configuration. Figure 5.22: \(\mu\)-RS measurements of the 3C-SiC film on a Si(100) substrate utilizing the conventional plane-view sample geometry for two different polarization configurations. The solid line represents the parallel configuration \(\overline{0}0(0\overline{1}1,0\overline{1}1)100\) and the dotted line the crossed configuration \(\overline{0}0(011,011)100\). Besides the second order phonon structures of the silicon substrate the SiC TO and LO phonon features are visible. The polycrystalline nature of the SiC is indicated by the barely traceable influence of the polarization configuration on the phonon feature intensities. The TO phonon structure at \(794.9\text{cm}^{-1}\) has a FWHM of about \(7.5\text{cm}^{-1}\). Its asymmetric broadening is likely to be induced by the effect of a minor crystal quality and thus a reduced correlation length (see section 2.1.2 and ref. [Sas89]). Using the relation given by Y. Sasaki *et al.* [Sas89] a correlation length of about \(27\text{nm}\) is obtained. This reduced correlation length results in a down-shift of the frequency position of \(\approx 0.7\text{cm}^{-1}\). The remaining frequency shift of \(0.5\text{cm}^{-1}\) is now entirely attributed to the strain giving thus a tensile stress of about \(125\text{MPa} [\text{Fen88a, Fen88b}], \) which correlates very well to the value of \(134\text{MPa} \) determined by the bending plate method [Got97].

In order to clarify the results obtained with the bending plate method (see figure 5.21) \(\mu\)-RS measurements in the cross-sectional sample geometry were performed. For that purpose two cross-sectional scans were taken. The first one was measured with the TiW metallization
layer on top of the SiC film and the second one after etching off the TiW. Figure 5.23 displays the 3D representation of the scan across the layered structure of the 3C-SiC layer

![3D representation of a scan in 100nm steps across the 3C-SiC/Si sample with the TiW layer etched off.](image)

Figure 5.23: 3D representation of a scan in 100nm steps across the 3C-SiC/Si sample with the TiW layer etched off.

on the silicon substrate after etching off the TiW. The spectra were subsequently taken in steps of 100nm starting in the surrounding atmosphere (front spectrum), while the rear spectrum corresponds to a laser beam position in the Si substrate well away from the 3C-SiC/Si interface. Four features can be distinguished corresponding to the silicon first order optical phonon ($\approx 520\text{cm}^{-1}$), the 3C-SiC TO phonon ($\approx 796\text{cm}^{-1}$), and the Si second order optical phonon band (from $930\text{cm}^{-1}$ to $1000\text{cm}^{-1}$), superimposed by the 3C-SiC LO phonon feature ($\approx 973\text{cm}^{-1}$). The phonon parameter variations derived from the curvefitting routine are displayed in figure 5.24. Panel a) shows the variations of the phonon structure intensity, b) the FWHM, and c) the frequency positions. In each panel the symbols represent the measurements. The FWHMs were used to estimate the shift due to the finite sizes in the materials as described for the plane-view measurements. The straight lines in panel b) and c) represent the bulk values for the FWHM and the frequency positions, respectively (solid: 3C-SiC and dashed: Si [Wei75, Fen88a]). The intensity variations in panel a) were simulated using the model described in section 2.5.2 and given as straight lines (solid: silicon phonon feature for the sample with the TiW layer on top, dashed: silicon phonon feature after TiW etching, dotted: 3C-SiC TO phonon feature with TiW layer, and dash-dotted: 3C-SiC TO phonon structure after TiW etching).
Figure 5.24: The variations of the phonon feature parameters depending on the laser beam position: Panel a) intensity, b) FWHM, and c) frequency position. The symbols represent the measurements (squares: silicon with the TiW layer on top, circles: silicon after TiW etching, diamonds: 3C-SiC TO with TiW layer on top, and stars: 3C-SiC TO after TiW etching), while the straight lines in panel a) give the simulations of the intensity variation. The straight lines in panels b) and c) represent the bulk values of the silicon (dashed lines) and the SiC (solid lines).
The silicon phonon feature intensity variations show in both cases an enhancement at the interface between the 3C-SiC layer and the Si substrate introduced by the larger light penetration depth in the SiC than in Si (see figure 2.20). Moreover, the variations of the silicon phonon feature intensity shows in both cases a shoulder. This shoulder only can be explained by an additional silicon rich layer of a few nanometers thickness on top of the SiC layer [Wer97b, Wer97d]. SEM measurements were performed to proof this assumption (see figure 5.25). Unfortunately this second layer is not visible in the SEM photograph. However, for this second layer a thickness of 15nm was used in the simulations, which is likely to small to be observable in the SEM measurements. The $\mu$-RS simulations reveal a SiC layer thickness of about 600nm, which corresponds quite well with the visible thickness by SEM. In contrast to this, the bending plate method needs the nominal thickness of 1.9$\mu$m [Got97]. The assumption of a second Si layer on top of the 3C-SiC layer is corroborated by the investigation of another 3C-SiC/Si sample for which no TiW metallization was performed. Figure 5.26 displays the phonon feature intensity variations for the cross-sectional scan across the sample heterostructure. The open symbols represent the measured phonon intensity variation and the straight lines give the simulations. Clearly the enhancement of the silicon phonon feature intensity in the vicinity of the interface to the 3C-SiC layer and the distinct maximum in front of the 3C-SiC phonon feature intensity variation maximum can be observed. This second maximum was simulated using a second Si layer thickness of 3nm. For the 3C-SiC layer a thickness of 1.6$\mu$m was obtained in good agreement to the layer thickness of 1.9$\mu$m estimated from the growth conditions. Moreover, the existence of this Si top layer is corroborated by the Si phonon features displayed in the insert of figure 5.26. Obviously the upper spectrum taken at the maximum of the Si top layer is broaden and exhibit a slight asymmetry compared to the lower spectrum taken in the Si substrate well away from the interface. A simulation using the model described in section 2.1.2 gives a correlation length of 5nm, which correlates very well to the thickness obtained from the simulations.

Figure 5.25: SEM photograph of the multilayer system: 1: TiW, 2: SiC, 3: Si.
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5.2.4 **Implanted 6H-SiC**

The samples investigated in this section were produced by co-implantation of aluminum (Al) and nitrogen (N) into 6H-SiC (0001) wafers at different doses to produce buried (SiC)$_{1-x}$(AlN)$_x$ layers with compositions of about $x=0.04$ and $x=0.20$. After the implantation procedure an annealing cycle in the temperature range from 1300°C to 1700°C was carried out to recrystallize the implanted samples. The samples were measured using the cross-sectional sample geometry to provide additional depth-resolved information, since the transparency of the 6H-wafer material disables an investigation of the buried layer. This is visualized in figure 5.27. The figure shows typical Raman spectra taken in the conventional plane-view sample geometry with the part a) the spectrum of a virgin 6H-SiC wafer, b) two spectra of as-implanted samples with a low and a high dose implantation, and c) the spectra of the samples implanted with two different doses and annealed at three different temperatures. Considering the spectrum of the virgin sample (part a) all phonon features allowed in the chosen polarization configuration can be observed: The $E_2$(TO) (768.0cm$^{-1}$), the $E_2$(TO) (789.0cm$^{-1}$), and the $A_1$(LO) (967.5cm$^{-1}$). In contrast to the selection rules
Figure 5.27: The Raman spectra of the virgin a), the as-implanted b), and the implanted and annealed c) samples measured in the conventional plane-view sample geometry.

[Fe168a, Fe168b] for the chosen polarization configuration (z(y)x)z with x=[1100], y=[1120], and z=[0001]) an additional weak structure can be observed at 795.5 cm\(^{-1}\) (E\(_1\) (TO)). This is related to the large aperture of the objective lens resulting in a partial lifting of the selection rules [Bru89]. In panel b) only very weak (low dose) or no sharp phonon features (high dose) are observable, while two broad bands appear at about 500 cm\(^{-1}\) and 750 cm\(^{-1}\). An additional broad band appearing around 1250 cm\(^{-1}\) is not displayed. These changes can be explained by an amorphization of the 6H-SiC in the surface region and a strongly reduced light penetration depth. The broad features appearing in the spectra are correlated to Si-Si/Si-Al/Si-N (\(\approx\)500 cm\(^{-1}\)), Si-C/Al-N (\(\approx\)750 cm\(^{-1}\)), and C-C/C-N vibrations (\(\approx\)1250 cm\(^{-1}\)) in the amorphous layer [Mor84, Bu187, Lam91, Che94, Per96]. As the amorphous layers have similar thicknesses for low and high dose implantation (see ref. [Hee95a]) the different light penetration depths are likely to be related to a difference in the density of the amorphous layers. Considering the spectra in figure 5.27c) only minor differences of the phonon intensities
between the spectra of samples annealed at different temperatures are visible. In addition, the spectra are similar to that in panel a). This can be explained with a high transparency of the recrystallized material. As a result the changes in the \((\text{SiC})_{1-x}(\text{AlN})_x\) region cannot be distinguished.

To overcome the difficulties of the plane-view sample geometry cross-sectional scans across the sample heterostructures were performed. Since these buried layers are expected to exhibit a cubic content (see for example ref. [Pez92b]) the polarization configuration \(-x(zy,zy)x\) for the cross-sectional scans was chosen to distinguish between the overlapping phonon features of the 3C-SiC TO phonon mode and the 6H-SiC \(E_1(\text{TO})\) phonon mode [Fel68a, Fel68b]. Figure 5.28 displays the cross-sectional \(\mu\)-Raman scan taken in steps of 100 nm in a 3D representation of a low dose implanted sample annealed at 1300°C (left hand side). The spectra in the front show zero signal due to the laser beam being entirely in the ambient atmosphere, while the rear spectra are taken in the unaffected 6H-SiC wafer. At the right hand side the intensity of the three phonon features appearing in the 3D plot are given: \(A_1(\text{TO})+E_2(\text{TO})\) (up triangles), \(E_2(\text{TO})\) (circles), and the superposition of the \(E_1(\text{TO})\) 6H-SiC with the TO 3C-SiC (down triangles). The straight lines give the simulation obtained using the model described in section 2.5.2. For the simulation the 6H-SiC has to be build of several distinct layers produced by the implantation and the following recrystallization. Since the \(A_1(\text{TO})+E_2(\text{TO})\) and the \(E_2(\text{TO})\) only stem from the 6H-SiC their phonon intensity variation was used to examine the 6H-SiC content in the implanted sample. In order to obtain
any cubic content the simulated and scaled intensity variation of the $E_2(\text{TO})$ was subtracted from the measurement. The resulting variation (given by the diamonds) can be related to the implanted layer $(\text{SiC})_{1-x}(\text{AlN})_x$.

Figure 5.29 displays the intensity variations depending on the laser beam position obtained from the scans across low dose (left part) and high dose (right part) implanted samples annealed at temperatures between $1300^\circ\text{C}$ and $1700^\circ\text{C}$. Considering the low dose implanted sample set the intensity variation of the sample annealed at $1300^\circ\text{C}$ can be simulated using four subsequent 6H-SiC layers. In view of their different participation in the intensity variation these layers can be interpreted as 6H-SiC with different defect densities with no cubic content. The assumption of a high defect density in the top 6H-SiC layer and a subsequent reduction for the deeper layers is corroborated by the high background intensity as well as by the enlarged FWHM of the phonon features near the surface, which can be seen in the
3D plot in figure 5.28. This phonon feature FWHM variation is additionally displayed in figure 5.30. The FWHMs are decreasing with increasing distance from the surface to a value of 2.90 cm\(^{-1}\) in the bulk typical for single crystals [Fel68a, Fel68b]. This indicates a decreasing defect density with increasing depth of the sample. Y. Sasaki et al. [Sas89] determined the FWHM in dependence of the correlation length in small 3C-SiC particles. Applying their formula for 6H-SiC the correlation length in the SiC increases from 1 nm in the top layer to \(\geq 50\) nm in the layer describing the unaffected 6H-SiC wafer. Such a layered system, namely top layer/two intermediate layers/bulk was found to be appropriate to simulate the ion implantation modifications of the 6H-SiC wafers [Zah96].

Thicknesses of \(\approx 120\) nm for the top layer and about 950 nm and 630 nm for the intermediate layers were evaluated by the simulations [Zah96]. In the case of 1500°C and 1700°C the thicknesses are 100 nm/870 nm/900 nm and 20 nm/700 nm/1200 nm, respectively [Zah96]. Obviously for the last two cases a cubic content due to the implanted layer can be observed. The shaded bar gives the region in which this implanted layer is located. For the sample annealed at 1500°C a thickness of \(\approx 300\) nm starting in a distance of about 110 nm from the surface and for the 1700°C sample a thickness of \(\approx 330\) nm starting in a depth of about 20 nm were estimated [Zah96]. The thicknesses and positions of the implanted layer correspond to results obtained by reflection high electron energy diffraction (RHEED) [Pez92a, Pez93], Rutherford backscattering (RBS) [Hee95a, Hee95b, Hee96], Auger electron spectroscopy (AES) [Hee95a, Hee95b, Hee96], and TEM but are a little larger [Zah96] (see

![Figure 5.30](image_url)

Figure 5.30: The variation of the phonon feature FWHM for the low dose implanted sample annealed at a temperature of 1300°C.
This small discrepancy is likely to be related to the different investigation methods, which are in the case of AES and RBS additionally destructive and modifying thus the investigated sample. Moreover, the modified depth in the 6H-SiC wafers up to \( \approx 2 \mu m \) is in contrast to the findings of these methods. On the other hand, results obtained by Positron Annihilation Spectroscopy for Ge\(^+\) implanted 6H-SiC reveal modifications up to depths of \( 2.5 \mu m \) correlated to induced vacancies \([Pac96a, Pac96b]\). For the high dose implanted samples similar results were obtained: 190nm/870nm/860nm \((1300^\circ C)\), 110nm/510nm/1250nm \((1500^\circ C)\), and 20nm/350nm/1540nm \((1700^\circ C)\), respectively \([Zah96]\). As in the case of low dose implantation for the 1300\(^\circ C\) sample no cubic content is detectable in contrast to RHEED and TEM investigations \((see \ refs. \ [Hee95a, Pez92a, Pez93]\)\), while for the 1500\(^\circ C\) and the 1700\(^\circ C\) samples implanted layers with thicknesses of \( \approx 290nm \) and \( \approx 330nm \) starting in depths of about 130nm and 50nm from the surface, respectively, were detected \([Zah96]\). This can be explained by a high defect density in the implanted 6H-SiC as well as in the transformed regions. For the interpretation of these phonon parameter variations one has to taken into account the different investigation methods.
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account that the assumption of distinct layers is a simplification because of the gradual implantation profiles [Hee96]. In spite of this simplification the model describes the measured variations quite well.

The measurements in this section demonstrate the ability of Raman spectroscopy for investigations in the silicon carbide material system though the Raman scattering efficiency for silicon carbide is very low. The measurements were performed for single crystalline material of 5 different polytypes as well as deposited films of 3C-SiC and implanted 6H-SiC wafers. The dependence on the incident laser light energy measured for the single crystalline materials gives on the one hand a resonant enhancement at about 2.46 eV due to the fundamental bandgap of 3C-SiC polytype and \( \omega^3 \) dependencies on the other hand for three of the remaining 4 polytypes (4H, 6H, and 15R) indicating the large bandgap energies of these polytypes. In contrast to this, the 21R-SiC polytype shows an increasing difference between the \( \omega^3 \) dependence and the measured dependence which is discussed as a beginning resonance enhancement. The SiC phonon feature frequency position dependence on the temperature exhibit a behaviour which shows a very good agreement to a quadratic approximation. This quadratic dependence was determined for all polytypes and optical phonon modes and was measured, apart from the 3C-SiC and the 6H-SiC polytype, for the first time - to my knowledge. As in the case of the diamond films on silicon substrates the advantages of a cross-sectional sample geometry for the investigation of transparent materials was demonstrated. Considering the 3C-SiC films deposited on silicon substrates the Raman spectroscopy measurements enables the detection of additional layers in the sample heterostructure, whose existence were obscured in the conventional plane-view sample geometry. The measurements in the cross-sectional sample geometry also gives the deposited layer thickness in comparison to the nominal layer thicknesses estimated from the growth conditions. For several samples quite large discrepancies were found (see for example figure 5.25) demonstrating the uncertainties in the layer thickness determination by this method. Furthermore the measurements of these samples demonstrates the application of Raman spectroscopy for the stress measurements in a heterostructure. The measurements in the plane-view as well as the cross-sectional sample geometry yield similar results as the bending plate method, which is a widely used method for this sort of measurements. Since the polycrystalline nature of the deposited films induces an additional phonon feature frequency position shift, this shift was separated from the frequency position shifts caused by the stress in the heterostructure. As a result the crystalline quality as well as the stress in the sample heterostructure was determined. In the case of the implanted 6H-SiC wafers the one-dimensional scans across the sample heterostructure in the cross-sectional sample geometry yield information about the polytype formation in the \((\text{SiC})_{1-x} (\text{AlN})_x\) layers in dependence on the annealing temperature and the implantation conditions. A layered system, namely layer/two intermediate layers/bulk was found to sufficiently describe the measured phonon intensity variations. The non-proportional intensity increase of the \( E_1 (\text{TO}) \) 6H-SiC phonon mode superimposed by the TO 3C-SiC phonon mode can be attributed to the formation for the 3C polytype in the implanted region near the surface. The coincidence between the cross-sectional \( \mu \)-RS scans and other measurement methods, like RHEED, RBS, and TEM is quite good. Furthermore, the cross-sectional
scans yields a distortion of the 6H-SiC wafer up to depths of approximately 2\(\mu\)m corroborating results obtained by PAS. These measurements demonstrate the advantages of this cross-sectional sample geometry for the detection of thin buried layers.

### 5.3 Boron and Boron Carbide (B\(_4\)C)

For the deposition of the boron nitride films in the following section several boron containing target materials are used, namely boron, hexagonal boron nitride, and boron carbide [Hah96, Hah97a, Hah97b, Sch95, Sch96] (see also chapter 4). In contrast to the hexagonal boron nitride target, with the boron carbide target carbon can be incorporated in the growing film. In addition, the formation of boron-boron bonds could not be excluded. To get information about the phonon features, which has to be expected for boron-boron and boron-carbon bonds in the grown film survey measurements of polycrystalline boron and B\(_4\)C bulk material were performed.

Figure 5.32 shows the Raman spectra taken with identical measurement conditions as for the boron nitride film measurements in the following section. While in the spectrum of the boron target only two broad bands at approximately 760\(\text{cm}^{-1}\) and 1090\(\text{cm}^{-1}\) are observable, in the B\(_4\)C spectrum there are several phonon features. The two broad bands in the boron...
spectrum correspond very well to structures in the B₄C spectrum. These structures thus
are correlated to boron-boron bonds, while the other phonon modes correspond to different
vibrations of the B₄C bonds. Since the carbon in the B₄C is always located in a tetrahedron
of 4 boron atoms no carbon-carbon vibrations can be observed. They should appear in the
spectral region from $\approx 1350 \text{cm}^{-1}$ to $\approx 1600 \text{cm}^{-1}$ (see for example figure 3.2). At this point
no further discussion of these materials is given.

It should be mentioned that these boron-boron bond correlated phonon modes can also be
observed in boron doped diamond [Age95]. This will be discussed in further detail in a
forthcoming paper for highly boron doped homoepitaxially grown diamond films.

5.4 Boron Nitride (BN)

In this section the investigation of the boron nitride films are discussed. Before the films are
discussed itself, some survey measurements of crystalline material of the cubic as well as the
hexagonal boron nitride modification are demonstrated.

5.4.1 Cubic Boron Nitride (c-BN)

Raman spectroscopy investigations were so far mainly performed for high pressure and
high temperature (HPHT) synthesized single crystals [Bra68, San83, Luk87, Her93, Kni95,
Wer97a] and only a few publications deal with deposited c-BN layers [Hal90, Wer97c]. This
is mainly due to the large band gap ($E_{g\text{, indir}} \approx 6.5 \text{eV}$) resulting in low light dispersion and
thus in a low Raman scattering efficiency. As a consequence survey investigations on the
dependence of the Raman scattering on (i) the incident laser light energy, (ii) the incident
laser light power, and (iii) the crystal size for c-BN HPHT single crystals were made. Single
crystals of four different sizes were investigated: 1mm, 100µm, 1µm, and 100nm. These sizes
were given by the producer of these single crystals (deBeers). No additional information
about the synthesis and the material was obtained. All the measurements were performed
using the conventional plane-view sample geometry.

Dependence on the Incident Laser Light Energy

Due to the large band gap of c-BN no resonance Raman condition can be utilized and thus
Raman spectra were taken in a first step of an 1mm c-BN single crystal for various laser lines
to find the most effective one. Figure 5.33 displays a selection of the Raman spectra measured
with HeCd, Ar⁺, and Kr⁺ laser lines. Clearly two phonon features can be observed. They are
related to the crystalline phonon structures of c-BN and correspond to the TO ($\approx 1055 \text{cm}^{-1}$)
and the LO phonon mode ($\approx 1304 \text{cm}^{-1}$), respectively. The multiplication factors given in the
plot mirror the decrease of the monochromator sensitivity in the red and the blue spectral
regions (see figure 2.13). Using the sensitivity factors of figure 2.13 the corrected dependence of the TO phonon feature intensities can be calculated. Figure 5.34 shows this dependence for the TO phonon feature as open symbols. The straight lines represent the calculation of $\omega^3$ (solid line) and $\omega^4$ (dashed line). Obviously the $\omega^3$ dependence on the incident laser light energy fits the measured dependence best. This corresponds to the discussion of equation (2.12) since photon counting was applied for the scattered photon detection. The arrow in figure 5.34 (E≈2.45eV) marks a possible impurity induced absorption in the HPHT synthesized c-BN. In contrast to this, other investigation of HPHT synthesized c-BN shows no absorption in this spectral region [Gie67, Chr74, Miy89, Ere95]. For that reason the origin of this weak maximum in the measured energy dependence is still unknown.

Concerning figure 5.33 and 5.34 the 482.5nm (2.57eV) of a Kr$^+$ laser (not displayed) or the
488.0nm (2.54eV) of Ar$^+$ laser were found to exhibit the best distinguished LO and TO phonon features with a sufficient signal to noise ratio and thus all following investigations of c-BN were performed using one of these two laser lines.

**Dependence on the laser light power**

In this subsection the second dependence, the influence of the incident laser light power on the phonon feature lineshape is discussed. This dependence was measured for the smallest crystal (L=100nm), since in the following subsection the dependence of the particle size of the c-BN crystals is investigated. For these crystallites the largest influence is expected, because the transmitted light is multiple reflected inside the crystallites, heating thus the investigated material. In larger crystals this introduced heat can be dispersed into the whole crystal leading thus to a decreased heating.

The maximum temperature increase induced in the material can be given as follows [Lax77]

$$\Delta T_{\text{max}} = \frac{P}{2\sqrt{\pi} k \omega_o}$$  \hspace{1cm} (5.5)

with P the laser light power in the crystal, k the thermal conductivity, and $\omega_o$ the ideal focus radius of the incident light beam given in section 2.4. On the other hand, for these investigations the c-BN crystallites with sizes of $\approx 100$nm were taken and thus this value has
to be inserted for $\omega_0$. For the calculation of the laser light power in the crystal the reflection was taken into account, giving thus

$$P = \left(1 - \frac{n - 1}{n + 1}\right)P_o$$

(5.6)

with $P_o$ the incident laser light power and $n$ the refractive index of c-BN at 2.71 eV (2.1 [Gie67]). For this temperature rise a phonon feature frequency position shift towards lower frequencies and an increase of the FWHM is expected (see section 2.1.3). Figure 5.35 shows the frequency position (squares) and the FWHM (circles) depending on the incident laser light power measured at the 100nm sized c-BN single crystals. The incident laser light power was measured in front of the microscope in the optical setup, leading thus to a reduction of the power to about 25% under the microscope. This reduced power was used in figure 5.35 and the calculations. The straight lines represent quadratic polynomial regressions to the data:

$$\text{CENTER } = 1056.10\text{cm}^{-1} - 0.18\frac{\text{cm}^{-1}}{\text{mW}}P_o - 5.36\frac{\text{cm}^{-1}}{\text{mW}^2}P_o^2$$

$$\text{FWHM } = 6.67\text{cm}^{-1} - 0.13\frac{\text{cm}^{-1}}{\text{mW}}P_o - 3.45\frac{\text{cm}^{-1}}{\text{mW}^2}P_o^2$$

(5.7)

Using the linear term in equation (2.27) and the value for the temperature dependent shift of the phonon mode in table 3.1 ($1 \times 10^{-2}\text{cm}^{-1}/\text{K}$ [Her93]) the temperature rise in the different
spectra is determinable. Transforming equation (5.5) as follows

\[ k = \frac{P}{2 \sqrt{\pi} \Delta T_{\text{max}} \omega_0} \]  

(5.8)

the thermal conductivity \( k \) can be calculated. Table 5.2 gives the thermal conductivities

Table 5.2: The absorbed laser light power \( P \), the temperature rise \( \Delta T_{\text{max}} \), and the thermal conductivity \( k \) for the incident laser light power of the measurements in figure 5.35. The \( \overline{k} \) means the average of the subsequent thermal conductivities.

<table>
<thead>
<tr>
<th>( P_0 ) (mW)</th>
<th>( P ) (mW)</th>
<th>( \Delta T_{\text{max}} ) (K)</th>
<th>( k ) (W mK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.3</td>
<td>10</td>
<td>90.3</td>
</tr>
<tr>
<td>1.25</td>
<td>0.8</td>
<td>6</td>
<td>376.1</td>
</tr>
<tr>
<td>5</td>
<td>3.2</td>
<td>90</td>
<td>100.3</td>
</tr>
<tr>
<td>12.5</td>
<td>8.1</td>
<td>40</td>
<td>571.2</td>
</tr>
<tr>
<td>50</td>
<td>32.3</td>
<td>840</td>
<td>108.5</td>
</tr>
<tr>
<td>125</td>
<td>80.7</td>
<td>1730</td>
<td>131.7</td>
</tr>
<tr>
<td>( \overline{k} ) average &amp; 229.7 &amp; &amp;</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

for the measurements in figure 5.35. The average value for the thermal conductivity of \( \overline{k} = 229.7 \text{W mK} \) is located in the range of values given in the literature 200-700 \text{W mK} [DeV72, Sl73]. On the other hand, the formula used for the calculation of the thermal conductivity requires an infinite crystal so that the heat can disperse into the whole crystal. Since the very small c-BN crystallites (diameter \( \approx 100 \text{nm} \)) used in this investigation cannot radiate all of the incident laser light power to the surrounding atmosphere the determined temperature rise in the detected volume is higher than it would be in an infinite crystal and thus a reduced thermal conductivity is calculated with equation (5.8). This is corroborated by an experiment using the 1mm c-BN crystal, for which no shift or FWHM broadening depending on the incident laser light power up to 125mW could be observed. Concerning figure 5.35 incident laser light powers of maximum 5-10mW corresponding to power densities of 2.3-10\(^3\) \text{W m}^{-2}\), due to the laser beam diameter of approximately 1 \( \mu \text{m} \), can be used for the following investigations of c-BN to minimize the influence of laser light heating.

### Dependence on the crystal size

The third survey experiment series deals with the dependence on the c-BN crystal size. In figure 5.36 the Raman spectra obtained for the c-BN crystals with four different nominal crystal sizes (100nm, 1\( \mu \text{m} \), 100\( \mu \text{m} \), 1mm) are displayed. Again the two phonon features corresponding to the TO and the LO phonon of crystalline c-BN are visible. Additionally, the broad feature at the lower energy side of the LO phonon mode can be observed, too. Its intensity nearly keeps constant with decreasing crystal size, while the intensity of the
crystal phonon modes reduces drastically. Considering these phonon modes three significant variations beside the intensity reduction with decreasing crystal size are visible: (i) the phonon features broaden, (ii) they become asymmetric, and (iii) they shift towards lower frequency positions. These changes can be understood in the light of the spatial correlation model, of which the theoretical aspects were already discussed in section 2.1.2 in detail [Shu70, Ric81, Par84, Cam86, Wer97a]. Figure 5.37 shows as open symbols the LO phonon spectra of figure 5.36 normalized to equal height. The straight lines represent the calculated Raman lineshapes using equation (2.24) of the spatial correlation model in section 2.1.2. For the TO phonon mode (not displayed) a similar behaviour was found. The evaluated values for the correlation length $S$ are given in the figure together with the nominal crystal sizes given by deBeers. Since the confined phonons are not only influenced by grain boundaries but as well by defects like vacancies, interstitials, oxygen and argon incorporation, etc.
5.4. BORON NITRIDE (BN)

value \( S \) is a few orders of magnitudes smaller than the corresponding nominal crystal size as in the case of diamond and silicon [Gon85, Age91, As85]. Considering the spectra for the 1mm single crystal (squares and solid line) the Raman lineshape shows a bulk-like shape [Her93, San83]. This is caused by the transition of the confined phonon to bulk-like behaviour for correlation lengths exceeding \( S=50 \text{nm} \) [Wer97a, Wer97c]. In figure 2.10 the calculated Raman spectra for \( S=5, 10, 20, 50, \) and \( 100 \text{nm} \) are given in a larger frequency range than in figure 5.37. Figure 5.38 displays the evolution of the calculated Raman lineshapes for decreasing correlation lengths \( S \) with \( S=0.5, 1, \) and \( 5 \text{nm} \) in the frequency range of figure 2.10. Clearly the increasing width of the phonon feature around 1200\( \text{cm}^{-1} \) can be seen. For a correlation length of \( S=0.5 \text{nm} \) the Raman spectrum of amorphous material was calculated, since the lattice constant of c-BN is \( a=3.615\AA \) [Pea52]). The lineshape of the calculated Raman spectrum is centered between 1200 and 1250\( \text{cm}^{-1} \), which agrees very well with the frequency position of the broad structure in the figures 5.33 and 5.36 and thus these features are correlated to amorphous inclusions in the c-BN single crystals. This is understandable in the light of the HPHT synthesis process in which amorphous BN was transformed into c-BN.

Figure 5.37: The measured LO phonon intensity (open symbols) after the substraction of the additional broad feature and the calculations of the Raman lineshapes using the spatial correlation model (straight lines).
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Figure 5.38: The evolution of the calculated c-BN LO phonon feature lineshapes for decreasing and small correlation lengths $S$.

5.4.2 Hexagonal Boron Nitride (h-BN)

For hexagonal boron nitride (h-BN) only the dependence of Raman scattering on the incident laser light energy was investigated. A detailed discussion of the particle size dependence of the h-BN phonon features is given by Nemanich et al. [Nem81]. In contrast to the size dependence for c-BN the $E_{2g}^{(2)}$ phonon mode of h-BN shifts to higher energies, the FWHM broadens symmetrically, and they can be described by a Gaussian lineshape [Nem81]. This is caused by the unusual phonon dispersion relation of h-BN, i.e. the phonon frequency of the highest branch does not have a maximum at the $\Gamma$-point [Nem81]. The measurements of the dependence on the incident laser light energy were performed utilizing a part of a polycrystalline h-BN sputtering target in the conventional plane-view sample geometry.

Dependence on the Incident Laser Light Energy

As in the case of the c-BN, for the h-BN with a fundamental band gap of $E_{\text{g,dir}} \approx 5.8$ eV no resonance Raman conditions can be used with the obtainable laser lines and thus the dependence of the Raman scattering on the incident laser light energy was investigated. Figure 5.39 displays the Raman spectra of a polycrystalline h-BN target. Clearly the low frequency $E_{2g}^{(1)}$ phonon mode as well as the high frequency $E_{2g}^{(2)}$ phonon mode can be observed. In the two spectra for which no $E_{2g}^{(1)}$ phonon mode is shown, plasma lines of the Ar$^+$ or the Kr$^+$ laser appear near the frequency position of the $E_{2g}^{(1)}$ phonon mode. Similar to figure 5.33 the scaling factors at the spectra of figure 5.39 reflect the decreasing sensitivity of the monochromator in the red and the blue spectral region. The corrected intensities of the
Figure 5.39: Dependence of the Raman scattering on the incident laser light energy for the polycrystalline h-BN target.

$E_{2g}^{(2)}$ phonon feature are plotted in figure 5.40 as open symbols depending on the incident laser light energy. The straight lines represent fits with $\omega^3$ (solid line) and $\omega^4$ (dashed line). Obviously the $\omega^3$ dependence again fits the measured dependence best due to the photon counting detection (see section 2.1.1). As in the dependence of the c-BN TO phonon mode on the incident laser light energy in figure 5.34 a maximum in the measured dependence can be found. In the case of the h-BN $E_{2g}^{(2)}$ phonon feature this maximum is centered at $E \approx 2.51\text{eV}$. In contrast to this, optical absorption measurements usually show no absorption in this spectral region [Hof84] and thus the origin of the absorption is still unknown. Considering the figures 5.39 and 5.40 optimum incident laser lines of the Ar$^+$ laser: 476.5nm (2.60eV) or of the Kr$^+$ laser (not displayed): 482.5nm (2.57eV) are determined. This correlates quite well with the optimum incident laser lines for the c-BN. Due to this the investigation of the BN films are performed using the 482.5nm line of a Kr$^+$ laser or the 488.0nm line of an Ar$^+$ laser, since
most of the investigated BN films consist mainly of c-BN [Fri95, Ric95, Hah96, Roe97].

### 5.4.3 Boron Nitride films

As discussed for the single crystalline c-BN and h-BN material the BN films are transparent [Ste96]. Due to film thicknesses of maximum 200nm the measured Raman spectra utilizing the conventional plane-view sample geometry are dominated by the silicon substrate phonon features. Unfortunately the adhesion of the BN films on the silicon substrate is too low to use the cross-sectional sample geometry. Figure 5.41 shows the transmission electron microscopy (TEM) photograph of such a teared away c-BN film. Obviously the weakness of the interfacial amorphous layer causes the loss of adhesion of the layer [Kes93, Kes94, Roe97]. Figure 5.42 shows the SEM photograph of another c-BN film. In contrast to figure 5.41 the c-BN has partly disrupted the silicon substrate and deep holes remain in the silicon. On other regions the c-BN film is still adhering. Similar as for the film in figure 5.41 for films shown in figure 5.42 no cross-sectional measurements can be performed. Nevertheless the focus diameter of approximately 1μm enables the investigation of those regions in which the c-BN film is still adhering. The advantages of the xy-stage under the microscope were used to perform two-dimensional mappings on c-BN and h-BN films. The mappings were taken in steps of 100nm in a 10x10μm² array for the silicon phonon mode to investigate the influence of the hard coating on the silicon substrate. Before these mappings are described in further detail, single Raman spectroscopy measurements of the BN phonon modes in the films are discussed.

Figure 5.43 shows the Raman spectrum of a pure h-BN film deposited on a silicon substrate.
The steep increase on the hand left side of the spectrum stems from the second order phonon scattering of the silicon substrate. The straight line represents a Gaussian fit to determine the frequency position and the FWHM of the phonon mode. This enables the evaluation of the crystallite size in the film [Nem81]. The $E_{2g}^{(2)}$ phonon mode is shifted towards higher frequencies and has an increased FWHM compared to the spectra in figure 5.39. The shift gives a crystallite size of $L \approx 5 \text{nm}$ while the FWHM corresponds to a crystallite size of $L \approx 5.5 \text{nm}$ [Nem81] demonstrating the nanocrystalline nature of the deposited h-BN film. Considering the stress dependence of the $E_{2g}^{(2)}$ phonon mode in table 3.1 ($4 \text{cm}^{-1} \text{GPa}^{-1}$) the difference corresponds to an intrinsic stress of approximately 125 MPa in the h-BN film [Exa91].

In figure 5.44 the RS measurement of a c-BN film (open circles) in the LO phonon mode range is displayed. For comparison the spectrum of a reference silicon sample without a c-BN film measured under identical conditions is included. Calculations using equation (2.24)
with correlation lengths of $S=12$, 13, and 14nm and a natural linewidth of $2.1\text{cm}^{-1}$ are also shown as straight lines. Obviously the calculated lineshape for $S=13$nm fits the measurement best. As discussed for the asymmetry of the diamond phonon feature Raman lineshape for diamond films on silicon the increase of the natural linewidth leads to an improved fit of the simulated and the measured Raman lineshape. This is demonstrated by the dash-dotted line in figure 5.44, which was calculated with a correlation length of $S=14$nm and an increased natural linewidth of $5\text{cm}^{-1}$.

Considering now the two-dimensional mappings it should be mentioned, that a mapping of the BN phonon modes of the h-BN films as well as of the c-BN films was not performed. This is caused by the extreme weakness of the phonon modes, due to the transparency of these materials leading to a very low Raman scattering efficiency and thus the silicon substrate phonon feature was mapped with a 100nm stepwidth in a $10\times10\mu\text{m}^2$ array to investigate the influence of the deposited BN film on the silicon substrate [Wer97c]. Figure 5.45 shows the phonon feature intensity (a), the frequency position shift (b), the FWHM (c), and the asymmetry (d) of the silicon phonon feature for a nearly 100% c-BN film (see figure 5.44). The SEM photograph in figure 5.42 shows the same sample. Although the scanned array does not correspond to this visualized region, a similar appearance can be assumed. The scanned array includes a region with silicon similar to that found on an untreated substrate (1), a region with a still adhering (2), and regions with a teared away c-BN layer (3), (4). Considering the phonon intensity and frequency position shift the correlations can be identified easily. In contrast to point (1) with an intensity of about 2.5-3cts/mWs at point (2) the intensity is increased to about 4cts/mWs, while at both points no frequency position shift is observable.
Figure 5.44: Raman spectrum of a nearly 100% c-BN film deposited on a silicon substrate (open circles) and the model calculations with different correlation lengths and natural linewidths (lines). The featureless spectrum at the bottom represents a reference measurement under identical conditions of a silicon sample without a c-BN film.

This is caused by the so-called "Entspiegelungseffekt" induced by the adhering c-BN layer at point (2). The "Entspiegelungseffekt" is related to the reduced reflection of a high refractive material covered with a thin low absorbing layer with a lower refraction index [Hec87]. Thus more intensity can enter the substrate and the scattered intensity increases. Since this does not influence the silicon itself no variation of the frequency position can be measured. In contrast to this, the silicon substrate at point (3) is heavily disrupted. The teared away c-BN film has cracked out silicon material and thus the crystalline quality is drastically reduced near the former silicon substrate surface. This disruption of the silicon substrate can be observed in the SEM photograph on the right hand side. Since the intensity reduces to nearly zero, the phonon feature shifts to lower frequencies, and shows an asymmetric broadening this behaviour can again be explained in the light of the spatial correlation model. The observed modifications of the silicon phonon feature lineshape correlate to an average correlation length of about 20nm in these regions [Ric81, Cam86]. The spectra at point (4) exhibit a different behaviour. Unless the intensity is reduced the FWHM shows low values and nearly no asymmetry is observable, indicating a quite unchanged silicon material. On the contrary the frequency position is shifted towards higher frequencies, which is related to a compressive stress of about 200MPa (using the value of table 3.1). Taking the reduced scattering intensity into account, this region is likely to be covered by a rough and absorbing layer. The nature of the material forming this layer is unknown, but concerning figure 5.41
The phonon scattering intensity (a), the frequency position shift (b), the FWHM (c), and the asymmetry (d) of the silicon phonon feature mapped with 100nm steps in a 10x10µm² array. The numbers give correlation points discussed in the text: The untreated substrate (1), a region with a still adhering (2) and regions with a teared away c-BN film (3), (4).

The existence of remaining a-BN or h-BN on the silicon substrate after the film has teared away cannot be excluded. Compared to this inhomogeneous c-BN film, the mapping of an h-BN film presents a very homogeneous deposition on a silicon substrate [Roe97]. The phonon parameter variations are quite small with respect to those in figure 5.45 with the intensity varying between 2.2 and 2.8cts/mWs, the frequency position showing shifts between -0.2 and 0.6cm⁻¹, a FWHM of approximately 3.2cm⁻¹, and hardly any asymmetry (1.0 - 1.05).

Additionally BN films deposited on silicon substrates were supplied by A. Schütze from the Fraunhofer-Institut für Schicht- und Oberflächentechnik (FhGIST), Braunschweig. In figure 5.46 the Raman spectrum of a mainly h-BN film on a silicon substrate is shown (open squares). The components describing the h-BN and the c-BN content are given by the dashed lines and the resulting simulation with these components is shown as the solid line. For the
Figure 5.46: Raman spectrum of a mainly h-BN film (open squares). The solid line shows the simulation of the measured spectrum utilizing the two components given by the dashed lines.

h-BN component a Gaussian lineshape was calculated with a FWHM of 51.3 cm\(^{-1}\) and a frequency position of 1382.6 cm\(^{-1}\). This gives a correlation length for the h-BN of about 3 nm. Using equation (2.24) with a correlation length of 0.5 nm the component of the c-BN was calculated. It should be mentioned that the linewidth was increased from the natural linewidth of about 2.4 cm\(^{-1}\) to 5.8 cm\(^{-1}\) following the discussion of Yoshikawa et al. [Yos93] discussed in section 5.1. In the Raman spectrum given in the upper panel of figure 5.47 the presence of c-BN as well as h-BN can also be observed. Considering the h-BN component the simulated Raman lineshape was again calculated with a Gaussian lineshape for a correlation length of 2.5 nm. The Raman spectrum shown in the lower panel of figure 5.47 shows no feature related to h-BN, but a feature around 1100 cm\(^{-1}\), which can be assigned to B-B or B-C bonds in the deposited BN film (see figure 5.32). Since both Raman spectra given in figure 5.47 are taken of mainly c-BN films the dominating feature in the spectrum is the c-BN component. In the upper panel the c-BN component was simulated using a correlation length of 10 nm, while for the component in the lower panel a correlation length of 15 nm was used. For both c-BN components the linewidth was increased to 5.8 cm\(^{-1}\). However, the c-BN and h-BN components are not sufficient for the description of the measured Raman spectra. In both Raman spectra an additional peak or a shoulder around 1335 cm\(^{-1}\) can be observed. This feature is related to C-C bonds in the c-BN film introduced by the usage of a B\(_4\)C target [Sch95, Sch96] for the deposition of these films. The formation of B-B, B-C, and C-C bonds in BN films deposited using a B\(_4\)C target is corroborated by recent investigations of Johansson et al. [Joh96] with X-ray photoelectron spectroscopy.
Figure 5.47: Raman spectra of two mainly c-BN films (open squares). The solid line shows the simulation of the measured spectrum utilizing the simulated components given by the dashed lines.
In conclusion, this section demonstrates the suitability of Raman spectroscopy for the investigation of single crystalline as well as deposited cubic boron nitride material. Additionally, the influence of the hard coating on the substrate was measured. The measurements show that the laser lines in the blue spectral region are the most effective ones not only for the investigation of single crystalline material but also for thin deposited c-BN films. The observed effects of reduced particle size, i.e., asymmetric broadening and frequency position shift towards lower frequencies, are explained in the light of the spatial correlation model. This model was applied to c-BN for the first time, which was enabled by the recent publication of the phonon dispersion relation by K. Karch et al. [Kar96]. A similar relationship between the correlation length and the nominal particle size as in the case of diamond and silicon was obtained. It is worthy noting, that the evaluation of correlation lengths critically depends on the precise knowledge of the dispersion relation $\Omega(q)$ in equation (2.24). If, on the other hand, defect densities could be determined by other methods, then such Raman studies can be utilized as a test for the dispersion relation. The application of two-dimensional mappings was demonstrated to enable the investigation of the influence of the hard coating on the substrate: An "Entspiegelungseffekt" in regions with an adhering c-BN layer as well as disruption can be observed in regions with a teared away c-BN layer. Furthermore the influence of the deposition conditions, especially the modification of the sputtering target, was demonstrated for samples produced on the one hand by an h-BN target or a boron-target and on the other hand by a B$_4$C target. Additional phonon features appear in the Raman spectra of c-BN films deposited utilizing the latter target in comparison to films deposited with one of the former targets. These additional phonon features were related to B-C and C-C, respectively, indicating the incorporation of the carbon in the growing film.

### 5.5 Carbon Nitride

Many attempts have been made to synthesize carbon nitride (C$_3$N$_4$) since Liu and Cohen [Coh85, Liu89] predicted its existence. Up to now a large number of experiments were performed applying different methods such as magnetron sputtering [Che93], r.f. sputtering [Yu94], laser ablation [Niu93], ion beam deposition [Mar94b], CVD [Kou94], and arc deposition [Mat94]. As a result of these experiments it was demonstrated that the main difficulty is the increase of the N-content in the deposited film to the stoichiometry necessary for C$_3$N$_4$ and the films are thus called CN$_x$. For that reason the Raman spectra of these films exhibit only two broad bands centered around 1350 cm$^{-1}$ and 1600 cm$^{-1}$ [Che93, Nis94, Li95, Ren95, Lee96]. Recently, E.G. Wang's group at the Chinese Academy of Science in Beijing has successfully synthesized C-N films on both silicon and nickel substrates via bias-assisted hot filament chemical vapor deposition using a gas mixture of nitrogen and methane [Che96a, Che96b, Che96c, Che97a, Che97b, Che97c]. The films obtained on Ni(100) substrates were mainly composed of $\alpha$- and $\beta$-C$_3$N$_4$ [Che97a, Che97b, Che97c]. Furthermore, the different deposition conditions, such as methane concentration can lead to the selected growth of $\beta$- and $\alpha$-C$_3$N$_4$ [Che96b], for example, CH$_4 = 1.0$ and 2.0 vol% yield $\beta$- and $\alpha$-C$_3$N$_4$.
prominent growth, respectively. A detailed description of the experimental procedure is given in the refs. [Che97a, Che97b, Che97c].

In this section firstly samples supplied by C. Spaeth and M. Kühn are investigated. They were deposited using magnetron sputtering yielding CN\textsubscript{x} films on silicon substrates [Spa96, Spa97, Fri97a]. Figure 5.48 shows the Raman spectra of some selected CN\textsubscript{x} samples. The

![Raman Spectra](image)

Figure 5.48: Raman spectra of some selected CN\textsubscript{x} samples [Spa96, Spa97].

labels at the spectra describe the variation of the deposition parameters for the subsequent samples [Spa96, Spa97]. The voltage value gives the acceleration voltage for the nitrogen ions, \( Q_r \), the ratio of the arrival rates for nitrogen and carbon, and the temperature value corresponds to the substrate temperature [Spa96, Spa97]. The nitrogen concentration was measured by elastic recoil detection analysis giving values between 0.23 and 0.31 [Spa96, Spa97]. Spectrum a) gives the Raman spectrum of a tetrahedrally bonded amorphous carbon film (ta-C) for comparison. Only one or two broad bands appear in all spectra corresponding
to the broadened E$_{2g}$ mode of graphite around 1600 cm$^{-1}$ (the G-band) in combination with vibrations of the C=N bonds [Lin91] and the D-band around 1350 cm$^{-1}$ correlated to the high disorder in the CN$_x$ films (see also section 3.2.1). With increasing substrate temperature (spectrum c) or intensified ion bombardement (spectrum d) the D-band intensity increases, which is correlated with a decreasing graphite particle size [Kni89, Shr90, Pra96]. This increased amorphization leads to a relaxation of the graphite lattice and reduces thus the hardness of the deposited CN$_x$ films. As a result, the measured E-moduls of the samples (30 - 190 GPa, depending on the deposition parameters) are smaller than the E-modul of the ta-C sample (676 GPa) [Spa96, Spa97].

In contrast to the nearly amorphous CN$_x$ samples above the C$_3$N$_4$ samples supplied by E.-G. Wang are crystalline [Che96a, Che96b]. SEM photographs exhibit prismatic formed, but randomly oriented, carbon nitride crystals with sizes of several micrometers in length and of several hundred nanometers width [Che96b] and thus no polarization analysis in the RS experiments were performed. Figure 5.49 displays the Raman spectra of a $\beta$-C$_3$N$_4$ rich deposit (sample Ni18 in the upper panel) and of an $\alpha$-C$_3$N$_4$ rich deposit (sample Ni05 in the lower panel). The inserts show the spectral region from 700 - 1700 cm$^{-1}$ enlarged by a factor of 3. Several sharp phonon features are well distinguished with frequency positions of 843 cm$^{-1}$, 915 cm$^{-1}$, 1258 cm$^{-1}$, 1299 cm$^{-1}$, 1354 cm$^{-1}$, 1435 cm$^{-1}$, and 1593 cm$^{-1}$ [Wer97e]. In contrast to most of the other Raman investigations of carbon nitride films no broad structures in the spectral region from 1100 - 1700 cm$^{-1}$ are observed (see for example 5.48). As a result the formation of an amorphous material can be excluded as corroborated by X-ray diffraction (XRD), SEM, and TEM investigations [Che97a, Che97b, Che97c]. A comparison of the Raman spectrum with recent calculations of the vibrational density of states (VDOS) by J. Widan y et al. [Wid96] for four different C$_3$N$_4$ crystal modifications shows that all features in the measured spectrum can be related to maxima in the VDOS. A detailed discussion of the crystal modifications and the assignment of the VDOS features to vibrations is given in ref. [Wid96]. The lower panel in figure 5.49 shows the Raman spectrum of an $\alpha$-C$_3$N$_4$ rich deposit (sample Ni05). The spectrum is quite similar to that in the upper panel. However, some differences are visible: (i) The elastically scattered light (increase towards lower frequencies) is drastically enlarged. This can be explained by a smoother surface and interface of the Ni18 sample. (ii) The phonon features at 1299 cm$^{-1}$ and 1354 cm$^{-1}$ and at 843 cm$^{-1}$ and 915 cm$^{-1}$ have different intensity ratios. (iii) Two additional phonon features appear at 900 cm$^{-1}$ and 1126 cm$^{-1}$, while the phonon feature at 1435 cm$^{-1}$ has vanished. The existence of the different phonon features and their varying intensities is likely to be induced by the different prominence of the $\alpha$- and the $\beta$-modification in the two C$_3$N$_4$ deposits, since the phonon features and their frequency positions and selection rules differs for the distinct crystal modifications.

These observed phonon features cannot be related to any other compound of the participating materials [Che97a, Che97b, Che97c]. This is corroborated by the very good correspondence of the calculated and the measured frequency positions shown in figure 5.50. Although the group theoretical calculations by Wada et al. [Wad81a] for Si$_3$N$_4$ reveal 42 Raman active phonon modes for the $\alpha$ modification, Raman measurements of Si$_3$N$_4$ yield only 30 up to
Figure 5.49: Raman spectra of a $\beta$-C$_3$N$_4$ rich deposit (sample Ni18 in the upper panel) and of an $\alpha$-C$_3$N$_4$ rich deposit (sample Ni05 in the lower panel). The insert shows the spectral region from 700 - 1700 cm$^{-1}$ enlarged by a factor of 3.
5.5. CARBON NITRIDE

Figure 5.50: Comparison of the measured frequency positions (open symbols) with calculated frequency positions using Hooke’s law and a factor 1.43 [Yen95] from the Si$_3$N$_4$ phonon feature frequency positions [Wad81a].

now. For the $\beta$ modification 21 Raman active phonon modes are calculated and measured [Wad81a] (for details see section 3.2.3). The calculated phonon modes are numbered with increasing phonon mode frequency. These respectively numbers are named phonon mode number in figure 5.50. Its theoretical frequency positions were calculated from the frequency positions of Si$_3$N$_4$ [Wad81a] using Hooke’s law [Wix90, Yen95]

$$\frac{\Omega_{C-N}}{\Omega_{Si-N}} = \sqrt{\frac{B_{C-N} d_{C-N} m^*_C}{B_{Si-N} d_{Si-N} m^*_Si}}$$

with $B$ the bulk modulus, $d$ the bond length, and $m^*$ the reduced mass ($\frac{1}{m^*} = \frac{1}{m_1^2} + \frac{1}{m_2^2}$) of the carbon-nitrogen (C-N) and the silicon-nitrogen (Si-N) bonds. A scale factor of 1.43 was calculated using the values given in table 5.3 [Liu90, Yen95]. In contrast to T.-Y. Yen et al.

Table 5.3: The bulk modulus $B$, the bond length $d$, and the reduced mass $m^*$ for the Si-N and the C-N bond [Liu90, Yen95]. In both cases the values are given for the $\beta$-modification.

<table>
<thead>
<tr>
<th>bond</th>
<th>$B$ (GPa)</th>
<th>$d$ (Å)</th>
<th>$m^*$ rel. atomic mass</th>
</tr>
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<tbody>
<tr>
<td>Si-N</td>
<td>256</td>
<td>1.74</td>
<td>9.35</td>
</tr>
<tr>
<td>C-N</td>
<td>427</td>
<td>1.47</td>
<td>6.47</td>
</tr>
</tbody>
</table>

[Yen95] who found only phonon features around 300cm$^{-1}$, the Raman spectra in figure 5.49
exhibit phonon features in a larger frequency range. Unfortunately the inelastic scattered light disables up to now a measurement of the low frequency phonon features.

The two broad bands observable in both Raman spectra in figure 5.49 at \( \approx 500 \text{cm}^{-1} \) and \( \approx 1100 \text{cm}^{-1} \) can be assigned to the formation of NiO\(_x\) [Die71, Far80], which is understandable since the samples were stored in air. In addition, a high incident laser light power had to be used to investigate the samples and thus the temperature rise in the laser beam center has to be calculated using equation (5.5). With a thermal conductivity of about \( \frac{8}{\text{W mK}} \) for nickel [Pow72], an absorbed power of \( P = 8.2 \text{mW} \) (due to a reflectivity of \( R \approx 0.45 \) [Lyn71]) and an ideal focus radius of \( \omega_0 = 0.58 \mu \text{m} \) the temperature increases by \( 499 \text{K} \), resulting in a sample temperature of \( \approx 530^\circ \text{C} \). Farrow et al. [Far80] measured Raman spectra of NiO\(_x\) on oxidated nickel substrates heated to temperatures of about \( 570^\circ \text{C} \). They found the formation of oxygen-rich NiO\(_x\) with broad bands near \( 560 \text{cm}^{-1} \) and \( 1100 \text{cm}^{-1} \) [Far80]. This corresponds very well with the frequency positions in the Raman spectra of figure 5.49.

These measurements of the different carbon nitride samples demonstrate the ability of Raman spectroscopy to distinguish between the different bonds available in carbon nitride films. In the mainly nanocrystalline or amorphous CN\(_x\) films C=C and C=N bonds dominate, inducing the broad bands around \( 1350 \text{cm}^{-1} \) and \( 1600 \text{cm}^{-1} \) [Lin91, Tam94] in the Raman spectra [Che93, Li95, Lee96]. Additionally, phonon features around \( 2200 \text{cm}^{-1} \) were reported for CN\(_x\) films [Ren95] representing C≡N bonds in the investigated film [Lin91]. In contrast to this the small crystallites in the C\(_3\)N\(_4\) films exhibit several quite sharp phonon features in a wide spectral range between \( 850 \text{cm}^{-1} \) and \( 1600 \text{cm}^{-1} \), which were detected for the first time in a Raman spectroscopy measurement. These phonon features are related to vibrations of the C-N bonds in the C\(_3\)N\(_4\) crystals [Wid96, Wer97c]. Further measurements including a variation of the incident laser light energy, of the polarization configuration, and the deposition parameters have to be performed to improve the information obtainable from this very new and promising material system.
Chapter 6

Conclusion

The results of this work are twofold. First, the suitability of Raman spectroscopy for the investigation of hard coatings, especially diamond, silicon carbide, boron nitride, and carbon nitride was demonstrated, although all these materials are wide bandgap semiconductors with fundamental bandgap energies between 2.46eV (3C-SiC) and 6.5eV (diamond) and thus the materials exhibit only very low Raman scattering efficiencies.

In this context, the Raman spectroscopy measurements of crystalline C\textsubscript{3}N\textsubscript{4} deposits yield for the first time sharp and well distinct phonon features in a wide spectral range. These phonon features could be related to maxima in theoretically calculated vibrational density of states as well as to theoretically predicted phonon frequency positions using Hooke's law and the frequency positions of Si\textsubscript{3}N\textsubscript{4}. Up to now in publications dealing with Raman spectroscopy of carbon nitride mainly two broad bands were measured confirming the amorphous or nanocrystalline, carbon-rich nature of the deposited CN\textsubscript{x} films.

In the case of boron nitride for the first time the dependence of Raman scattering efficiency on the incident laser light energy was evaluated. For cubic boron nitride as well as hexagonal boron nitride a non resonant $\omega^3$ dependence on the laser light energy was determined, as expected due to the transparency of both crystal modifications in the energy range 1.92eV to 2.81eV. Because of the highest monochromator sensitivity in the red-yellow spectral region and the $\omega^3$ dependence of both boron nitride modifications the laser lines in the blue spectral region, especially the 482.5nm (2.57eV) Kr$^+$ and 488.0nm (2.54eV) Ar$^+$ laser lines, were determined to be the optimum laser lines for the investigations in this material system. The Raman scattering dependence on the incident laser light power was additionally investigated for the c-BN modification resulting in a maximum laser light power density of 2-3 $10^6 \frac{W}{m^2}$ for the measurements. These dependence additionally reveals a value for the thermal conductivity of boron nitride, which was determined to $229.7 \frac{W}{mK}$. This value is well located in the range of values given in the literature. Furthermore, the dependence of the Raman scattering on the crystal size was described for c-BN for the first time in terms of the spatial correlation model. The measured asymmetric broadening and the frequency downshift were very well
simulated using a recently calculated phonon dispersion relation. This dependence was measured for single crystalline material of different size, but the results were also used for c-BN films deposited on silicon substrates, where they corroborate the nanocrystalline nature of the deposited films.

For the silicon carbide the incident laser light energy and the temperature dependences were measured for 5 different polytypes, namely 3C, 4H, 6H, 15R, and 21R - to my knowledge - for the first time. Due to the fundamental bandgap energies of 3C-SiC and 21R-SiC resonance enhanced Raman scattering was detected, while for the other polytypes ω³ dependences on the incident laser light energies were measured. In this context, the fundamental bandgap energy of 3C-SiC were determined to 2.46eV in contrast to theoretical calculations of 2.41eV. Together with other experimental results this corroborates that the theoretically calculated value is likely too low.

The second part of this work gives a theoretical model for the description of the phonon parameter variations in the cross-sectional scans across a sample heterostructure. This rarely used sample geometry combined with the conventional plane-view sample geometry was demonstrated to enable the detection of ultra-thin top layers and interfacial layers as well as buried layers with thicknesses in the nanometer range. For this model a convolution of the Gaussian laser beam intensity profile with several boxfunctions representing the distinct layers in the sample heterostructure is introduced. A further improvement of the simulation and the measured phonon feature parameter variations was obtained if the different light penetration depths in the different materials in the heterostructure were taken into account. Moreover the influence of diffraction was discussed in detail.

In the case of the diamond material system the interface formation to the substrate, which is still under discussion, was investigated. With varying growth conditions the formation of a graphitic interfacial layer with a thickness of 2nm as well as the direct nucleation of the diamond seeds in the silicon substrate was proofed. Due to the stepwidth of 100nm and the deconvolution with the Gaussian laser beam lineshape the obtained phonon parameter variations were discussed depth-resolved, which enables the determination of the material properties variations, like stress, crystal size and quality. For silicon carbide deposits on silicon substrates the identification of additional layers in the sample heterostructure with thicknesses in the nanometer range was performed. Furthermore, the formation of an intermixing layer in implanted 6H-SiC wafers with a cubic polytype was determined. These results were corroborated by investigations with other methods, like bending plate, TEM, AES, RBS, SEM, and PAS, demonstrating the very good suitability of the cross-sectional sample geometry for the investigation of buried and obscured thin layers in a sample heterostructure.

In conclusion, this work confirms the feasibility of Raman spectroscopy for the investigation of hard coating materials despite of their low Raman scattering efficiency and the improved interface assessment for these coatings deposited on substrates, utilizing various Raman spectroscopy tools.
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