Study in analytical glow discharge spectrometry and its application in materials science
1. Gutachter: Prof. Dr. Jürgen Eckert
2. Gutachter: Prof. Dr. Arne Bengtson
Tag der Verteidigung: 18. August 2011
# Content

Kurzfassung ........................................................................................................................ 3
Abstract .................................................................................................................................. 5

1 MOTIVATION AND DISSERTATION SCOPE ........................................................................ 8
2 INTRODUCTION .................................................................................................................. 11

2.1 The Glow Discharge (GD) .................................................................................................. 11

2.1.1 GD plasma .................................................................................................................... 11
2.1.2 GD sputtering vs. other sputtering techniques .............................................................. 15
2.1.3 GD sources .................................................................................................................. 16

2.2 Glow Discharge Optical Emission Spectrometry (GD OES) .............................................. 18

2.2.1 Basic principles of GD OES .......................................................................................... 18
2.2.2 Quantification in GD OES ............................................................................................ 19
2.2.3 GD OES vs. other depth profiling methods .................................................................. 23

2.3 Pulsed glow discharge (PGD) ............................................................................................. 24

2.3.1 Virtues and shortcomings of the pulsed mode ............................................................... 24
2.3.2 Rf or dc pulsing? ............................................................................................................. 26
2.3.3 How big is the thermal stress reduction when PGD is applied? ................................... 29

2.4 Measurement of the discharge gas temperature .................................................................... 31

2.4.1 What is the temperature of the GD gas? ....................................................................... 31
2.4.2 Determination of the GD temperature from the rotational spectra of the molecules .......................................................................................... 35
2.4.3 Determination of the GD temperature from the Doppler width of spectral lines .................................................................................. 37
2.4.4 Laser-light scattering technique for the measurement of the GD temperature .......... 37

2.5 Applications ....................................................................................................................... 38

2.5.1 CIGSe thin film solar cells ............................................................................................ 38
2.5.2 SAW devices ................................................................................................................. 43

3 EXPERIMENTAL DETAILS .................................................................................................. 46

3.1 Measurement of the electrical characteristics ..................................................................... 46
3.2 Measurement of the sputtered crater shapes ...................................................................... 47
Kurzfassung


Der Einfluss des Sputters auf Cu(In,Ga)Se$_2$ (CIGSe) Dünnschichten von Solarzellen wurde erstmals beschrieben. REM-Untersuchungen an GD-gesputterten CIGSe Schichten haben gezeigt, dass die Sputtereffekte durch die Variation der Pulsparameter reduziert werden können.


Abstract

Glow Discharge Optical Emission Spectrometry (GD OES) has proved to be a versatile analytical technique for the direct analysis of solid samples. The application of a pulsed power supply to the glow discharge (GD) has a number of advantages in comparison with a continuous one and thereby broadens the analytical potential of the GD. However, because the pulsed GD (PGD) is a relatively new operation mode, the pulsing and plasma parameters as well as their influence on the analytical performance of the GD are not yet comprehensively studied.

The aim of this dissertation consists in the investigation of the PGD features, which are crucial for both understanding the discharge plasma processes and analytical applications. The influence of the pulsing parameters on the PGD is ascertained and compared for direct current (dc) and radio frequency (rf) discharges. In the research attention is firstly paid on the electrical parameters of PGD, then on the sputtered crater shapes, sputtering rates and finally on the light emission. It is found that the sputtered crater shape is strongly affected by the duration of the applied pulses even when the duty cycle is fixed. The pulse length influences the intensity of the light emission as well (at constant duty cycle). Moreover this influence is different for emission lines of atoms and ions in the plasma. This phenomenon can be seen at the comparison of atomic and ionic lines of different elements.

The voltage–current plots of the PGD are found to indicate heating of the discharge gas when operating at high duty cycles. Using this feature a new method for the estimation of the discharge gas temperature from the voltage-current characteristics of the PGD is developed. The calculated temperature values are compared with another temperature measurement technique. Different temperature estimation procedures have shown that the discharge gas temperature can be reduced by around 100 K when PGD is applied. The temperature measurements have also confirmed that the gas heating can be adjusted by variation of the pulsing parameters.

The effect of sputtering on the Cu(In,Ga)Se$_2$ (CIGSe) layer surface of the solar cells is described for the first time. SEM investigations of the CIGSe layer of the solar cells have shown that sputter induced effects can be reduced by variation of the pulsing parameters.
With regard to the question whether dc and rf pulsed discharges behave similarly: nearly all phenomena found with dc discharges also appear in the rf case. Hence it is concluded that the pulsed rf and dc discharges are very similar in terms of the electrical properties, sputtered crater formation, light emission and temperature.

It is concluded that matrix specific, as well as matrix independent quantification principles and the intensity correction developed by Arne Bengtson can be applied for the pulsed mode, if special conditions are fulfilled. CIGSe solar cell samples and thin layered electrode metallizations of SAW devices are measured and quantified with application of PGD. The proposed quantification procedures are performed at commercial GD OES devices and can be used for the analysis with application of pulsed rf discharge.

The studies of the PGD performed in this dissertation are relevant for the application of the GD OES analysis in materials science. During the collaborative work with Helmholtz-Zentrum Berlin für Materialien und Energie and with the research group of Dr. Thomas Gemming at IFW Dresden the optimized pulsed GD OES measurements could be successfully applied at the investigation of thin film solar cells with CIGSe light absorbing layer and electrode metallizations of SAW devices. In case of solar cell samples pulsed GD OES depth profiling along with SIMS measurements reveal the role of the Al$_2$O$_3$ barrier layer in high efficiency solar cells consisting of a CIGSe/Mo/Al$_2$O$_3$/steel substrate layer stack (the barrier layer is to prevent the Fe diffusion into the CIGSe). The features of the CIGSe films growth are studied with help of pulsed GD OES and in situ synchrotron XRD measurements. The diffusion coefficient of Zn into the CuInS$_2$ layer is determined for the first time from the measured GD OES depth profiles of the corresponding solar cell samples. In case of SAW samples, pulsed GD OES measurements helped to evaluate the different SAW electrode preparation procedures and to select the most suitable one. In addition pulsed GD OES depth profiling along with XPS, TEM-EDX and electrode lifetime measurements indicate the possible mechanism of power durability and lifetime improvement of the SAW devices when a small amount of Al is added to the Cu-based electrodes.
1 Motivation and dissertation scope

Glow Discharge Optical Emission Spectrometry (GD OES) has proved to be a versatile analytical technique for the direct analysis of solid samples. The mild but at the same time fast sputtering glow discharge (GD) plasma lends itself to a wide range of analytical applications, including the analysis of bulk metals and alloys, non-conductive samples as well as depth-resolved analyses. The application of pulsed voltage to ignite and sustain the GD plasma broadens the analytical potential of the GD. Pulsed Glow Discharge (PGD) has some attractive features, as compared to the continuous discharge, in particular: (1) with additional discharge parameters (duty cycle, frequency and pulse duration) the sample removal rate can be controlled with greater precision; (2) due to the transient power there are fewer problems with overheating of the sputtered sample; (3) by recording of the emission at a certain time of the pulse one can either suppress or intensify the signal of plasma species.

Although the PGD offers a number of advantages, its use in commercial spectrometers has some limitations. Firstly, on the one hand, additional control parameters give bigger room for the sputtering control, but on the other hand, more parameters complicate the analysis. To find proper measurement conditions one should study the influence of all discharge parameters on the analytical discharge performance (depth resolution, light emission, quantification). As the PGD is a relatively new technique, the parameters of the PGD are not yet comprehensively investigated. Secondly, it is difficult to quantify the profiles measured with PGD, because the existing quantification model is established for the continuous discharge. Therefore, PGD is applied with modern commercial devices mostly for qualitative analysis.
Motivation and dissertation scope

Besides the limitations of the PGD use in the commercial scale there are two more fundamental aspects of the PGD which are until now not clarified: (1) It is well known that one of the outstanding possibilities of PGD is the reduction of thermal stress caused by sputtering. However, the extent of thermal stress reduction when pulses are applied is not often discussed and measured. Also the influence of the pulsing parameters (duty cycle, pulse duration and frequency) on the discharge gas and sample temperature is not known. (2) The ability of insulator sputtering is a well known difference between radio frequency (rf) and direct current (dc) discharges and widely applied for the analysis. The detailed comparison of dc and rf discharges is still a topic for debates. Some researchers suppose that ionisation and sputtering efficiencies are different in dc and rf modes, and others believe that both modes are similar.

Based on the above mentioned problems and questions regarding the PGD, which complicate and restrict its application in analytics, the goals of the present dissertation are formulated as follows:

• As one of the keys to understand the glow discharge is its electrical behaviour, the first task of the present work is to study the influence of the PGD parameters (pulse duration, pulse frequency and duty cycle) on the voltage–current characteristics and current and voltage signal shapes within the pulse.
• The next objective of the work is to reveal the influence of the pulsing parameters on the shape and roughness of the sputtered crater as well as on the sputtering rate. The correlation between the electrical parameters and the sputtered crater formation should be taken into account.
• The influence of the pulsing parameters on the spectra of both pulsed dc and rf discharges is to be investigated in present work. The correlation of electrical parameters with light emission effects should be taken into account.
• The important tasks of the work are to estimate the reduction of the GD gas temperature at the application of pulsed discharge and to ascertain the impact of the pulsing parameters on the discharge gas heating.
• To answer the question whether dc and rf pulsed discharges behave similarly all experiments concerning the electrical properties, sputtered crater formation, light emission and discharge gas temperature are to be performed for both modes.
• It is worthwhile to find an approach to quantify the depth profiles measured with PGD. First of all it should be examined whether the existing quantification principles, which are established for continuous discharge, are valid also for the pulsed mode.

• The studies of the PGD to be done in the course of the work are relevant for the application of the GD analysis in materials science. To demonstrate this, two types of layered materials analyzed by means of pulsed GD OES will be considered: thin film solar cells with Cu(In,Ga)Se$_2$ light absorbing layer and electrode metallizations of Surface Acoustic Wave (SAW) devices.

The dissertation is divided into five main parts: (1) Motivation and dissertation scope, (2) Introduction, (3) Experimental details, (4) Results and discussion and (5) Conclusions.

In the “Introduction” the fundamentals, as well as virtues and shortcomings of the glow discharge and GD OES analysis are introduced. The statement of the dissertation tasks is argued by the actual data known from the literature. With regard to the thin film solar cells and SAW devices, the state of the art as well as present challenges in the scientific and industrial fields of these two layered systems are shown. The importance of GD OES depth profiling with application of pulsed glow discharge is discussed.

The part “Experimental details” includes the description of the special equipment used for these studies, which is not introduced in the “Results and discussion”.

The chapter “Results and discussion” deals with the main results of the work and their interpretation. The study of electrical parameters of PGD, sputtered crater formation, sputtering rates, light emission and quantification are consequently described. Finally some examples are shown, where optimized pulsed GD OES measurements are helpful at the investigation of thin film solar cells and SAW devices.

The most outstanding results on the fulfilling of the above listed dissertation goals are summarized in the “Conclusions”.

2 Introduction

2.1 The Glow Discharge (GD)

2.1.1 GD plasma

In 1705 the English scientist Francis Hauksbee demonstrated a partly evacuated glass globe, which while charging by static electricity could produce a light bright enough to read by. It was the first demonstration of the discharge phenomenon in gas. In 1857 the German physicist and glassblower Heinrich Geissler invented the first low pressure glow discharge (GD) source – an evacuated glass cylinder with an electrode at each end, which was later called Geissler tube. Geissler tubes filled with different discharge gases were mass produced as entertainment devices, with various spherical chambers and decorative serpentine paths. The gas discharge phenomenon played an important role also for the science. William Crookes, the English chemist and physicist used the discharge tubes to study the properties of cathode rays. Later on (in 1897) the British physicist and Nobel laureate Joseph John Thomson identified the cathode rays as negatively-charged particles, later named electrons. In 1852 William Robert Grove discovered the sputtering of cathode material in a GD, which nowadays got a wide application area in industry and analytics.

The Geissler tube is the classical device serving the study of the discharge processes till nowadays. It consists of two metal electrodes immersed into a glass tube with some gas, typically Ar. When the voltage between the electrodes is raised, the current sharply increases at a certain voltage $U_b$ and light emission appears. These are the signs of a breakdown, where the insulating by nature gas becomes
conductive because of the avalanche ionisation in the electric field. As a certain portion of the particles in the gas is ionized, it is called plasma. According to the Paschen’s law,\(^1\) \(U_b\) depends on the distance between the electrodes and the pressure in the discharge cell. The type of discharge that forms after the breakdown is defined by the applied voltage and current: Townsend discharge, normal GD, abnormal GD or arc discharge (see Fig. 2-1). All these discharges are self-sustaining because no external ionization agent, such as heating or X-ray radiation, is needed to maintain them.

![Fig. 2-1 Voltage-current characteristics of different self-sustaining gas discharges.](image)

In Townsend discharge the voltage is equal to the ignition potential \(U_b\) and thus the ionization degree is so small that the charge density (or current) has no influence on the electric field. However at further current growth (for example at higher pressures) the voltage across the electrodes begins to decrease and after a certain current the fall stops indicating the normal glow discharge. The remarkable property of this mode is that the current density doesn’t change. What is changed is the area through which the current flows. When all the cathode area is exhausted the current density starts to increase providing also a voltage increase. This discharge is said to be abnormal and corresponds to the climbing area of the U-I curve in Fig. 2-1. When the discharge current is high enough (around 1 A) an arc appears.\(^2\) For analytical purposes the cathode is usually the sample itself. Hence the abnormal mode is most important,
because the current density over the whole cathode area is the same what favors homogeneous sputtering.

The GD develops under the following conditions: relatively low pressure of 1.3 - 13 hPa, low current of $10^{-6} - 10^{-1}$ A and a rather high voltage from hundreds to few thousands of volts.$^2$

The abnormal GD, hereafter called simply GD, has some altering dark and luminous regions (see Fig. 2-2). These regions are related to the different energy of electrons repelled away from the cathode due to the negative cathode potential and to the difference in the ionic and electronic speed. In the dark areas the electron energy is either too small (Aston dark space, Faraday dark space) or too high (cathode dark space) for the gas particles excitation. In the glowing regions the electron energy corresponds to the atomic and ionic excitation levels and thus electrons are capable to excite the gas particles. The small electrons move much faster than massive ions, therefore close to the cathode a region with high ion concentration is built – the cathode dark space. In the cathode dark space the electron energy is too high to excite the atoms but exactly right for the ionization.$^3$ A large number of slowly moving positive ions create a positive space charge, where most of the potential difference between the two electrodes is dropped (see Fig. 2-2 Electric field distribution). The cathode dark space is crucial for maintaining the GD, while the adjacent negative glow is analytically the most important region. In this area the electrons have moderately high energies to excite the atoms and ions.$^4-7$ The maximum of the emitted light intensity is in the negative glow region (see Fig. 2-2 Light intensity distribution); therefore the most analytical glow discharge devices employ short electrode distance so that only cathode dark space and negative glow remain. Such discharge is called obstructed and occurs when the electrode separation is only a few times larger than the thickness of the cathode dark space.$^5$ Despite the positive column is the most prominent area, it is not required to sustain a GD and collapses when the distance between the electrodes becomes small enough.$^2$
The processes taking place in the cathode dark space and in the negative glow are interdependent and fairly complex. The most important basic processes are summarized in Fig. 2-3. The positive ions of the plasma bombard the negatively charged cathode and thus give rise to secondary electron emission and release the atoms of the cathode material. The sputtering of the cathode atoms is caused not only by positive ions, but also by energetic argon atom (Ar$^{0}_{fast}$) bombardment. Due to the potential difference between the cathode and the anode, the electrons accelerate away from the cathode and collide with plasma particles. This collision can be elastic or inelastic. Inelastic collision results in ionization or excitation of the plasma particles. The Ar atoms are mainly ionized and excited by electron impact, whereas for the sputtered atoms there are some additional ionization and excitation processes such as Penning ionization by metastable Ar atoms (Ar$_m^+$) and asymmetric charge transfer with Ar ions. For the readers interested in a detailed description of the plasma processes there are a number of references,6-9 including some computational results.8,10-12
2.1.2 GD sputtering vs. other sputtering techniques

The ability to convert the solid samples directly into gaseous atoms and ions is a big advantage for the analysis since a time consuming and laborious sample preparation is avoided. The techniques which allow the direct analysis of solid samples are based on ion bombardment, laser ablation and plasma-based processes.\textsuperscript{13,14} Ion beam sputtering is used for depth profiling in SIMS, SNMS, XPS and AES. In these methods a focused ion beam (ion energies in the keV region) is applied at high vacuum conditions to sputter material from a specific location on a solid surface.\textsuperscript{15,16} Laser techniques are utilized in LIBS - the laser energy is transferred to the sample surface resulting in the ejection of atoms and ions; the ablated sample material generates a plasma and when local thermodynamic equilibrium is established, the characteristic atomic emission lines of the elements can be observed.\textsuperscript{17} Moreover the ablated material can be transferred to an ICP plasma and subsequently analyzed by a mass spectrometer (LA-ICPMS).\textsuperscript{18} However the forming plasma is not reproducible; therefore LIBS and LA-ICPMS suffer from poor precision. Among the plasma-based techniques there are spark, arc and glow discharges. Sparks and arcs coupled to...
optical emission spectrometry are widely used for bulk analysis.\textsuperscript{14} Nevertheless the erratic behavior renders them unable to depth profiling.

Sputtering in the GD is widely applied for both bulk and depth profile analysis in GD OES and GD MS.\textsuperscript{19-22} GD sputtering has a greater number of attractive features as compared to other sputtering techniques. Because of the relatively high operational pressure (several hPa), atoms and ions in the GD undergo numerous collisions transferring their kinetic energy and changing their trajectories (the mean free path of the ions in the GD is around tens of µm).\textsuperscript{23} Hence in contrast to high vacuum ion beam sputtering the atoms and ions in the GD strike the cathode with a wide angular distribution.\textsuperscript{24,25} This favours homogeneous sputtering over the sample surface, which in case of an ion beam can be reached only by sample rotation.\textsuperscript{26-28} Due to the frequent collisions the particles in the GD lose their energy and bombard the cathode with significantly lower energies than at high vacuum sputtering (< 100 eV vs >1 keV).\textsuperscript{25,29-31} The trajectories of low energy ions in the bombarded material are confined to a shallower depth. Also the number of collisions made by a projectile in the solid is much smaller at low energies.\textsuperscript{32-34} The ejected atoms usually originate from only few angstroms of the sample and have energies of 5 to 15 eV.\textsuperscript{35} Hence the sputtering induced surface changes like ion implantation, atomic mixing and surface topography formation\textsuperscript{36-40} are in case of GD less pronounced. As compared to high vacuum sputtering, the GD has much greater current densities (100 mA/cm\textsuperscript{2} vs 1 µA/cm\textsuperscript{2}) because of the higher pressure. Thus for GD sputtering the sample ablation rates are much higher but with far less lattice damage.\textsuperscript{24}

### 2.1.3 GD sources

The operation simplicity and the variety of analytical applications of GD led to the development of several source configurations. The oldest one is the hollow cathode.\textsuperscript{41} In this configuration a cylindrical hollow cathode is used so that the negative glows from the opposite cylinder walls coalesce. Hence the current density, the ionization and excitation efficiencies are much larger than the usual ones.\textsuperscript{42} The hollow cathode source provides great sensitivity but its disadvantages are the complicated sample geometry and exchange and the impossibility of depth profiling. Another GD source configuration is the “pin-type” source, which is capable to sputter
pin-shape samples or wires. This source is often used in mass spectrometry because of the ion extraction simplicity and easy sample preparation. However, depth profiling in the “pin-type” source is difficult.

In 1967 Grimm invented the GD source device which is widely employed till nowadays. In Fig. 2-4 the schematic cut of the original Grimm source is depicted, where 1 – cathode or sample; 2 – cathode body; 5 – anode body; 4 and 11 – pumping lines; 6 – Ar flow line; 15 – water cooling; 9,12,14,16 - sealing rings.

The main features of the source are obstruction and constriction of the GD plasma. As discussed in 2.1.1, the obstruction of the plasma is realized by the reduction of the distance between cathode and anode. Thus only the most important regions for ionization and excitation remain in the source: cathode dark space and negative glow. The plasma is also confined (constricted) in a circumference by the cylindrical hollow anode. This is realized by the small distance between anode and cathode and by its evacuation through the pumping line 11. The small value of the product of distance and pressure avoids the existence of plasma outside the anode according the Paschen law. Because of the relatively high pressure in the Grimm cell the cathode dark space is very thin and the anode body doesn’t affect the equipotential lines to a large extent. Computation studies have shown that the equipotential lines are parallel to each other and to the cathode surface so that the bottom of the crater is expected to be also flat. Hence the Grimm type source is capable for planar
sputtering of the sample at the proper discharge conditions\textsuperscript{46,47} and is well suited for the depth profile analysis.\textsuperscript{48} In addition the Grimm geometry allows easy and fast sample mounting.

For further improvement of the sputtered crater and thus of the depth resolution, various attempts have been made to modify the basic Grimm source.\textsuperscript{49} For example a floating electrode\textsuperscript{50} or an auxiliary cathode\textsuperscript{51} were introduced between cathode and anode. To increase the excitation efficiency boosted sources with secondary discharge,\textsuperscript{52} magnetic field\textsuperscript{53} or additional gas flow towards the sample surface\textsuperscript{54} have been designed. However the basic Grimm geometry is the most abundant till nowadays.

2.2 Glow Discharge Optical Emission Spectrometry (GD OES)

2.2.1 Basic principles of GD OES

GD OES is known since 1967 when Grimm published the first results from his analytical source.\textsuperscript{55} Starting from that time the interest in Grimm’s source in combination with optical emission spectrometry has steadily grown. Nowadays GD OES is employed for the analysis of steels and steel surfaces, other metallic coatings and metals, PVD/CVD coatings, semiconductors, polymers, ceramics, lacquer layers, etc.\textsuperscript{21}

The principle of GD OES is the following: atoms of the sample are sputtered, ionized, excited and emit characteristic light in the GD plasma (discharge gas - Ar); this characteristic light is detected by an optical spectrometer. The detectors can be either PMTs or CCD arrays mounted into a Rowland-circle or in combination with a monochromator. In Fig. 2-5 there is a schematic representation of a modern commercial GD OES spectrometer (Spectruma, GDA 750). As can be seen from Fig. 2-5 the modern GD cell is nearly identical with the source invented by Grimm in 1967 (see Fig. 2-4).
GD OES is suitable for the analysis of nearly all elements (including the light elements H, C, N, O) in films of 1 nm up to more than 100 µm thickness. The depth resolution of the method is 5-10 % of the sputtered depth, but higher than the ultimate depth resolution\textsuperscript{38,56} (3 nm). However it should be mentioned that to reach the best depth resolution, the shape of the sputtered crater should be optimized (by varying the discharge parameters, in the simplest case - voltage, current and pressure). In addition GD OES is characterized by a high sensitivity (detection limit 0,1-10 µg/g) and high dynamic range (µg/g up to main components).\textsuperscript{21}

2.2.2 Quantification in GD OES

For some analytical applications it is important to convert the measured intensity-time profile into the concentration-depth form. There are several approaches to quantify the measured depth profile.\textsuperscript{57} In the following text the most frequently used GD OES quantification model will be described.
In GD OES there are three independent processes which contribute to the
generation of the analytical signal: (1) the supply of the sputtered atoms; (2)
excitation – de-excitation of the atoms and ions in the plasma; (3) detection of the
emitted light. Hence all these processes are included into the equation of the emitted
light intensity \( I_i \) (see 2-1).

\[
I_i = k_i S_i R_i c_i q + b_i
\]

First of all the intensity \( I_i \) of the characteristic light of element \( i \) depends on the
concentration of this element in the sample \( c_i \) [m\%]. The sputtering rate of the sample
\( q \) [µg/s] is responsible for the supply of the sputtered atoms and is a constant when
the sputtered matrix doesn’t change. The process of excitation – de-excitation is
characterized by the emission yield \( R_i \) of the element \( i \) in the plasma and by the
correction of self-absorption \( S_i \). The detection process is taken into account by
introduction of the instrumental detection efficiency \( k_i \). \( b_i \) – is a background value
which depends on the individual instrument. In any analysis it should be assumed
that the concentrations of all elements will add up to 100% (see 2-2).

\[
\sum_i c_i = 1
\]

The emission yield \( R_i \) is the number of photons with defined wavelength emitted per
atom or ion of element \( i \) in the plasma. \( R_i \) can be determined from the measurement
of standard samples with known concentration of element \( i \). The advantage of GD
sputtering is that the sputtering and excitation processes are separated in space and
time; therefore the excitation or the emission yield of the sputtered particle is
independent of the sputtered matrix. Thus the emission yield determined from the
measurement of a standard sample is valid also for an unknown sample with different
matrix and can be used for quantification. However this assumption is valid only
when standard and unknown sample are sputtered under the same electrical
conditions, particularly the same voltage and current. This theory is known as “the
concept of constant emission yield” with the main principle that the emission yield is
almost matrix- and pressure-independent but strongly influenced by voltage and
current.

Summarizing, the \( R_i \) is determined from the standards, the \( k_i, S_i, b_i \) and
sputtering rate \( q \) (only when the sputtered matrix is the same) are constants, the \( I_i \) is
determined from the measurement of the sample and there are two unknown values - 
$c_i, q$. Hence the concentration $c_i$ can be calculated from the two equations with two 
unknown values: 2-1 and 2-2.

In practice the determination of the sputtering rate is avoided, if possible. This 
can be done at so called matrix specific calibration, when the sample and the 
standards have the same matrix. In the case of matrix specific calibration, the matrix 
element, which can be used as a reference, is present in all samples. Thus by 
ratioing the intensity values of some element $I_i$ and the matrix element $I_m$ from one 
sample (minus background $b_i$ and $b_m$), the sputtering rate is cancelled:

$$\frac{(I_i - b_i)}{(I_m - b_m)} = \frac{k_i S_i R_i c_i q}{k_m S_m R_m c_m q} = const \cdot \frac{c_i}{c_m}$$  \hspace{1cm} (2-3)

Because both intensities are measured at the same sample, the sputtering rate $q$ is 
absolutely the same and can be cancelled. Depending on the sample purity the 
concentration of the matrix must be taken into account or is simply set to 1. When all 
elements in the sample are measured, 2-2 and 2-3 are used to calculate the 
concentration of the matrix element and finally the absolute concentrations of all 
other elements in the sample.

Nevertheless, the described quantification procedure can be applied only 
when the matrixes of the sample and the standards are the same or very similar. 
especially, ratioing to the intensity of one element can be only done, if this element is 
present in all samples and layers. If this is not the case, the sputtering rate of the 
samples and standards with different matrixes will strongly differ. Therefore for the 
quantification the sputtering rate of each standard must be measured and included 
into 2-1. For the convenient comparison of the sputtering rates at different 
instruments the relative sputtering rate which is the ratio of sputtering rate of 
reference matrix (usually pure Fe) $q_{ref}$ and the calibration sample $q_s$ is usually 
considered $q_{rel}$.$^{60}$ The relative sputtering rate is included in the well known multi-
matrix calibration algorithm or matrix independent calibration.$^{61}$ It is important that the 
sputtering rates are determined at the same voltage and current. The reason is that 
according to the Boumans’ law$^{62}$ the sputtering rate is proportional to the voltage $U$ 
and current $I$, thus they can be cancelled when the ratio of two sputtering rates $q_{ref}$ 
and $q_s$ is considered (see 2-4 and 2-5).
In the equation 2-4 \( U_0 \) is a material dependent threshold voltage; \( C \) is a constant depending on the material.

In some cases it is not possible to keep \( U \) and \( I \) constant within the measurement. Therefore a special algorithm to compensate the variations of the excitation conditions by means of empirically derived expressions was developed.\(^{63}\) For this the emission intensities were measured at different voltages and currents. The observed dependencies were fitted to mathematical models giving the empirical intensity expression (see 2-6 and 2-7).

\[
I_i = k_i c_i C I^4 f(U) \tag{2-6}
\]

\[
f(U) = a_0 + a_1 U + a_2 U^2 + a_3 U^3 \tag{2-7}
\]

The equations 2-6 and 2-7 show that the experimentally deduced intensity depends exponentially on current and polynomial on voltage. The matrix-independent constants \((A, a_0, a_1, a_2, a_3)\) are experimentally determined for a number of spectral lines. Thus with known \( U \) and \( I \) one can normalize the emission intensity to a standard voltage and current.

After conversion of the emission intensity to the concentration, the sputtering time should be converted into the depth. For this the density of the sample is calculated as the sum of the pure element densities \( \rho_i \) multiplied by their atomic fraction \( c_{Ai} \) in the sample:

\[
\rho = \sum_i c_{Ai} \rho_i \tag{2-8}
\]

This assumption about the sample density is valid for metals and alloys;\(^{64}\) however for the light elements it can bring some errors into the calculated depth. The calculation of the sputtered depth \( \Delta d \) within the time interval \( \Delta t \) and at an anode area \( O \) [cm\(^2\)] is done according to 2-9:

\[
\Delta d = q \Delta t / (O \rho) \tag{2-9}
\]
The quantification algorithm is repeated for each time interval $\Delta t$. Thus the overall sputtered depth $d$ is the sum of all $\Delta d$ (see 2-10).

\[ d = \sum_j \Delta d_j \]  

2.2.3 GD OES vs. other depth profiling methods

Along with GD OES, GD MS, SIMS, SNMS, AES and XPS are also often used for depth profiling. The choice of the method depends on several criteria: the concentration range to measure, the analysis time, the elements to detect, the thickness of the layers in the sample, the required spatial resolution and of course the measurement cost. For the trace element analysis in the ng/g concentration range the mass spectrometric methods like GD MS, SIMS and SNMS are beyond comparison. But up to µg/g concentrations GD OES is preferable. In comparative studies GD OES was reported to be the fastest depth profiling method. The reason is the previously discussed fast erosion rate in the GD plasma (see paragraph 2.1.2). In addition, GD OES devices are easy to use and have a high sample throughput because no ultrahigh vacuum is required and the sample can be simply exchanged. This also results in a reduction of the analysis costs – 100-150 euro for the measurement. For comparison a MS measurement costs 500-1000 euro.

As compared to the depth profiling methods, which are using high vacuum ion beam sputtering, GD OES has less matrix effects and therefore the quantification procedure is less complicated for GD OES. Nevertheless, in contrast to XPS and AES, GD OES doesn’t provide any information about the chemical bonds in the sample. The lateral resolution of GD OES is limited by the anode diameter (minimum 1 mm) whereas the lateral resolution of SIMS, SNMS, XPS and AES is in the nm to µm region. Good lateral resolution is a big advantage for the analysis of the thin and ultrathin layers. In addition, ion beam sputtering allows avoiding the effect of the sputtered crater on the depth resolution by exclusion of the crater edges from the area of investigation. On the other hand, GD OES is proved to be also a reliable depth profiling method for very thin (nm region) layered samples. Since the GD OES is a relatively new depth profiling technique, there are several possibilities to improve its depth resolution. The depth resolution is mostly affected by the non
planar sputtered crater. Thus the measured depth profile is a function of the true depth profile and some response function, which is determined by the sputtering crater shape. There are several works where the response function was mathematically described and deconvoluted from the measured depth profile, providing evident improvement of the depth resolution.\textsuperscript{70-72} The depth resolution in GD OES can be improved also experimentally by the application of novel sputtering conditions. Nowadays pulsed glow discharge is becoming more and more popular in GD OES and GD MS due to the ability to control the sputtering rates and crater shapes with greater precision. Pulsed glow discharge will be detailed discussed in the following paragraphs.

\textbf{2.3 Pulsed glow discharge (PGD)}

\textbf{2.3.1 Virtues and shortcomings of the pulsed mode}

In PGD the power is not applied continuously but only periodically. Frequency, duration of the power on time (pulse length) and duty cycle are the main parameters of the PGD which determine its analytical performance (see Fig. 2-6).

Nowadays PGD is becoming evermore popular for analytical applications. From the PGD benefits not only GD OES, but also Atomic Fluorescence / Absorption Spectrometry and Mass Spectrometry.\textsuperscript{73,74} The reason is that PGD has a greater number of attractive features, as compared to the continuous discharge, which broaden its analytical potential.\textsuperscript{75} In the following text the advantages of the PGD, which have been highlighted in the literature, will be listed.

\textbf{Fig. 2-6 Schematic illustration of the pulsed voltage applied to the GD and the main parameters of the PGD.}
Additional control parameters Besides the common GD parameters – voltage, current and pressure - the pulsed discharge has a duty cycle, pulse duration and frequency. With these additional parameters the sample removal rate can be controlled with greater precision. Thin films that would be immediately removed in the continuous discharge, show moderate sputtering rates with PGD.\textsuperscript{76-79}

Reduction of the sample heating In steady-state discharges the sample being analyzed must continuously dissipate heat that is produced in the sputtering process, which leads to the sample heating. Thus the continuous discharge is limited by the power level which can be tolerated by the sample. It was found that the sample and the discharge gas temperature affect the depth resolution and the sputtering rate.\textsuperscript{80,81} Too high temperature can even partly melt\textsuperscript{82} or mechanically destroy the sample. The application of PGD reduces the sample heating during the analysis and thereby promotes a good depth resolution. Thus with PGD also thermally fragile samples can be analysed.\textsuperscript{83-87}

As a result of the reduced sample heating, PGDs allow higher transient powers than continuous discharges. Typical voltage ranges are 600 – 1200 V and 600 - 3000 V for the continuous and pulsed dc modes respectively. Likewise, the currents are also considerably different – tens of mA for the continuous mode versus tens to hundreds of mA of transient current in the pulsed dc discharge.

Enhanced ionisation and excitation efficiency Because of the higher voltages and transient currents of PGD the ionisation and excitation efficiency within the pulse is also higher. By gating the detector to acquire the signal only during the pulse, the analytical signal may be maximized.\textsuperscript{88-90} The gated detection and investigations of the temporal emission and ionisation within the pulse revealed a number of useful effects. For example an interesting feature of PGD is the reduction of self-absorption at the very beginning of the pulse (first µs). This effect is relevant for the GD OES quantification, because the curvature of the calibration curves was observed to be reduced when only the first microseconds of the pulse are detected.\textsuperscript{74,91}
**Temporal resolution** The pulsing process initiates different excitation and ionization mechanisms at the beginning, during and after the pulse with strong, medium and soft plasma conditions. Using this feature and time-of-flight mass spectrometry one can extract elemental and molecular information from gaseous samples. Recent studies have shown that the direct oxidation state determination is also possible in solid state materials. In addition by measuring the emission at a defined time of the pulse one can discriminate the impact of contaminations or other species in the plasma.

In spite of the above-listed advantages of the PGD, its use in commercial spectrometers has still some limitations. Firstly, on the one hand, additional control parameters give bigger room for the sputtering control, but on the other hand, more parameters complicate the analysis. To find proper measurement conditions one should study the influence of all discharge parameters on the analytical discharge performance (depth resolution, light emission, quantification). As the PGD is a relatively new technique, the parameters of the PGD are not yet comprehensively investigated. Secondly, it is difficult to quantify the profiles measured with PGD, because the existing quantification model (see 2.2.2) is established for the continuous discharge. Therefore, PGD is applied in modern commercial devices mostly for qualitative analysis. In addition there are two more questions, which are discussed in the following text (see 2.3.2 and 2.3.3).

### 2.3.2 Rf or dc pulsing?

PGD, as well as continuous discharge, can be operated either in direct current (dc) or in radio frequency (rf) mode. The main difference between rf and dc modes is that the rf discharge is able to sputter nonconductive samples. The simplified description of the rf discharge processes is given in the following text. For analytical applications, the rf voltage is delivered to the source through a capacitor. When the rf voltage is applied, the surface is bombarded alternatively by positive ions and negative electrons. The rf voltage is sinusoidal and bipolar. Therefore the ionic bombardment, which is necessary for sputtering, should take 50% of the whole rf cycle. However after some rf cycles the surface potential shifts to a negative value providing almost
continuous ion bombardment. The reason for this is that the electrons in the plasma move much faster than massive ions and consequently the electron current is greater than the ionic one. Because of the capacitive coupling no net current can flow through the cathode. Therefore the electrons remain at the cathode surface within the positive rf cycle. The slow ion flux within the negative rf cycle is not sufficient to compensate this negative charge formed by electrons. So the excessive negative charge remains at the cathode surface and the surface potential gets a negative offset, which is also called dc bias. In this way in case of a conductive sample (cathode) the capacitor between the rf generator and the source is responsible for the biasing of the rf voltage to a negative value and sputtering of the sample by positive ions. In case of a nonconductive sample (cathode) the sample itself acts as a capacitor, preventing the net current flow through the system. Thus the bombarding electrons also form an electron sheath on the sample surface, responsible for the cathode sputtering.

Sometimes the rf mode is advantageous for the analysis of conductive samples as well, because it is less affected by nonconductive surface oxide contamination.

The ability of insulator sputtering is the only difference between rf and dc discharges which is well known and widely applied for the analysis. Further comparison of the dc and rf discharges is still the topic of debates. In the following text references will be highlighted where some authors suppose that ionisation and sputtering efficiencies are different in dc and rf modes, and others which believe that both modes are similar.

It has been reported that in rf discharges two different discharge regimes exist: α and γ. In the α regime the electrons in the bulk plasma are heated by the rf field oscillations. The energy of these electrons is high enough to cause ionisation and to sustain the plasma. In case of the γ regime the discharge is sustained by the electrons emitted from the cathode (secondary electrons). In dc discharges only the γ regime exists. The absence of the α regime and also computational results indicate that the ionization in dc mode is less efficient than in the rf one. However, later modelling studies have shown that the calculated Cu atom and ion densities, optical emission spectra, sputtering rates and sputter crater shapes are similar for rf and dc
mode. These computational results are in good agreement with experimental data.\textsuperscript{111} Lewis et al. studied the temporal emission characteristics of pulsed dc and rf discharges and found only negligible differences between dc and rf mode.\textsuperscript{112} Präßler et al. have observed that the GD OES intensity-time profiles, crater shapes and depth resolution are similar for rf and dc discharges.\textsuperscript{113} Alberts et al. have investigated the emission pre-peak of the pulsed discharge and observed similar behaviour for both rf and dc modes.\textsuperscript{91} On the other hand, a Langmuir probe study of the rf glow discharge has shown that the electron energy and temperature are higher for the rf mode than those for the dc one.\textsuperscript{114} In addition Harrison et al. have mentioned that the efficiency of sputtering by an rf discharge is somewhat less than that obtained by dc.\textsuperscript{88}

Thus, from the literature it is difficult to conclude whether the dc and rf modes are different or similar. At this point it is extremely important to emphasize at which electrical conditions these two modes are compared. Two discharges can be compared at the same pressure and only in the case when the power they are consuming is the same. Hence, for the case of rf discharges equivalents to the dc-voltage and dc-current are necessary. Bogaerts et al. have made the first mention about the conditions at which rf and dc discharges should be compared: “in the dc discharge a higher operating voltage was needed to yield the same amount of power, compared to the corresponding dc bias voltage in the rf discharge”.\textsuperscript{109} Additional studies\textsuperscript{115} and subsequent work\textsuperscript{105} have shown that the rf equivalent of the dc voltage is the effective voltage $U_{\text{eff}}$, which is the cycle root mean square value of the periodic voltage signal $U_p(t)$ plus bias $U_{\text{bias}}$ (see 2-11). Indeed, as Bogaerts mentioned, the $U_{\text{eff}}$ is a little higher than the dc bias. The equivalent for the current value $I_{\text{eff}}$ is the rf power $P$ divided by the effective voltage (see equations 2-12, 2-13, 2-14).

\begin{equation}
U_{\text{eff}} = \frac{1}{T_p} \int_{t_p}^{t_p'} (-U_{\text{bias}} - U_p(t))^2 \, dt 
\end{equation}

\begin{equation}
P(t) = U_p(t) \cdot I_p(t) \tag{2-12}
\end{equation}

\begin{equation}
P = \frac{1}{T_p} \int_{t_p}^{t_p'} P(t) \, dt \tag{2-13}
\end{equation}
\[ I_{\text{eff}} = \frac{P}{U_{\text{eff}}} \]

It must be mentioned that the determination of power, rf voltage and dc bias deteriorates with increasing thickness of insulating samples. The quality of the power measurement at fixed frequency generator systems depends on the power losses in the matchbox and the quality of the used correction – the so-called subtraction method. The rf voltage becomes lower throughout nonconductive samples, depending on sample thickness, frequency and current. In principle, this voltage loss can be corrected, if voltage and current are measured. The direct measurement of the dc bias becomes totally impossible and calculation procedures\textsuperscript{105} or estimations\textsuperscript{115} must be used.

In conclusion, there is no work where the dc and rf discharges are comprehensive compared. The pulsed discharge is even less studied. However it is shown that for the comparative studies the effective voltage in the rf mode should be used as an equivalent to the dc voltage.

### 2.3.3 How big is the thermal stress reduction when PGD is applied?

One of the outstanding possibilities of PGD is the reduction of thermal stress caused by sputtering (see 2.3.1). The heating of the discharge cell, in particular of the cathode and the discharge gas, is a phenomenon frequently associated with GD studies and applications. A number of publications, experimental and modeling studies, have reported the considerable impact of the discharge gas and sample heating. For example, it has been observed that the GD OES depth profile of a Zn-on-steel thin film sample is changing being analyzed either with or without sample cooling.\textsuperscript{80} Windawi has found a variation of the Cu sputtering yield when its temperature is varied.\textsuperscript{81} Heyner et al. have shown that too high temperature can even partly melt the sample.\textsuperscript{82} The cathode temperature has been identified as an important parameter influencing the mass loss due to evaporation for zinc cathodes in analytical glow discharge.\textsuperscript{116} Wilken et al. have found that the sample expands at the moment of the plasma ignition and explained this effect by the increased sputtered surface temperature.\textsuperscript{117} Experimental studies have shown that the
discharge gas temperature influences the discharge current at constant voltage and pressure: a temperature rise results in a decrease of the gas density, and thus causes a decrease of the discharge current.\textsuperscript{2,118-121} This phenomenon has also been confirmed by modeling results.\textsuperscript{122-124}

In spite of the above-listed thermal effects and their considerable impact on the GD performance, gas temperature and cathode (or sample) temperature measurements are not often made in analytical GD spectrometry. However, for the fundamental studies and analytical applications of PGD it is worthwhile to determine the extent of thermal stress reduction when pulses are applied. It is also important to study how the pulsing parameters (duty cycle, pulse duration and frequency) influence the discharge gas and sample temperature. As of today there are only few papers where the temperature in the PGD is measured.\textsuperscript{87,125} Pollmann et al.\textsuperscript{87} have measured the temperature of µs- and ms- pulsed and continuous discharges such a way that the pulse width was gradually increased, filling the time gap between on-times of 10 µs up to continuous dc operation (see Fig. 2-7). It was observed that for pulse lengths of 1 ms and higher the pulsed discharge is very close to the continuous one in terms of temperature. However it should be mentioned that by filling the gap between the pulses one changes not only the pulse length but also the duty cycle. Therefore it is difficult to attribute the observed phenomenon of temperature increase either to the pulse width or to the duty cycle.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{Fig_2-7.png}
\caption{Temperature of the glow discharge gas measured for µs-, ms- and continuous dc GD.\textsuperscript{87}}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{Fig_10.png}
\caption{N\textsubscript{2} \textsuperscript{+} rotational temperature versus pulse width for an argon GD. Cu cathode, 1.5 Torr argon and 0.3 Torr nitrogen; µs-pulse, 100 W (peak), 30 Hz; ms-pulse, 0.25 W; dc, 2.5 W}
\end{figure}
Jackson et al.\textsuperscript{125} and Gamez et al.\textsuperscript{126} have also measured the gas temperature of the ms-pulsed GD, but have paid more attention on the spatial temperature distribution above the cathode than on the influence of the pulsing parameters.

The lack of temperature studies in PGD is caused by the complexity of the temperature measurement techniques. In the following chapter the methods of the discharge gas temperature measurement and the corresponding complications are briefly discussed.

2.4 Measurement of the discharge gas temperature

2.4.1 What is the temperature of the glow discharge gas?

Temperature relates to the thermal energy held by a matter, which is the kinetic energy of the random motion of the particle constituents of matter. The empirical definition of temperature arises from the conditions of thermodynamic equilibrium, expressed as the zeroth law of thermodynamics: “Systems are in thermal equilibrium if they do not exchange energy in the form of heat.” Hence the gas temperature is characterized by the kinetic energy of the gas particles when these particles are in the thermodynamic equilibrium (TE) with each other. Therefore, to understand what is the temperature of the GD gas one should examine the particles in the GD and their temperatures as well as the conditions of TE. It is well known that the GD gas contains several types of particles: electrons, photons, ions, neutral atoms, excited atoms and ions and also molecules or radicals. Thus the GD can be characterized by different temperatures:

1. The \textit{electron temperature}, which represents the kinetic energy of the electrons;
2. The \textit{neutral atom temperature}, which characterizes the kinetic energy of the neutral atoms;
3. The \textit{excitation temperature}, which describes the population of the various energy levels;
4. The \textit{ionization temperature}, which governs the ionization equilibrium;
5. The \textit{rotational and vibrational temperatures} of the molecules.
If the GD gas were in TE, a single temperature value might describe all the above-listed temperatures. Also the conditions of the TE would have to be fulfilled for the GD:

1. The velocity distribution of all kinds of free particles (molecules, atoms, ions and electrons) in all energy levels satisfies the Maxwell’s equation;
2. For each separate kind of particle the relative population of energy levels conforms to Boltzmann’s distribution law.
3. Ionization of atoms, molecules and radicals is described by the Saha’s equation and dissociation of molecules and radicals by the general equation for chemical equilibrium.
4. Radiation density is consistent with Planck’s law.\textsuperscript{127-129}

Nevertheless it is well known that in the GD the electron temperature is much higher than the temperature of the other massive particles in the plasma: 10000 K versus less than 1000 K.\textsuperscript{9,130,131} The reason is that the electrons continuously acquire the energy in the electric field, but the energy transfer by means of elastic collisions from the light electrons to the much heavier particles in the plasma is inefficient. In addition the walls of the GD cell have a temperature different from the GD gas and the discharge gas flow brings cold gas into the plasma; thus there is a heat exchange in the system and some processes cannot be in equilibrium with their converse. Also the velocity of the charged plasma particles depends not only on the temperature, as it should be in TE, but also on the applied electric field. So it can be concluded that the GD gas is not in thermodynamic equilibrium.\textsuperscript{130} It has to be noted that when the gas is not in the TE a physical meaning for the gas temperature becomes vague. Nevertheless the TE approach allows using the well known equations (see conditions of TE above) to interpret the spectral line intensities and to simulate the plasma, what is much simpler and faster than solving the non-thermal equations.\textsuperscript{132,133} Therefore for plasmas which are close to thermal ones different approximations are usually done. However one should be cautious in using these approximations because they can cause unexpected errors for plasmas strongly departing from the TE. Thus there are several criteria which help to estimate whether the plasma is predominantly thermal or not.\textsuperscript{134-138} For the plasmas where the temperature gradient is small (comparable with the distance at which the excited atom diffuses during its
relaxation) and where the particles exchange their energy very frequently (collision frequency is 10 times larger than the radiation frequency) each small portion of the gaseous body can be characterized by a unique temperature. The equilibrium conditions in such a non-homogeneous gas are called local thermodynamic equilibrium (LTE).\textsuperscript{128,129,137} For the LTE the Boltzmann and Saha’s equations are valid. The particle temperatures in the GD plasma, especially when comparing electrons with atoms or ions, differ from each other. Therefore the GD gas is not in LTE. On the other hand the GD is a weakly ionized plasma with an ionization degree of less than 1 % and the number of electrons and ions in the plasma is much smaller than the neutral atoms.\textsuperscript{7,139} Thus the particle velocity in the GD gas depends to a lesser extent on the electric field than on the temperature. Also the huge electron temperature has a small effect on the establishment of the LTE in the GD gas, because the electrons are not capable to change the kinetic energy of the other much heavier plasma particles significantly. So the GD gas can be assumed to be close to the LTE. LTE can only be expected if collisional processes are more important than radiative decay and recombination, and if the velocity distributions of the colliding particles are thermal. Since most collisional excitations and ionizations and their inverses involve electrons, the electron density mostly determines how close the GD gas is to the LTE.\textsuperscript{137}

In Fig. 2-8 (a) the calculated ionization degree in a hydrogen-like plasma is plotted against the electron density (for electron temperature 16000 K).\textsuperscript{135} For low electron densities the radiative decay rates predominate over collision induced decay rates. Such plasmas are called nonthermal or cold plasmas and are far away from the LTE because of the collisions lack. An example of such cold plasma is the Solar Corona (see Fig. 2-8 (b)) which has a temperature of millions of degrees, but it is 10 billion times less dense than the atmosphere of the earth. The extremely high ionization states observed in the Solar Corona as well as the excitation are induced by the enormous temperature (due to the solar magnetic field) and not by the collisional processes.
The other extreme case is on the right side of Fig. 2-8 (a) and (b), which correspond to high electron densities and thus to a complete LTE. In this area collision induced decay dominates and all atomic levels have a thermal population, i.e. the Boltzmann and Saha equations are valid. An example of a thermal plasma is the Sun Core (thermal fusion plasmas in Fig. 2-8 (b)). The core is made of hot dense gas in the plasmic state, which has a density of up to 150000 kg/m³ (150 times the density of liquid water) and a temperature close to 15000000 K.

The GD plasma has an electron density of around $10^{15}$ cm$^{-3}$ as can be seen from Fig. 2-8 and is between the nonthermal and thermal plasmas.\textsuperscript{7,141,142} From Fig. 2-8 one can see that depending on the electron density the GD plasma is either close to a nonthermal or to a thermal plasma (dashed lines). Consequently the further the GD plasma deviates from thermal one, the higher is the error which one introduces using the thermal equations. For the GD and also similar plasmas it is useful to apply the concept of partial LTE where only a limited range of energy levels of electrons in the atoms and ions can be described by the Boltzmann and Saha equations. It is known that in the collisional-radiative processes the upper levels reach a thermal distribution with a continuum of free electrons more easily than the lower levels. Thus one assumes that ions or atoms are in partial LTE if the population density of one of theirs levels and all higher-lying levels can be described by the Boltzmann and Saha equations.\textsuperscript{134} Therefore, an energy level for the electrons in
ions or atoms exists, which can be called “thermal limit”, above which the
distributions approximate to thermal and below which they are approximately
nonthermal. As the electron density increases, the “thermal limit” drops lower and
lower; at sufficient high densities it reaches the ground level and all levels have
thermal population.\footnote{135}

In conclusion, it was shown that the definition of the GD gas temperature is not
trivial. However it can be assumed that the GD gas temperature is characterized by
the kinetic temperature of the plasma particles which are mostly close to the thermal
gas particles, in particular – neutral atoms, metastable atoms, some ions (generally in
the negative glow region where the electric field is not very strong) and molecules.
The approximation of the nonthermal GD gas to the thermal one can cause some
inaccuracies or even errors in both computational studies and interpretation of the
emission spectra.

\subsection{2.4.2 Determination of the GD temperature from the rotational spectra of the
molecules}

The discharge gas temperature is often determined from the rotational spectra of
diatomic molecules in the plasma (usually N\textsubscript{2} or OH radicals).\textsuperscript{87,125,143-149} The
rotational temperature \( T_{\text{rot}} \) is assumed to have generally the same magnitude as the
gas kinetic temperature because of the low energies involved in the rotational
process and the rapid exchange between rotational and kinetic energy of the
molecule. In other words when the discharge gas is in LTE, the rotational
temperature of the molecule in this gas should be equal to the kinetic gas
temperature. In this case the ratio of population or number density \( n_k \) of bound
electrons at the rotational level with energy \( E_k \) and total number density of the
rotational states \( n \) is described by the Boltzmann distribution:

\begin{equation}
    n_k / n = \frac{[g_k \exp(-E_k / kT_{\text{rot}})] / Q(T)}
\end{equation}

where \( g_k \) is the statistical weight of level \( k \) and \( Q(T) \) is the partition function which is
very close to the statistical weight of the ground state \( g_o \) at low temperatures.
The emission line intensity \( I \) is the product of number density \( n_k \) and transition
probability \( A \ (s^{-1}) \) for spontaneous emission:
\[ I = \left(\frac{h \nu}{4\pi}\right) An_k \]  

Thus the intensity of a rotational line can be deduced from the equations 2-15 and 2-16:

\[ I = D \nu^3 S \exp\left(-\frac{E_k}{kT_{rot}}\right) \]

where the coefficient \( D \) contains the rotational partition function, the statistical weight \( g = (2K' + 1) \) and universal constants, \( S \) is the oscillator strength. \( E_k \) is the rotational energy:

\[ E_k = B_{\nu}hcK'(K'+1) \]

where \( B_{\nu} \) is a rotational constant belonging to the vibrational quantum number \( \nu \), and \( K' \) is the quantum number of the rotational level or the angular momentum. From the 2-17 and 2-18 follows:

\[ \log(I / S) = -\frac{B_{\nu}hc}{kT_{rot}} K'(K'+1) + \text{const} \]

The line strength \( S \), the constants \( B_{\nu}, h, c, k \) and \( K' \) are known from the literature. Thus the rotational temperature \( T_{rot} \) of the molecule can be determined from the slope of the plot: \( \log(I / S) \) vs \( K'(K'+1) \) plotted for the measured intensities of the rotational lines from one vibrational band of the molecule.\(^{150}\)

The Boltzmann plot method is often used for the determination of the discharge gas temperature, because of its simplicity and the possibility of spatial resolved measurements (e.g. at side-on intensity measurements). This method doesn’t require a very high spectral resolution; therefore the rotational spectra can be measured with common commercial spectrometers (resolution of around 20 pm). Moreover when the measured spectrum is partially resolved, a special procedure of the spectral contour fit can be applied to deduce the rotational temperature.\(^{151-153}\) On the other hand the determination of the gas temperature by the measurement of rotational emission line intensities is prone to error. Firstly the rotational temperature of the molecule may not be similar with the kinetic gas temperature because of the lack of LTE. In addition the accuracy with which one knows the transition probabilities of the measured rotational lines is critical. It should be also mentioned that to obtain measurable rotational spectra of the molecular species it is necessary to add enough of those species, which can alter the temperature.
2.4.3 Determination of the GD temperature from the Doppler width of spectral lines

The phenomenon of Doppler broadening of the spectral lines due to the thermal motion may be also applied for the determination of the discharge gas temperature.\textsuperscript{152,154,155} When the GD gas particles are in thermal motion, i.e. in LTE, the broadening depends only on the wavelength of the spectral line $\lambda$, the mass of the emitting particles $M$, and their temperature $T$, and therefore can be used for inferring the temperature of an emitting gas:

$$\Delta\lambda_{1/2} = 7,16 \times 10^{-7} \frac{\lambda T}{M}$$

where $\Delta\lambda_{1/2}$ is the full emission line width at half intensity.\textsuperscript{154,156}

The Doppler method of the GD temperature determination requires extremely high spectral resolution which can be only achieved at special (e.g. Fourier transform) spectrometers. The operation of these spectrometers is much more complicated and spectrum measurements are time consuming in contrast to the commercial low resolution spectrometers. Similarly to the rotational temperature, the Doppler temperature can deviate from the kinetic gas temperature introducing an error into the deduced kinetic gas temperature value.

2.4.4 Laser-light scattering technique for the measurement of the GD temperature

The Rayleigh scattering of the laser on the plasma particles is frequently used for the determination of the discharge gas temperature.\textsuperscript{126,131,157-160} Rayleigh scattering of incident light occurs only from very small particles, and is proportional to the concentration of the scatterers in the observation volume. In the GD, where the ground-state argon atoms are by far the most prevalent scatterers, the Rayleigh scattering is the measure of the localized argon number density. Thus, with known number density the gas kinetic temperature can be calculated from the ideal gas law.

The laser-light scattering method requires special equipment and can not be performed with a common GD source at a commercial spectrometer. However the
Rayleigh scattering approach of the gas temperature measurement offers several advantages, in particular better spatial resolution and accuracy.

2.5 Applications

In this chapter two types of layered materials analyzed by means of pulsed GD OES are introduced: thin film solar cells with Cu(In,Ga)Se₂ (CIGSe) light absorbing layer and electrodes of Surface Acoustic Wave (SAW) devices. State of the art as well as present challenges in the scientific and industrial fields of these two material systems are shown. The importance of the GD OES depth profiling with application of PGD is discussed.

2.5.1 CIGSe thin film solar cells

Due to the application of light absorbing materials with high absorption coefficients, the thin-film technologies reduce the amount of material required in creating a solar cell. This greatly reduces the material costs. In addition thin film solar cells (TFSC) have become popular due to the flexible substrate, lighter weight, ease of integration, long-term stability, cheap and multiple pathways for deposition with room for innovation and evolutionary improvement. The above listed features give TFSC an advantage over c-Si (crystalline Si) in two specific markets: small rural solar home systems and building integrated photovoltaic installations.

In 1981 or 1982, four TFSC technologies crossed the 10 % efficiency barrier and thus became serious contenders for commercialization: Cu₂S/CdS, amorphous Si, CdTe and CIGSe (the most abundant sunlight-absorbing materials are listed). CIGSe has produced the highest efficiency TFSC devices and is the only TFSC that can be expected to compete with c-Si efficiencies. The largest CIGSe installation is on the roof of Shell Solar’s manufacturing building in Camarillo CA in the USA. The schematic view of the typical CIGSe solar cell and SEM image of its transverse cut are shown in the Fig. 2-9.
In contrast to the CdS and ZnO semiconducting layers, which act as windows for the sunlight, the band-gap energy of the CIGSe layer (1.4 – 1.6 eV) is exactly right for the effective absorption of the solar radiation. In addition CIGSe is a direct semiconductor and it has a high absorption coefficient. Therefore the absorber (CIGSe) thickness of 1-2 µm is sufficient to completely absorb the light which is responsible for the charge carrier formation. Hence according to the photoelectric effect the sunlight produces the electron-hole pairs in the CIGSe layer. These charge carriers are separated by the electric field formed in the space-charge region of the p-n junction (at the CdS and CIGSe interface) and move into opposite directions: electrons – forwards the ZnO front contact and the holes forwards the Mo back contact. Thus, the electric current is produced.\textsuperscript{162}

The main characteristics of the solar cells are determined at standard test conditions: the illumination intensity 1000 W/m\textsuperscript{2}, temperature of the solar cell of 25 °C. The solar cell is illuminated by a standard light source (AM 1.5), with spectrum similar to that of the sunlight, while the I(V) curve of the cell is measured (see Fig. 2-10).
Fig. 2-10 Typical voltage-current characteristics of the non illuminated (dark) and illuminated solar cell with main electrical parameters of the solar cell.

This measurement gives the following important values: the maximal power $P_m$ at voltage $V_m$ and current $I_m$, the open-circuit voltage $V_{OC}$ at which the current under the constant irradiation is zero, and the short circuit current $I_{SC}$ which flows at zero voltage. The fill factor $FF$ and the efficiency of the solar cell $\eta$ are calculated using the following equations, where $P_{in}$ is the power:\[162\]

\[FF = \frac{I_m V_m}{I_{SC} V_{OC}}\]  \hspace{1cm} 2-21

\[\eta = \frac{P_m}{P_{in}} = \frac{I_{SC} V_{OC} FF}{P_{in}}\]  \hspace{1cm} 2-22

One more important characteristic of the solar cell is its quantum efficiency ($QE$). $QE$ is the percentage of photons hitting the photoactive material that will produce an electron-hole pair, which is collected at the contact. The $QE$ is measured over a range of different wavelengths to characterize the device efficiency at each photon energy. The quantum efficiency of a solar cell is an important measure as it gives information on the current that the cell will produce when illuminated by light with a particular wavelength.

The most important layer of the solar cell, which has the greatest influence on its efficiency, is the sunlight absorbing layer Cu(In,Ga)Se$_2$. CIGSe is a solid solution of CuInSe$_2$ and CuGaSe$_2$. These two compounds have a chalcopyrite lattice
structure, which is similar to the sphalerite structure but with an ordered substitution of the group II on the groups I (Cu) and III (In or Ga) elements.

![Diagram](image)

**Fig. 2-11** (a) Ternary phase diagram of the Cu-In-Se system and (b) pseudobinary \( \text{In}_2\text{Se}_3-\text{Cu}_2\text{Se} \) equilibrium phase diagram for compositions around the \( \text{CuInSe}_2 \) phase. \( \text{Cu}_2\text{Se} \) exists as a room-temperature (RT) or high temperature (HT) phase.

The possible phases in the Cu-In-Se system are indicated in the ternary phase diagram and the tie-line near \( \text{CuInSe}_2 \) is described in the literature by the pseudobinary phase diagram (see Fig. 2-11). Thin films are usually grown at 500 °C and 22-24 at. % of Cu. \( \text{CuInSe}_2 \) as well as ordered defect compounds (ODC) are located on the \( \text{Cu}_2\text{Se}-\text{In}_2\text{Se}_3 \) tie line. The lattice structure of ODC is the chalcopyrite-type but with an ordered insertion of intrinsic defects: atoms occupy the sites of other atoms and vacancies. These defects can produce either donor or acceptor defect energy levels. Hence the electronic properties of \( \text{CuInSe}_2 \) and consequently the efficiency of the solar cell are controlled largely by the intrinsic defect chemistry of the material. For example, it is known that Cu and In vacancies in excess of Se yield strongly p-type material. Therefore, CIGSe solar cells are always grown at an excess of Se. In general, the defect chemistry is complex and until today under investigation.

The band-gap energy of \( \text{CuInSe}_2 \) can be increased from 1.04 to 1.69 eV by substituting Ga for In.\(^{164}\) Similarly, the binary phase \( \text{In}_2\text{S}_3 \) at the end point of the pseudobinary tie line can be alloyed to form \( \text{(In,Ga)}_2\text{Se}_3 \). In high performance
devices, the \([\text{Ga}] / ([\text{Ga}] + [\text{In}])\) ratio is typically between 0.2 and 0.3. Substituting Se for S increases the band gap energy. Further improvements are obtained by incorporating Na into the CIGSe layer, although the Na role in improving the device efficiency is not yet completely understood. Soda-lime glass used as substrate provides uncontrollable source of Na, since during the layer growth at high temperatures Na diffuses through the Mo layer into the CIGSe. There is a theory that the chalcopyrite phase field \(\alpha\) is increased by the addition of Ga or Na. However the influence of Na and Ga as well as other elements (for example Zn or Fe) on the CIGSe solar cells performance is still under study.\(^{162,163,165}\)

Summarizing, the elemental composition of the absorber layer has great influence on the intrinsic defect formation and the band gap of the light absorbing material, which are crucial for the solar cell efficiency. Also the lateral distribution of the elements in the absorbing layer has an influence on the solar cell performance.\(^{166,167}\) Therefore the measurement of the elemental depth-distribution is relevant for the study of the CIGSe and for a better understanding of its mode of operation. As shown above, GD OES is a suitable and fast method providing either qualitative (intensity-sputtering time) or quantitative (concentration-depth) depth profiles (see 2.2).

Depth profiling is also useful for the development of the solar cells manufacture as well as for controlling the quality of the deposited layers. There are two common deposition methods for the CIGSe absorbers: multisource coevaporation\(^{166,167}\) and two-stage processes of precursor deposition followed by Se annealing.\(^{168,169}\) Junction and device formation is typically performed by chemical bath deposition (CdS) and sputtering (ZnO). Despite the level of effort on developing manufacturing processes, a large discrepancy remains in efficiency between the laboratory-scale solar cells, and the best large-scale modules. For example, it may be more cost effective to operate at much higher deposition rate in large-scale manufacture and to accept a lower efficiency compared with a slower process optimized for higher efficiency. Hence there is a necessity for developing new processes and equipment for the large-area and high-throughput deposition, which is complicated by the lack of a comprehensive scientific base for CIGSe materials and devices.\(^{163}\)
It was already discussed before that the sputtering procedure at the GD OES analysis causes heating of the sputtered sample (see 2.3.1). The most abundant CIGSe substrate is soda lime glass, which is thermally fragile. Therefore, to avoid the local overheating of the glass during sputtering and its damage due to the thermal stress, application of the pulsed glow discharge is preferable. The effect of thermal stress and sputtering on the CIGSe layer is not described in the literature and is discussed for the first time in the experimental part of the present work.

2.5.2 SAW devices

SAW (Surface Acoustic Wave) devices have got a wide application spectrum due to their small size and suitability for the large scale production. They are used as high frequency filters in TV sets, mobile phones, keyless-entry systems, wireless-LAN products, GPS navigation etc. A schematic drawing of the SAW frequency filter is shown in the Fig. 2-12.

![Fig. 2-12 Schematic drawing of the SAW filter and surface wave transduction by electrodes on piezoelectric substrate.](image)

The electromagnetic radiation is received by the antenna of the SAW filter. If the frequency of this radiation corresponds to the resonance frequency of the SAW system, the acoustic surface waves with a well-defined wavelength appear along the top of the piezoelectric substrate via the inverse piezoelectric effect. Another electrode system, which is used as a receiver, transforms the mechanical information of the acoustic wave back into an electrical signal. This way the electromagnetic radiation with a defined frequency is filtered.
With the miniaturization of modern electronic devices, the resonance frequencies of SAW filters are shifted from the MHz to GHz range; also the power density at the electrodes is increased due to the smaller device size. Thus the probability of electrodes damage is higher. On the other hand the device performance should not degrade. The SAW devices of the next generation should have excellent filtering properties, high power durability and life time. The common Al electrodes are damaged under the high power loads. Hence the technological requirements of SAW electrodes have been increased. Different investigations have already shown the possibility of power durability improvement for Al electrodes. To prevent the acoustic migration and diffusion of the Al atoms, various Al alloys (Al-Cu, Al-Ge, Al-Ti, Al-Mg etc.) or layered systems (Al/Ti-, Al/Cr-, Al/Cu- etc. structures) are applied for the SAW electrodes.\textsuperscript{172-174} Nowadays a transition from Al- to Cu- based alloys takes place for certain SAW devices with operating temperatures of ca. 80 °C.\textsuperscript{175} Cu as compared to Al has a higher mass density, a lower electrical resistivity, a higher thermal conductivity and power durability.\textsuperscript{176} However Cu diffuses much easier than Al under the power load (Fig. 2-13 (a)).

A combination of Al with Cu-based materials could lead to a further improvement of SAW device performance. The study of the Cu-based electrodes is directed towards the layered Al/Cu systems (see Fig. 2-13 (b)). Al prevents both the diffusion of Cu to the electrode surface and Cu oxidation. Furthermore the Al atoms diffuse to the Cu grain boundaries and block the diffusion of Cu atoms.\textsuperscript{177} However too much Al in Cu (more than 19,7 at. %) causes formation of Cu-Al intermetallic phases which are very hard and brittle\textsuperscript{178} and thereby hinder the SAW device performance. In addition the Cu electrodes with more Al have higher electrical resistivity than pure Cu...
Introduction

Hence it is essential to find an optimal Al to Cu ratio which provides both reduced Cu diffusion and oxidation and low electrical resistivity of the electrodes. GD OES depth profiles of the Al/Cu/Al layer stacks allow controlling the distribution of Al in Cu. As can be seen from the Fig. 2-13(b) the layers are in the nm region. Such thin layers would be sputtered within some milliseconds in the continuous discharge. Therefore to slow down the sputtering of the sample and to have more control over the sample removal rate, pulsed discharge should be applied.

To characterize the life time of the SAW device the time-to failure (TTF) value is used. To measure this value the high power loads (1-2 W) and temperatures (50-100 °C) are applied to the electrodes until they are failing within some acceptable time. The indicator of the electrode failure is the shift of the SAW filter resonance frequency (50 kHz-2 MHz).
3 Experimental details

3.1 Measurement of the electrical characteristics

For dc and pulsed dc measurements a 4 mm Grimm-type source from Spectruma is used. The discharge pressure is measured in the anode body by a Pirani gauge, calibrated by a Baratron manometer (MKS Baratron Type 127; range 0–100 hPa). A high voltage generator (MCN 350-2000, FUG) is used to produce the continuous dc GD. The pulsed dc GD is excited with a high voltage pulse generator (RUP 3-3a, GBS Elektronik GmbH) and synchronized by an external TTL pulse generator (33120A, HP). The discharge voltage and the current of the pulsed discharge are transferred via a digital oscilloscope (11201, Tektronix) to a computer for further evaluation.

For rf and pulsed rf measurements a modified Grimm-type glow discharge source with a 4 mm anode tube is used. The GD is excited with a free running rf generator (Forschungstechnik IFW, 3.37 MHz). The measurements of the transient voltage and current are made by voltage and current probes integrated into the source. The experimental setup and the measurement system are described in detail in the paper of Wilken et al.\textsuperscript{179} The rf voltage is additionally measured by a 1:100 voltage divider (GE 3425, General Elektronik GmbH). The signals from the voltage and current probes are fed into a high speed oscilloscope (LC584A, LeCroy) from which they are subsequently transferred to a PC, where further evaluation is conducted. For all electrical experiments 10 mm thick pure Cu samples or 0.7 mm thick Si samples are used.

One part of the present work is dedicated to the optimization of the experimental setup. This step is essential before performing any experiments to
ensure that the measured signals correspond to the real ones and to reveal possible measurement artefacts. Possible artefacts which are not caused by the discharge processes, but by the electrical circuit of the pulsed system are described in the published papers.\textsuperscript{180-182}

### 3.2 Measurement of the sputtered crater shapes

The 3D measurements of the sputtered craters are performed with the optical profilometer FRT MicroProf (see Fig. 3-1) with chromatic sensor. The profilometer is set such that it scans the 8 mm x 8 mm area around the crater with a resolution of 200 x 200 points. Further the data of the 3D crater are saved in ASCII format and opened with a special evaluation program written in HP-VEE, which calculates the crater volume and the average crater shape exploiting the rotational symmetry of the crater.

![3D profile of the sputtered crater, 2D profile of the sputtered crater](image)

**Fig. 3-1** Optical profilometer FRT MicroProf and examples of 3D and 2D profiles of a sputtered crater.

The lateral resolution of the FRT Microprof is about 1 µm and the depth resolution about 20 nm. A depth of up to 600 µm can be measured in one scan. Because of the working principle (no movement of the sensor in depth direction is needed) a crater with the above mentioned dimensions and resolution is measured within 5 min and the volume (and thus also the sputtering rate) can be determined with an accuracy of 1%.\textsuperscript{183}
3.3 Light emission and spectra measurement

The measurement of the spectra (see 4.1.5) are performed at the spectrometer GDA 650 from Spectruma with CCD arrays (spectral resolution of 20 pm) at 700 V 4 hPa using the standard sample IARM 93B (Cu 85,42 m%, Al 10,33 m%, Fe 3,87 m%). To avoid the saturation of strong spectral lines the dynamic detection mode with integration time of 3 s is applied. In this mode 10 spectra of 10 ms, 5 of 20 ms, 8 of 50 ms, 9 of 100 ms and 6 of 250 ms are recorded and the intensity of all non saturated pixels is used to calculate the intensity for a 10 ms integration time. This means that e.g. the intensities measured with 100 ms integration time are divided by 10 before they are used to calculate the average intensity of all measured spectra.

The fast time resolved measurements of the characteristic emission lines during the pulse are made at the Spectruma GDA 750 spectrometer with the monochromator Digikröm DK480 and PMT detector R6357, Hamamatsu. A Standford Low-Noise Current Preamplifier SR570 with a maximum bandwidth of 1 MHz in the 1 mA/V range was used to convert the PMT current into a voltage, which was measured by the 11201, Tektronix oscilloscope. In the used amplification range (2 µA/V) the bandwidth is still higher than 500 kHz.

3.4 GD OES depth profiling and quantification

Depth profiles of the solar cell samples are measured at the spectrometer GDA 650 with 100 ms integration time of the CCD detectors. The internal free running Spectruma rf generator working at 5.9 MHz is used. Due to the low duty cycles applied for the analysis of the thermally fragile solar cell samples, the GD plasma is often not ignited or ignited with a long delay (up to some minutes) after switching on the voltage. To avoid this and to provoke the plasma ignition at the beginning of the analysis a special spark-generating device was developed, which generates a single 100 µs long high voltage pulse of 5 kV amplitude. This voltage generates a spark in the anode body, strong enough to ignite the GD plasma.
Quantitative depth profiling is implemented at various spectrometers:

- Spectruma GDA 750 is applied for the quantitative analysis of the SAW samples, prepared by the co-evaporation of Cu and Al and by evaporation of a Cu-Al ingot (see 4.2.2.1). The standard samples used for the quantification are presented in Table 3-1. This instrument is equipped with the commercial free running rf generator from Spectruma, working at 6.4 MHz. A turbo pump evacuates the GD source up to a pressure of about $10^{-5}$ hPa in order to assure a clean source and to avoid in influence of leakages. During sputtering only the Triscroll dry pump from Varian is active.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Cu</th>
<th>Al</th>
<th>Cr</th>
<th>Fe</th>
<th>Mn</th>
<th>Ni</th>
<th>P</th>
<th>Pb</th>
<th>Sb</th>
<th>Si</th>
<th>Sn</th>
<th>Ti</th>
<th>Zn</th>
<th>Bi</th>
<th>Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>CU10</td>
<td>0.35</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WSB1 (BATCH F)</td>
<td>0.47</td>
<td>82.7</td>
<td>1.9</td>
<td>0.02</td>
<td>0.1</td>
<td>0.1</td>
<td>0.08</td>
<td>0.04</td>
<td>0.55</td>
<td>0.03</td>
<td>5.95</td>
<td>0.23</td>
<td>7.55</td>
<td>0.34</td>
<td></td>
</tr>
<tr>
<td>WSB3 (BATCH C)</td>
<td>0.46</td>
<td>82.4</td>
<td>0.7</td>
<td>0.05</td>
<td>0.51</td>
<td>1.44</td>
<td>0.36</td>
<td>0.04</td>
<td>0.39</td>
<td>0.07</td>
<td>3.48</td>
<td>0.6</td>
<td>9.66</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>WSB6 (BATCH D)</td>
<td>0.36</td>
<td>94.7</td>
<td>0.06</td>
<td>0.06</td>
<td>0.03</td>
<td>0.25</td>
<td>0.12</td>
<td>0.02</td>
<td>0.95</td>
<td>0.01</td>
<td>2.48</td>
<td>0.06</td>
<td>0.88</td>
<td>0.01</td>
<td>0.25</td>
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<tr>
<td>WSB7 (BATCH B)</td>
<td>0.46</td>
<td>72.7</td>
<td>3.87</td>
<td>0.01</td>
<td>1.95</td>
<td>3.39</td>
<td>3.03</td>
<td>0.19</td>
<td>0.03</td>
<td>0.64</td>
<td>4.25</td>
<td>1.93</td>
<td>7.58</td>
<td>0.19</td>
<td>0.01</td>
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<td>NBS-1767</td>
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<td></td>
<td>99.8</td>
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<td></td>
<td>0.03</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
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<td></td>
<td></td>
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<tr>
<td>Al pure</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti-5-2-5</td>
<td>2.15</td>
<td>0.01</td>
<td>5.48</td>
<td>0.02</td>
<td>0.32</td>
<td>0.03</td>
<td>0.01</td>
<td>0.01</td>
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<td></td>
<td></td>
<td>0.04</td>
<td>2.4</td>
<td>91.6</td>
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</table>

Table 3-1 The list of standard samples, their Relative Sputtering Rates (RSR) and element concentrations in m%. These standards are used for the quantification of the depth profiles of SAW electrodes measured with continuous dc discharge.

- Spectruma GDA 650 is applied for the quantification of the solar cell samples (the list of standards is given in Part 4.1.6.1). This instrument is equipped with the commercial free running rf generator from Spectruma, working at 5.9 MHz. Before each measurement a Triscroll dry pump evacuates the GD source up to a pressure of about $10^{-2}$ hPa.

- LECO GDS 850A device at Swerea KIMAB (Corrosion and Metals Research Institute in Stockholm) is applied for the quantitative depth profiling analysis of the 10nmAl/100nmCu/10nmAl/5nmTi/LiNbO$_3$ layer stacks of the SAW devices (see 4.1.6.2). The list of standards used for the quantification is shown in Table 3-2.
### Experimental details

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Mo</th>
<th>N</th>
<th>Nb</th>
<th>Ni</th>
<th>O</th>
<th>P</th>
<th>S</th>
<th>Sb</th>
<th>Si</th>
<th>Ti</th>
<th>W</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>NIST - KIMAB/C1145A</td>
<td>0.48</td>
<td>0.62</td>
<td>0.215</td>
<td>0.191</td>
<td>0.001</td>
<td>0.001</td>
<td>11</td>
<td>0.044</td>
<td>0.063</td>
<td>0.011</td>
<td>4,87</td>
<td>32,4</td>
</tr>
<tr>
<td>INST-MF - KIMAB/CU0X</td>
<td>0.01</td>
<td>0.012</td>
<td>0.001</td>
<td>0.002</td>
<td>0.006</td>
<td>0</td>
<td>0.132</td>
<td>0.97</td>
<td>0.66</td>
<td>0.138</td>
<td>0.211</td>
<td>1,15</td>
</tr>
<tr>
<td>INST-MF - KIMAB/ST4</td>
<td>1</td>
<td>0.25</td>
<td>0.008</td>
<td>0.001</td>
<td>0.008</td>
<td>0.049</td>
<td>0.07</td>
<td>1.07</td>
<td>0.67</td>
<td>0.138</td>
<td>0.211</td>
<td>1,15</td>
</tr>
<tr>
<td>INST-MF - KIMAB/T4</td>
<td>0.35</td>
<td>0.14</td>
<td>0.016</td>
<td>0.017</td>
<td>19.45</td>
<td>1.44</td>
<td>47.5</td>
<td>0.012</td>
<td>0.001</td>
<td>0.011</td>
<td>4,87</td>
<td>32,4</td>
</tr>
<tr>
<td>INST-MF - KIMAB/ST4</td>
<td>1</td>
<td>0.25</td>
<td>0.008</td>
<td>0.001</td>
<td>0.008</td>
<td>0.049</td>
<td>0.07</td>
<td>1.07</td>
<td>0.67</td>
<td>0.138</td>
<td>0.211</td>
<td>1,15</td>
</tr>
<tr>
<td>INST-MF - KIMAB/JK41-1N</td>
<td>0.15</td>
<td>94.5</td>
<td>3.1</td>
<td>0.095</td>
<td>1.6</td>
<td>0.38</td>
<td>0.23</td>
<td>4.67</td>
<td>4.67</td>
<td>4.67</td>
<td>4.67</td>
<td>4.67</td>
</tr>
</tbody>
</table>

**Table 3-2** The list of standard samples, their Relative Sputtering Rates (RSR) and element concentrations in m%. These standards are used for the quantification of the depth profiles of SAW electrode metallizations measured with pulsed rf discharge.
4 Results and discussion

4.1 Study of pulsed glow discharge

4.1.1 Defining the range of the PGD parameters

The parameters of PGD can be varied within a wide range providing either weak or strong plasma with µs or ms pulse length. Therefore for the particular application it is reasonable to select some narrow parameter ranges which favour reliable analysis results. In the present work the studies are oriented to the analysis of layered and thermally fragile samples. Therefore the main criteria for the selection of the parameter ranges are: flat sputtered crater, moderate sputtering rates and minimal thermal stress.

Voltage, current and pressure ranges In the introduction it was already mentioned that the parameters of PGD are: voltage (U), current (I), pressure (p), duty cycle, pulse length and frequency (see 2.3.1). The first three are fairly investigated for continuous discharge. It is well known that U, I and p are not separately variable and one can not change one of the parameters keeping two other immutable. But it was found out that the pressure is a less important parameter for GD-OES. Also the main sputtering equation of Boumans contains only U and I, which means that U and I are the most convenient parameters to describe GD sputtering. If one assumes that U and I have the greatest impact also for the pulsed discharge, the task of defining the U, I and p ranges for PGD is simplified to only U and I.

For all analytical applications of the Grimm-type source, the GD is operated in abnormal mode, where the sputtering is most stable and homogeneous. In this mode
a voltage increase leads to an increase of the current.\(^2\) This is reflected in the voltage-current (U-I) plots measured for continuous and pulsed discharges at different pressures (see Fig. 4-1). Hence the U and I ranges of glow discharges suitable for analysis can be defined from an examination of U-I characteristics. The measurement of the U and I of continuous dc discharge is easy to perform (Fig. 4-1 (a)). In case of pulsed dc discharge the simplest way to get the current value is to measure the total input current of the pulse generator. In this way the average current over the whole pulse period (on- and off-time) is measured including the power losses in the pulser. Thus the current values are significantly lower than those of the continuous mode (Fig. 4-1 (b)).

![Fig. 4-1 U-I plots of the (a) continuous dc discharge and (b),(c) pulsed dc discharge (0.2 duty cycle, 200 µs pulse width, 1 kHz frequency). In the plot (c) the measured current values from the plot (b) are divided by the duty cycle / 0.2.](image)

Division of the current values from the Fig. 4-1 (b) by the duty cycle normalizes the pulsed current to the duty cycle and makes it comparable with the current of the continuous mode (see Fig. 4-1 (c)). The measured U-I plots of pulsed discharge are very similar with the continuous discharge plots. Hence it can be concluded that, at
the same pressure range from 3-9 hPa, the voltage range of pulsed discharge, where the U-I plots indicate the abnormal mode, is the same as in continuous discharge: 500 - 1400 V. It should be mentioned that the upper voltage limit for the pulsed discharge can be higher and depends on the power supply. Nevertheless 1400 V were chosen to be able to compare pulsed discharge with the continuous one, because the maximum voltage of the continuous mode is limited to around 1400 V due to the strong heating at high powers.

From the *Fig 4-1* (a) and (c) can be seen that the slopes of the U-I plots of continuous and pulsed discharges differ: U-I plots of the pulsed mode are steeper than those of the continuous one. Also at high powers the U-I plots are more curved. This important phenomenon is thoroughly analyzed in the following text and parts 4.1.2 and 4.1.3.1.

Measurement of the U-I plots of the pulsed rf discharge is even more complex than for dc mode and will be discussed in the next parts. In this work the considered voltage range for the pulsed rf discharge is the same as in dc mode – 400-1400 V.

The current range, similarly with voltage, can be deduced from the U-I plots. For example for a 20 % duty cycle and 200 µs pulse length the total input current values where observed to be from 1 to 7 mA. With these current values the U-I plot is nearly linear, what indicates the abnormal mode. The corresponding pressure is 6 hPa. At commercial spectrometers or experimental setups in case of pulsed discharge it is easier to measure pressure than current. Therefore, for most experiments in this work the current is not recorded but the pressure is set to a value close to 6 hPa.

**Duty cycle, pulse length and frequency ranges** The range of the pulse parameters duty cycle, pulse length and frequency is not so often discussed as the electrical parameters U, I and p. The applied frequencies can be from the Hz\(^{77}\) region to several kHz,\(^{184}\) the pulse durations – from µs\(^{185}\) to ms.\(^{98,186}\) Correspondingly the duty cycle may vary from 0 to 100 %. Studying the PGD within all these parameter ranges can take a lot of time and makes no sense, because the analysis conditions of layered or thermally fragile samples have limitations. It is worthwhile to determine these limitations.
Similarly to U, I and p the duty cycle, pulse length and frequency are interdependent. One cannot change for example the duty cycle without changing pulse length or frequency. Analogous to the pressure in this work the frequency was found to be a less important parameter. The reasons are: (1) The duty cycle is directly correlated with the power introduced into the discharge. Thus this parameter is responsible for the heating of the discharge system and is important for the analysis of thermally sensitive samples. Also the sputtering rate depends on the duty cycle. (2) It is found that the current signal depends on the pulse duration (see 4.1.2). So this parameter can influence the sputtering conditions even though operating at constant duty cycle. Hence in the present study of the PGD, duty cycle and pulse duration are independently varied while the frequency is allowed to reach its own value depending on the first two parameters.

The duty cycle value should be determined for each application individually depending on the thermal stability and thickness of the sample. To find the appropriate pulse duration range one should take into account the plasma processes within the pulse and their temporal characteristics. The most significant physical processes are: field-electron interaction, electron-neutral collisions, diffusion processes and thermal effects. The first three occur and stabilize in up to some µs after the plasma ignition. But the kinetic temperature of the discharge gas stabilises in the ms range.\(^\text{74}\) Thereby the discharge gas is heating within the pulse and reaches its maximum temperature in the ms region.\(^\text{87}\) Pollmann et al.\(^\text{87}\) found that the N\(_2^+\) rotational temperature rises from 400 to 575 K when the pulse duration changes from several µs to 1 ms. But from 1 ms to continuous mode the temperature change was observed to be only around 100 K (see Fig. 2-7). The U-I plots measured in the present work indicate a similar effect. In Fig. 4-2 the U-I plots measured at different pulse durations but at constant duty cycle are depicted. In the following text it is shown that the longer the pulse the lower the average current value within the pulse (see also 4.1.2.2 Fig. 4-13). In Fig. 4-2 the current difference (offset) at 500 V is subtracted from the measured current values to bring the first points of all the plots together. In such representation one can clearly see that the pulse duration influences the slope of the U-I plots (see Fig. 4-2). The slope is directly connected with the resistance of the discharge gas. According to the ideal gas law, at constant
pressure and volume the gas density decreases and thus the resistance grows with temperature. In the Fig. 4-2 the slope of the U-I plot is going down at longer pulses. This confirms that at longer pulses the plasma is hotter. In addition the difference of the slope is getting smaller at longer pulses reaching its constant value at 1 ms. The plots which correspond to 1 and 4 ms pulse length are congruent and very close to the plot of continuous discharge. In continuous mode the kinetic temperature is stabilized and has its maximum value, which is apparently close to the temperature of the ms pulsed discharge. Thus to take profit of the PGD and to reduce the thermal stress of the sample one should apply pulse lengths less than 1 ms. This is valid also for the rf discharge because the behaviour of the rf current is observed to be very similar to the dc one.

The lower limit of the pulse length region is considered to be 10 µs – the time of the transition from ignition to the stable plateau region.

The main deductions of the part are:

- Pressure and frequency are less important parameters for sputtering.
- Voltage and current should be chosen such to provide abnormal discharge and minimum thermal stress. The U-I plots of pulsed discharge, similarly to continuous discharge, indicate the abnormal mode and plasma heating. The voltage range defined for the investigation in the present work is 400 - 1400 V. The current range should correspond to the chosen voltage range at the pressures around 6 hPa.
- The duty cycle should be determined individually for each sample. The application of pulses longer than 1 ms causes a discharge gas heating close to that of the continuous discharge. The pulse length range defined for the study is 10 – 1000 μs.

### 4.1.2 Electrical properties of PGD

One of the keys to understand the glow discharge is its electrical behaviour. The electrical properties, in particular the U–I characteristics, current and voltage signal shapes within the pulse, are important for the understanding of the processes taking place in the glow discharge. Electrical properties are also closely related to the analytical performance of PGD, due to their effect on the sputtering rates, sputtered crater shapes and emission yields. In addition in the previous part (see 4.1.1) it was shown, that the voltage–current plots indicate whether the discharge is operating in the abnormal mode, which is extremely important for homogeneous sample sputtering and efficient excitation and ionization. Electrical parameters of the discharge are also necessary for the plasma modelling studies. Nevertheless in case of PGD there is a lack of studies where the current and voltage signals are considered in detail. Even though the influence of the pulse parameters on the crater shape and emission intensity is considered, less attention is paid on the electrical properties of the PGD. Therefore, in this dissertation the 4.1.2 part is dedicated to the electrical properties of PGD. The influence of the PGD parameters (duty cycle and pulse duration) on the electrical properties is examined. The pulse frequency is not considered because it is the less important parameter (see above section 4.1.1) and is allowed to reach its own value depending on the duty cycle and pulse duration.

In the introduction the question, whether dc and rf discharges behave similarly is brought up (see 2.3.2). This question is actual till nowadays and for the PGD it is even less studied. Therefore in this work the comparative studies of the electrical properties of the dc and rf pulsed discharges are made. Nearly all experiments are performed for both dc and rf pulsed discharges, keeping in mind that the effective voltage should be used in the case of an rf discharge in order to obtain the same plasma conditions as in dc mode.
4.1.2.1 Voltage-current plots of PGD

The importance of the abnormal discharge mode for the analytical applications has been already discussed in the introduction and in the previous section. In this mode the discharge conditions are selected such that the current flows homogeneously through the cathode surface thus providing flat craters and high power. The expansion of the plasma over the cathode is obstructed by the anode. Therefore, at higher voltages more electrons are extracted from the surface per unit area and the current increases. This process defines the form of the U–I characteristics of the GD: the current increases with voltage. The U–I plots of the PGD are found to resemble the U–I plots of the continuous discharge (see Fig. 4-1). However whereas for the continuous dc mode the measurement of the U–I plots is experimentally simple and straightforward, for the pulsed mode there are several measurement options. It is essential to choose a convenient type of current signal acquisition. This acquisition is also different for the dc and rf pulses. Therefore in the following text the measurement of the U–I plots of pulsed dc and rf discharges will be sequentially described.

Dc pulsed discharge With the high voltage dc pulse generator RUP 3-3a, applied in this work, there are two possibilities to record the current signal. One of them provides a high time resolved measurement of the current within the pulse. The other gives the total input current of the pulser. So, for the voltage–current plots one can either measure the current within the pulse and calculate the average value during the pulse on-time (method 1) or measure the input current and divide it by the duty cycle (method 2). The second method is used in the section 4.1.1 (see Fig. 4-1 and Fig. 4-2). Both methods produce an averaged current value during one pulse. Experiments have shown that the current measured by method 2 exceeds the current from the method 1 by about 15% (see Fig. 4-3).
A part of this difference is explained by the heating of the pulse generator due to the power consumption. In general, method 1 is preferable, if accurate currents are needed. However, as the ratio between both currents is stable and does not depend on the voltage, it is possible to correct the current measured by method 2. Because method 2 is much easier to perform and even possible at a commercial scale, this later current recording option is used in the present work.

**RF pulsed discharge** The measurement system developed at the IFW allows recording the rf current and voltage within the pulse. In the Fig. 4-4 (a) the measured voltage and current correspond to two oscillation periods of the rf current and voltage at the end of the 200 µs pulse. Plotting the measured voltage versus current gives the U-I plot of the pulsed rf discharge shown in the Fig. 4-4 (b). The voltage signal is shifted to the negative region and only a small part is higher than the zero value. This important property of the rf voltage is due to the bias formation when the discharge source is capacitive coupled. The bias formation mechanism is described in the introduction (see 2.3.2).
Results and discussion

In the region where the voltage is negative the current is also negative. This current is called ionic current because when the cathode is negatively charged, the positive ions are accelerated towards its surface. The negative voltage and current region takes around 85% of the whole rf period and is responsible for the cathode sputtering. When the voltage is positive the electrons, accelerated by the electric field, move in the direction of positively charged electrode. Because the small electrons are much faster than massive ions, the electronic current is 3 times higher than the ionic one, despite the short positive region time (Fig. 4-4). In the electronic part of the U-I plot the cathode sputtering is absent. Hence for the analytical applications the ionic part is more important.

The electrical behaviour of a dc discharge is described by a resistor. Therefore the U-I plots of the dc discharge represent one line in a certain voltage range. For the rf discharge the equivalent circuit is more complex. In the rf case besides the resistance the capacity of the sheaths (cathode dark space with positive space charge see Introduction 2.1.1), which are periodically contracted and expanded in front of the electrodes, have significant contribution to the complex impedance of the plasma.\(^\text{105,201}\) The presence of the capacitor in the equivalent circuit of the rf plasma causes a \(90^0\) phase shift between rf voltage and current. However due to the additional impact of the plasma ohmic resistance this shift is less than \(90^0\). Hence the hysteresis of the U-I plot of the rf discharge in Fig. 4-4 (b) is caused by the phase

![Fig. 4-4 (a) Current and voltage signals of the rf discharge measured in the last 600 ns of the 200 µs pulse (effective voltage 700 V, pressure 6 hPa, duty cycle 0.2, frequency 1 kHz) and (b) corresponding U-I plot.](image)
shift between the voltage and current, which appears because of the sheaths capacity.

In the external circuit of the rf system the charges oscillate between the electrodes of the coupling capacitor. Thus the current integrated for one rf cycle is zero. In case of rf pulsed discharge it makes no sense to acquire the average current value within the pulse, as it is done for the dc pulses, because the average rf current within the pulse is zero. Therefore in the present study the voltage–current plots of pulsed rf discharge correspond to a few oscillation periods of the rf current and voltage at some defined time within the pulse (see Fig. 4-4).

According to the described measurement procedures, the U-I plots of the pulsed dc and rf discharges are measured at different pressures and duty cycles. The pulse duration is kept constant.

In Fig. 4-5 the U-I plots of pulsed dc discharge are depicted. According to the previously described current measurement principle the current in this figure represents the averaged current value within the pulse (pulse length 200 µs). From Fig. 4-5 follows that at a constant pulse duration (200 µs) the average current during the pulse on-time depends on the duty cycle. In particular, at 3 hPa the plot, which corresponds to the 0.4 duty cycle, is placed lower than the plots for the 0.2 and 0.1 duty cycles. At 6 and 9 hPa the decrease of the current is already seen for the 0.2 and 0.4 duty cycles. One more attention worthy effect is that the plots are more curved when higher powers are applied.

![Fig. 4-5 Voltage–current plots of pulsed dc discharge presenting the averaged current values within the 200 µs pulse (measured using method 2).](image)
**Fig. 4-6** U-I plots of pulsed rf discharge measured in the last 600 ns of the 50 µs pulse at 700 V effective voltage. (a) – electronic part of the U-I plot, (b) – ionic part of the U-I plot.

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**Results and discussion**

Fig. 4-6 contains measured U-I plots of pulsed rf discharge. For the better view the electronic and ionic parts are depicted in two different plots – Fig. 4-6 (a) and (b) correspondingly. The slope of the electronic part is weakly influenced by the duty cycle: the current slightly grows at application of a lower duty cycle. Pressure has stronger influence on the electronic current than duty cycle: at higher pressures the current in the electronic part is higher. The same effect can be seen in the ionic part of the rf U-I plots as well as in the dc U-I plots. Higher pressure means more gas particles and thus higher current.

The powered electrode is negatively charged in the ionic part of the rf U-I plot, therefore the ionic part corresponds to the dc discharge with negative cathode potential. Rf plots in the ionic part look similar to the dc plots: as in the dc case, a decrease of the current and thus of the slope at higher duty cycles can be seen.
However, in contrast to the dc case, voltage–current characteristics measured for rf discharge show a linear behaviour without any current saturation at higher powers.

The experimental results of U-I plots measurement raise the question: why the voltage–current graphs (of both dc and rf modes) for different duty cycles, despite the normalization of the current to a duty cycle (see 4.1.2.1 method 2), are not congruous? In the previous section it is shown that the pulse duration affects the slope of the U-I curve (see 4.1.1). It is concluded that the reason is the discharge gas heating when long pulses are applied. In this section experiments are performed at constant pulse duration, but different duty cycles. Similarly with long pulses, high duty cycles cause a current decrease. So the effect of duty cycle on the U-I plots can be also attributed to the discharge gas heating.

The phenomenon of current suppression at high powers is already known for the continuous discharge (see 2.3.3).\textsuperscript{2,118,119} According to the ideal gas law at constant voltage and pressure a temperature rise results in a decrease of the gas density, and thus causes a decrease of the discharge current. Hence the reduction of the current in case of pulsed discharge indicates discharge gas heating when long pulses or high duty cycles are applied. The curvature of the U-I plots in the pulsed dc case at high powers indicates heating as well (see Fig. 4-5). However voltage–current characteristics measured for rf discharges within the last 600 ns of the pulse show a linear behavior without saturation in the ionic part (see Fig. 4-6 (b)). This means that during the short time of some rf periods the gas temperature stays constant.

It is shown that U-I plots of pulsed discharge contain important information about the discharge gas heating mechanism and its dependence on the duty cycle and pulse duration. They are also testifying whether the discharge is in abnormal mode or not. However when measuring the average current within the pulse or acquiring the U and I signals only at some short time of the pulse the information about the U and I signal shapes is lost. It has been observed that plots measured at the beginning and at the end of the same pulse are different. Moreover, this difference depends on the pulse parameters.\textsuperscript{182} On the other hand, it requires a lot of work and time to study the voltage–current characteristics at different times of the pulse, varying duty cycle and pulse duration. It is much easier in terms of
Results and discussion

experimental work and also useful to look at the current and voltage signal shapes during the pulse.

4.1.2.2 Voltage and current signal shapes within the pulse

The dc pulse generator used in this work (RUP 3-3a) produces a rectangular voltage signal. Therefore this part will focus on the current shapes during the pulse. Nevertheless there is one essential aspect concerning the rf voltage, which should be mentioned here. Contrary to the dc mode, the voltage signal produced by an rf generator is not rectangular at the beginning of the pulse (see Fig. 4-7).

![Fig. 4-7 Rf voltage signal measured at different pulse durations (effective voltage 800 V, pressure 6 hPa, duty cycle 0.2).](image)

The reason of this phenomenon is the previously described bias formation procedure\textsuperscript{105} (see also 2.3.2). At the beginning of the pulse the electrons remain at the cathode surface and charge it up to a negative bias voltage. For the experimental setup used in this work this procedure takes around 50 µs time. The time of the bias development depends on the capacitance of the system and thus can differ for different devices. The described effect is not a measurement artefact and should be taken into account when pulsed dc and rf discharges are compared. It is also relevant for the analytical applications, because when very short pulses are chosen (shorter than 50 µs) the voltage is not reaching its prescribed value (see Fig. 4-7). This may lead to a decrease of the sputtering rate.

The influence of the discharge parameters on the current signal shapes during the pulse is studied and described below. The following discharge parameters are considered: voltage, duty cycle and pulse duration.
Influence of the voltage on the current shapes In the previous section 4.1.2.1 for the presentation of U-I characteristics of the pulsed dc discharge the average current value over the pulse is evaluated. Such averaging hides possible effects within the pulse. In the Fig. 4-8 the measured current shapes during the dc pulse are presented at different voltages. The other discharge parameters pressure, duty cycle, and pulse duration are fixed.

As expected the current within the pulse in Fig. 4-8 increases with increasing voltage. However there is one more effect which was invisible at the U-I plots study: the current peak at the beginning of the pulse becomes more pronounced at higher voltages. The high current peak at the beginning of the pulse has already been mentioned by several authors.\textsuperscript{101,126,202} Because of its strong excitation and ionization conditions, the region at the beginning of the pulse is often used in time-gated measurements to get elemental information about the sample.\textsuperscript{97} But the origin of the high current after the plasma ignition is not yet absolutely clear. In the modelling studies in order to predict the high current peak at the beginning of the pulse, a considerable rise of the gas temperature in this region has been supposed.\textsuperscript{196} But later on the theory about the temperature has been denied and it has been assumed that the initial current peak is attributed to the measuring circuit and not to the real plasma current.\textsuperscript{203} There is a theory that a part of this high current is the capacitive current caused by charging of a capacitor (the discharge source without the plasma).\textsuperscript{74} The discharge source used in this work, including cables, has a capacitance $C$ of around 230 pF. The resistance value $R$ which is between the power...
Results and discussion

supply and the source is 35 Ohm. So in this case the application of a voltage $U_0$ (for example 800 V) across the 230 pF capacitor will really produce a huge current peak $I_{\text{max}}$ of several Ampere, but it will decay in some ns (see Fig. 4-9).

\[ I_{\text{max}} = \frac{U_0}{R} \quad I = I_{\text{max}} \cdot e^{-\frac{t}{RC}} \quad I_{\text{max}} = \frac{800V}{35\Omega} = 22.9\ A \]

**Fig. 4-9** Simplified equivalent circuit of the dc discharge system (which includes the dc power generator, the resistance of the generator and the cables and the source capacity) and calculation of the corresponding capacitor charging time.

The huge peak of 22.9 A in the first ns of the pulse is very likely existing, but it is not possible to record it with the equipment used in the present study (the applied voltage probes are not made for such high frequency and current). Thereby the assumption about the capacitive current doesn’t explain the often observed current peak in the μs region, like in the Fig. 4-8. Therefore further work, especially computational studies on this topic are necessary.

Compression of the time scale of the measured rf current signal from the Fig. 4-4 (a) gives the rf current shape within the pulse. In this way the rf current signal shapes at different effective voltages, but constant duty cycle and pulse duration are measured (see Fig. 4-10). It is interesting that the behaviour of the pulsed rf discharge is rather like in the dc case (see Fig. 4-8) and current peaks appear in the prepeak region as well in the both electronic (positive) and ionic (negative) parts. In comparison with the plateau region the current peak at the beginning of the rf pulse is not so high as in dc case. But one can clearly see the similarity between rf and dc pulses: the peaks disappear at lower voltages.
Influence of the duty cycle and pulse duration on the current shapes In this part firstly the influence of the duty cycle on the current is studied at fixed pulse duration. Afterwards the influence of the pulse duration at fixed duty cycle is investigated. The frequency is allowed to seek its own value depending on the duty cycle and pulse length.

Fig. 4-11 Dc (a) and rf (b) current signals within the pulse measured at different duty cycles (6 hPa, 800 V (in case of rf $U_{\text{eff}}$ 800 V), pulse duration 200 µs).

Fig. 4-10 Rf current signal within the pulse measured at different effective voltages (pressure 6 hPa, duty cycle 0.2, pulse duration 200 µs, frequency 1 kHz).
Results and discussion

smaller the current level for both dc and rf modes. This result confirms the observations made at the U-I plots study.

Lowering of the current level caused by the duty cycle increase is correlated with the fact that the U-I characteristics measured at different duty cycles are not congruous in spite of the normalization to the duty cycle (see 4.1.2.1 Fig. 4-5). This normalization gives the average current value within the pulse. As can be seen from the measured current shapes, the average current is not the same for different duty cycles. U-I plots of pulsed rf discharge, which represent the current values in the last 600 ns of the pulse, are also not congruous (see 4.1.2.1 Fig. 4-6). This phenomenon is explained by the lowering of the rf current level as well (Fig. 4-11 (b)).

To remind the decrease of the current is attributed to the discharge gas heating at high powers. The power can be heighten e either by an increase of the voltage and current or by an increase of the duty cycle. In the first case one observes a curvature of the U-I plots (Fig. 4-5) and in the second case – a decrease of the current within the pulse despite voltage and pressure are fixed (Fig.4-11).

In 4.1.1 it was shown that the pulse length also affects the U-I plots (see Fig. 4-2). To get deeper insight of this effect the correlation of the current shape and pulse duration is studied. In Fig. 4-12 the dc and rf currents measured at different pulse durations but at fixed duty cycle, voltage (in case of rf discharge – effective voltage) and pressure are presented. First of all it should be emphasized that the current for all pulse durations follows the same trajectory and doesn’t sink as in the case of higher duty cycles in Fig. 4-11.
However the current signal changes with time and long pulses look completely different than short pulses. In general one can see a decrease of the current with the time of the pulse. Therefore in spite of the same duty cycle, longer pulses mean lower average current and very probably also lower sputtering rate and emission intensity.

Fig. 4-13 demonstrates the dependence of the total input current on pulse duration at fixed duty cycle for the dc case. The reduction of this current from the shortest to the longest pulse is around 75 %. This phenomenon, as well as U-I plots measured at different pulse durations (see Fig. 4-2), indicate that the long pulses produce the hottest plasma.
It should be mentioned that the current decreases not gradually within the pulse. In Fig. 4-12 one can see the reproducible oscillations of the current signal. Moreover the oscillations appear for both dc and rf pulses. A very similar phenomenon has already been mentioned by Nelis et al.. Periodical variations of the Cu 224.7 nm light emission with a period of 200 µs and damping after 1 ms have been found. Nelis suggested that the observed oscillations are caused by a variation of the discharge gas particle density due to changes in either pressure or temperature. This explanation can be also valid for the current oscillations observed in this work. The main question is why the pressure or temperature oscillates after discharge ignition? A possible mechanism responsible for the generation of pressure waves is discussed in the paper of Voronov et al.. He investigated the pressure vibrations in pulsed discharge in a Grimm-type source by the direct insertion of a microphone into a discharge chamber. The microphone has recorded the oscillating acoustical signal. It has been proven that this signal is generated by the application of the high voltage to the source and ignition of the discharge at the beginning of the pulse. The frequency of current oscillations has been found to be the same as the acoustical signal frequency.

**Fig. 4-14** Dc (a) and rf (b) current signals within the pulse measured at different voltages (in the rf case - effective voltages) (duty cycle 0.2, pulse duration 1000 µs, frequency 0.2 kHz, pressure 6 hPa); (c) - is zoomed ionic current from the plot (b).
Observation of Voronov et al.\textsuperscript{204} can likely be an explanation of the current oscillations found in this work for both dc and rf discharges. If a sharp voltage rise induces the pressure waves in the discharge chamber, the oscillations should disappear at lower voltages. This supposition is confirmed by the experimental results in \textit{Fig. 4-14}: oscillations, as well as the current peak at the leading age of the pulse, are going down at lower voltages. In the rf case the pressure waves are expected to affect both ionic and electronic current, which is also confirmed by the experiment: electronic and ionic current show symmetrical oscillations (see \textit{Fig. 4-14} (b) and (c)).

In summary, part 4.1.2 covers the electrical features of the PGD which are crucial for both understanding of the discharge processes and analytical applications.

Nearly all phenomena found for the dc discharge also appeared in the rf case. No significant difference between rf and dc pulsed discharges have been found. The current signal shape within the pulse has shown a similar behaviour in the rf and dc modes: (1) growth of a current peak at the beginning of the pulse at higher voltages, (2) sinking of the current level within the pulse when a higher duty cycle is applied and (3) oscillations of the current signal within long (up to 1 ms) pulses. Thereby in terms of the electrical properties the pulsed rf and dc discharges are very similar.

It has been found, that the current signal is not constant during the pulse. Thus the pulse duration is an important parameter. The experimental results have shown that at fixed duty cycle the average discharge current depends on the pulse duration. The shorter is the dc pulse the higher is the average current. Presumably, the sputtering rate and emission intensity are also influenced by the pulse length, in spite of the fixed duty cycle. An important feature of the rf mode is that the rf voltage needs around 50 µs to reach its prescribed value because of the bias formation. So the choice of very short pulses can cause a decrease of the sputtering rate. The detailed investigation of the sputtering rates and the emission intensities of the PGD considering the results of the electrical properties is described in the parts 4.1.4 and 4.1.5.

For both, rf and dc discharges, a decrease of the current caused by a heating of the discharge gas at higher powers has been observed. This effect provoked an
idea of estimation of the discharge gas temperature from the U-I plots of PGD, which is described in the next part (4.1.3.1).

4.1.3 Measurements of the PGD gas temperature

In 2.3.3 it is shown that knowledge of the discharge gas temperature is relevant for the analysis of thermal fragile samples and for the fundamental studies as well. For example the depth resolution and the sputtering rate depend on the temperature of the sample and the discharge gas.\textsuperscript{80,81} Too high temperature can even partly melt\textsuperscript{82} or mechanically destroy the sample. The application of PGD allows reducing the sample heating during the analysis and thereby promotes a good depth resolution. In this part the reduction of the GD gas temperature at application of pulsed discharge is estimated.

4.1.3.1 Voltage-current plots of the PGD as a thermometer for the GD gas

According to the previously made suggestion, the decrease of the current amplitude with the duty cycle is due to the influence of discharge power on the temperature of the gas. When the duty cycle increases the mean power consumption increases too. This leads to a heating of the plasma gas. Under constant pressure according to the thermodynamic law $p=nkT$ an increase of the gas temperature leads to the decrease of Ar atom concentration and therefore of the current. Processes like different secondary electron emission yield at the sample surface caused by temperature changes of the sample or changing concentration of the sputtered material in the plasma are considered as less important.

The phenomenon of the current decrease at high powers gives an approach to the estimation of the discharge gas temperature. The impedance of the plasma depends strongly on the Ar atom concentration. But the concentration at low temperature and low pressure corresponds to the same concentration at certain higher temperatures and higher pressures: $p_{\text{high}}/T_{\text{high}}=p_{\text{low}}/T_{\text{low}}$. In this equation $p_{\text{low}}$ can be assumed to correspond to the discharge gas with the room temperature $T_{\text{low}}$. $p_{\text{high}}$ is the pressure of the hot discharge gas with unknown temperature $T_{\text{high}}$. $p_{\text{high}}$ and $p_{\text{low}}$ are easy measurable. Thus the only unknown value is $T_{\text{high}}$, which is deduced from the: $p_{\text{high}}/T_{\text{high}}=p_{\text{low}}/T_{\text{low}}$. In Fig. 4-15 the temperature estimation principle is
The schematically shown. The U-I plots of the pulsed dc discharge are measured at three different duty cycles and two different pressures. The current represents the average current during one pulse normalised to 100% duty cycle. The plot of the 0.4 duty cycle and 6 hPa pressure corresponds to the higher discharge gas temperatures, which are unknown. The plot of the 0.1 duty cycle and 5 hPa pressure correspond to the cold plasma. The temperature of the discharge gas at low duty cycle can be assumed to be the room temperature (20°C).

The temperature of the GD gas for the pulsed rf discharges is determined according to the described principle. The slopes of the ionic part of the U-I curves are used for the temperature estimation (see Fig. 4-16 (a)). The plots which correspond to the lowest duty cycle 0.01 are assumed to represent the cold plasma at 20°C.

Fig. 4-15 Schematic representation of the temperature estimation from the measured U-I plots of pulsed discharge.

Fig. 4-16 (a) Ionic part of the U-I plots of pulsed rf discharge measured in the last 600 ns of the 50 µs pulse at 700 V effective voltage; (b) the slope of the ionic part of the U-I curves at 0.01 duty cycle plotted versus pressure.
To simplify the determination of $p_{\text{low}}$, the dependence of the U-I slope on pressure at room temperature (0.01 duty cycle) is plotted (see Fig. 4-16(b)). From this plot $p_{\text{low}}$ is determined for each U-I plot at duty cycles higher than 0.01. Further, with known $p_{\text{high}}$, $p_{\text{low}}$ and $T_{\text{low}}$, the temperature $T_{\text{high}}$ is calculated using equation:

$$p_{\text{high}}/T_{\text{high}} = p_{\text{low}}/T_{\text{low}}.$$

In case of pulsed dc discharge the U-I plots are measured for the same pressures and duty cycles as for rf mode (see Fig. 4-17(a)), using method 2 described in 4.1.2.1. However the temperature estimation from the slope of these plots makes no sense because each point of the U-I plots corresponds to a different power and therefore to a different temperature. To remind, the U-I plots of the rf discharge are measured in the last 600 ns of the 50 µs pulse at constant effective voltage (700 V). As already said in part 4.1.2.1, the U–I characteristics measured for rf discharges within the last 600 ns of the pulse show a linear behavior without saturation in the ionic part. This means that during the short time of some rf periods the gas temperature stays constant. Hence the estimation of the discharge gas temperature from the slope of the U-I plots is reliable for the rf discharge, but not for the dc one.

To estimate the discharge gas temperature in case of pulsed dc discharge the same principle as for rf mode is used, but instead of the slope just the current value at 700 V is used. The 700 V voltage is taken for a better comparison of the temperature of the dc and rf modes (the U-I plots of rf mode are measure at 700 V effective voltage). Similarly to the rf mode, the current values (instead of the slope values) measured at 700 V and 0.02 duty cycle are assumed to correspond to the room temperature and plotted versus pressure (see Fig. 4-17(b)). From this plot $p_{\text{low}}$ is determined.

In Fig. 4-18 the temperature values determined from the U-I plots for dc and rf pulsed discharges are plotted versus duty cycle. For both dc and rf mode the temperature increases with increasing duty cycle. However in case of dc discharge the gas is warming up faster with increasing duty cycle, which is most pronounced at 5 hPa. At higher pressures (6 and 7 hPa) the cold Ar flow which enters the discharge chamber may affect the temperature of the discharge gas: the higher is the pressure the colder is the discharge gas (see Fig. 4-18(a)). This phenomenon doesn’t appear
in the rf mode and the pressure has no influence of the temperature (see Fig. 4-18 (b)). The observed difference between dc and rf modes can be caused by two facts: (1) in case of dc mode 200 µs pulses are applied while for the rf case – 50 µs; (2) the dc current is measured and averaged over the whole pulse length while the rf current is acquired at the last 600 ns of the pulse.

![Duty cycle](image.png)

**Fig. 4-17** (a) Voltage - normalized current plots of pulsed dc discharge at 200 µs pulse length measured using method 2, described in 4.1.2.1; (b) the current at 700 V of pulsed dc discharge at 0.02 duty cycle plotted versus pressure.

![Current at 700 V](image.png)

**Fig. 4-18** Temperature of the glow discharge gas determined (a) from the U-I plots of pulsed dc discharge in Fig. 4-17(a); (b) from the U-I plots of pulsed rf discharge in Fig. 4-16(a).
In general it can be concluded that the highest temperature reduction which can be achieved for both dc and rf discharges is around 100 °C (see the difference between 0,01 and 1 duty cycles in Fig. 4-18). Interesting is that the rf plasma starts heating at 0,1 duty cycle and at lower duty cycles the discharge gas temperature doesn’t change, while in dc case the temperature increase can be seen already at 0,05 duty cycle.

The developed temperature estimation procedures are simple and seem to be reliable. The observed temperature effects are similar for dc and rf modes. However it is important to prove the estimated temperature values with another temperature measurement method. Therefore in the next section the temperature of the discharge gas is determined from the rotational spectra of N₂ molecules and compared for pulsed and continuous modes.

4.1.3.2 Determination of the GD temperature from the rotational spectra of nitrogen species

For the estimation of the discharge gas temperature the method described in the introduction is used (see 2.4.2). This temperature estimation method can be used at common commercial spectrometers with normal spectral resolution (e.g. 0,02-0,05 nm). Because commercial spectrometers can only operate in pulsed rf regime, this mode was investigated at the beginning and all experiments in this section are performed only for rf discharge. Temperature measurements for pulsed dc discharges were started and made in cooperation with the London Metropolitan University, but are not yet finished.

For the experiments 2 vol. % of nitrogen are introduced in the discharge gas (Ar). The rotational spectral bands of the nitrogen species are measured with an optical spectrometer. The CCD detection is faster than the monochromator with PMT, therefore the optical spectrometer with CCD detection is applied for the recording of the rotational spectra. However to check the correctness of the spectra acquired with CCD, it is additionally scanned by a monochromator with PMT detection (see Fig. 4-19). The spectra measured with two different spectrometers show a good agreement. Therefore the CCD detection can be used for the further measurements.
In the Fig. 4-20 one can see the rotational spectra of the $\text{N}_2^+$ and $\text{N}_2$ species, which are also called first negative and second positive systems correspondingly. For the identification of the particular spectral lines which is necessary for the Boltzmann plot, the FTS (Fourier transform spectrometry) spectra are used.
Results and discussion

The FT spectrometer provides spectra with high wavelength accuracy and resolution. For example, in the second positive system one can see that each line actually consists of three unresolved lines, which are perfectly resolved in the FTS spectrum (see Fig. 4-20 (b)). In this case the average peak intensities of the unresolved lines are used for the Boltzmann plot.

The FTS spectra are in good agreement with the CCD spectra. This helped to find the spectral lines which correspond to the R-branch of the rotational spectra (the transitions where the change of the total angular momentum is 1 $\Delta J=1$). For the R branch the following equations are valid: $K'=K''+1$ so $S=2*(K''+1)$ and $K'(K'+1)=(K''+1)(K''+2)$. The angular momentum $K''$ is a known value and can be used for the calculations.

For the comparison of the continuous and pulsed discharges the first negative and second positive systems are measured for both modes (see Fig. 4-21). The numbers above the lines are the corresponding $K''$ values.

![Fig. 4-21 (a) Rotational spectrum of second positive system of nitrogen; (b) rotational spectrum of first negative system of nitrogen. The spectra are measured with Spectruma GDA 650 spectrometer with CCD detection using Ar discharge gas with 2 vol. % of nitrogen. Spectra of continuous (1000 V, 2 hPa) and pulsed (1000 V 2 hPa, duty cycle 10 %, pulse length 200 µs, frequency 500 Hz) discharge are compared.](image)

From these measurements the intensities of the lines which belong to the R-branch are determined and used for the Boltzmann plot (see Fig. 4-22). According to the principle described in the introduction the slope of the Boltzmann plot is inversely proportional to the rotational temperature of the nitrogen species (see 2.4.2). The rotational temperature can be assumed to be the discharge gas kinetic temperature when this gas is in local thermodynamic equilibrium (LTE).
Results and discussion

Fig. 4-22 Boltzmann plots for the determination of the nitrogen rotational temperature plotted using spectra from the (a) Fig. 4-21(a) - second positive system and (b) Fig. 4-21(b) - first negative system.

The temperature values calculated from the second positive system strongly exceed the temperatures calculated from the first negative one. The difference is around 1500 °C. Also the absolute temperature values are very unlikely for the gas kinetic temperature.\(^{122}\) Especially at the temperature deduced from the second positive spectra (around 2000 °C) the Cu sample used for the experiments and the GD source itself would melt. The observed temperature difference as well as enormous temperature deduced from the second positive system can have several reasons, e.g. (1) the considered nitrogen species are not in LTE with the discharge gas (see also 2.4.1); (2) the rotational spectra are overlapped with the spectra of other rotational bands. In addition it should be emphasized that in this work the rotational spectra are measured from the front of the discharge. It is known that the gas temperature profile varies in the axial direction. Hence, probably the result will differ if the spectra are measured from the side like it is done by Ohorodnik and Harrison.\(^{149}\) Unfortunately side-on measurements are not possible with a commercial GD spectrometer. There is one more point which should be taken into account: in the works where the discharge gas temperature is determined with the Boltzmann plot method relatively low discharge pressures are used (around 1.3 hPa).\(^{87,149}\) In the current work much higher pressures are applied (6 hPa) to get sufficient emission intensity. At higher pressure the rotation of the nitrogen molecules may be distorted due to the numerous collisions. In this case the calculated rotational temperature may not be equal to the discharge gas temperature.
There is one important result of the rotational temperature measurements. The temperature difference between pulsed and continuous mode calculated from the spectra of second positive system is 78 °C and from the spectra of first negative system – 90 °C. These values are also close to the temperature difference deduced from the U-I plots of the pulsed and continuous discharges - 100 °C (see 4.1.3.1). Hence there are three different temperature estimation procedures (U-I plots, rotational spectra of N\textsubscript{2} and N\textsubscript{2}\textsuperscript{+}) which indicate that the discharge gas temperature can be reduced by around 100 °C when PGD is applied.

However the study of the discharge gas temperature is not completed. More attention should be paid to the absolute value of the discharge gas temperature and at the cathode (sample) temperature as well.

**4.1.4 Study of the sputtered crater formation in the PGD**

The advantages of GD sputtering (see 2.1.2) make GD OES to a suitable and fast method for depth profiling of thin layers.\textsuperscript{48,66,205,206} Mild surface sputtering and fast sampling time of commercial light detection systems should theoretically provide an exceptionally high depth resolution in sub-nanometre level. Nevertheless the real depth resolution of GD OES is limited by the ultimate depth resolution\textsuperscript{56} (some nm\textsuperscript{38,207-209}), formation of a nonplanar sputtered crater\textsuperscript{210-213} and sputter induced roughening of the sample surface.\textsuperscript{82,214,215} Hence to reach the best possible depth resolution (ultimate depth resolution) at GD OES depth profiling it is necessary to optimize the analysis conditions such a way to get a most flat and smooth crater.

Besides the common discharge parameters of the GD – voltage, current and pressure, in the case of PGD there are additional parameters – duty cycle, pulse duration and pulse frequency (see 2.3.1). On the one hand, more discharge parameters enable to control the heating and sputtering rate of the sample with greater precision. But from the other hand it complicates the optimization procedure. As a consequence, one should study the influence of all the PGD parameters on the crater shape and roughness.

For the continuous discharge the influence of voltage, current and pressure on the crater shape and depth resolution is well investigated.\textsuperscript{51,187-195} Also a number of modelling works studied the crater formation and corresponding depth
profiles. But in case of pulsed discharge very few authors consider the PGD parameters. Oxley et al. suppose that pulse width and frequency have little influence on crater shape, but Martin found that the pulse width plays an important role in producing a good crater. The effect of pulsing parameters on the sputtering rate and depth resolution is also studied, but only small pulse length and frequency ranges are examined.

Apparently, PGD is a promising tool for GD OES depth profiling of thermally sensitive and thin layered samples. Nevertheless to find optimal analysis conditions more systematic studies on the relation between discharge parameters and crater formation are necessary. Therefore, in the following sections the influence of all PGD parameters (pulse duration, duty cycle as well as the electrical parameters voltage and current) on the crater formation is studied. Pulsed dc and rf discharges are compared in terms of sputtering rates and crater shapes. The observed changes of the crater shape are reflected in depth profiles measured at different discharge conditions (4.1.4.3).

### 4.1.4.1 Investigation of the sputtering rates

In this part the dependence of the sputtering rates on U, I, duty cycle and pulse length is studied. These PGD parameters are sequentially considered following the principle of varying only one parameter under investigation and keep all others constant. In this way one can correlate the observed effect with a distinct operating parameter.

**Influence of voltage and current on sputtering rate** It has been already mentioned that voltage and current are very often considered and well studied for the continuous discharge. As far back as 1972 Boumans found that the sputtering rate \( q \) linearly depends on voltage and current (equation 2-4). The pressure is defined by the U and I values and implicitly included in the formula. This result of experimental and empirical work represents the dependence of the sputtering rate on voltage and current and is especially used at quantitative GD OES analyses, where standards with different matrix are used for calibration (see 2.2.2). Therefore it is reasonable to check if it is valid also for pulsed discharge. For this one should consider such
Results and discussion

electrical parameters of the pulsed discharge, which can reliably represent the voltage and current values. For pulsed dc discharge the total input current of the pulse generator and the sputtering rates of pure Cu samples are measured at different voltages (see Fig. 4-23). For pulsed rf discharge the rf equivalent of the dc voltage and current are the effective voltage $U_{\text{eff}}$ and the effective current $I_{\text{eff}}$ (see 2.3.2). Therefore for the Boumans plot the effective voltage and power are measured within the pulse. Afterwards, the power value is divided by the effective voltage giving the effective current value. The $I_{\text{eff}}$ is multiplied by the duty cycle to get values equivalent to the total input current of the dc pulse generator (see Fig. 4-23).

![Fig. 4-23 Boumans plots](dependence of the reduced sputtering rate $q$ on voltage) measured for dc and rf discharges (duty cycle 0.2, pulse duration 100 µs, frequency 2 kHz, pressure 6 hPa, Cu sample).

Fig. 4-23 shows that the sputtering rate $q$ divided by the current is linear dependent on the voltage. Thus the Boumans equation, originally deduced for continuous dc discharge, is valid also for both pulsed dc and rf discharges. Nevertheless the dc and rf plots are not congruent. The electrical conditions of dc and rf discharges are the same, but the sputtering rate of the rf discharge is systematically lower. This effect is explained by that fact that dc voltage sharply increase at the beginning of the pulse in less than 1 µs, whereas the rf voltage needs some more time to reach its prescribed value (see 4.1.2.2 Fig. 4-7). In the present work this time is around 50 µs. So in the dc case sputtering starts from the beginning of the pulse, but in the rf case only after 50 µs. Therefore, rf sputtering is observed to be slower than the dc one despite the same pulsing parameters.
Influence of duty cycle on sputtering rate

The influence of duty cycle on the sputtering rate has been previously described by some authors. Nelis\textsuperscript{184} studied the impact of the duty cycle on the sputtered depth and observed different tendencies for Al and Sn/Pb matrixes. The sputtered depth of the low melting alloy Sn/Pb decreased with higher duty cycle while the Al matrix revealed higher sputtering rates at higher duty cycles. Such sputtering rate degradation of Sn/Pb at high duty cycles can be related to the previously discussed discharge gas and sample heating at higher duty cycles. There is a theory that the sputter yield tends to decrease with increasing sample temperature. The explanation is that at surface temperatures approaching the melting point the efficiency of momentum transfer from the bombarding particle to the sample atoms decreases because of lattice relaxation. Hence less atoms get sufficiently large momentum to leave the surface.\textsuperscript{7,81,82} The Sn/Pb alloy has a lower melting point than Al and therefore its sputtering may be greater affected by sample heating.

Wagatsuma observed a non proportional rise of the sputtering rate with increasing duty cycle using a steel sample. In his study the duty cycle was varied with pulse duration at constant frequency.\textsuperscript{79} Because in this work the importance of the pulse duration has been previously discussed and shown (see 4.1.1 and 4.1.2), the study of the duty cycle effect is done at constant pulse length of 500 µs (see Fig. 4-24).

![Crater shapes measured at three different duty cycles for both pulsed dc and rf discharges](image)

\textbf{Fig. 4-24} Crater shapes measured at three different duty cycles for both pulsed dc and rf discharges (pulse duration 500 µs, voltage 800 V, pressure 6 hPa). Dc measurements are made with Cu and rf – with Si.
In Fig. 4-24 the crater shapes measured at three different duty cycles are shown. All craters are sputtered the same time. It is found that at higher duty cycles the craters are deeper, therefore for a better comparison the crater depths in the Fig. 4-24 are multiplied by factors. These factors are the same with the ratio of the corresponding duty cycles. Thus it can be concluded that the sputtering rate is proportional to the duty cycle for both dc and rf pulsed discharges and Cu and Si matrixes.

**Influence of pulse duration on sputtering rate** The influence of the pulse length on the sputtering rate is studied. For this comparison the sputtering rates of continuous dc and rf discharges are also measured and multiplied by the duty cycle used for pulsing.

![Graph showing sputtering rate vs pulse length for both Cu and Si samples](image)

**Fig. 4-25** Dependence of sputtering rate on the duty cycle measured for (a) dc and (b) rf discharge for both Cu and Si samples (duty cycle 0.05, pressure 6 hPa).
In the *Fig. 4-25* (a) for the case of dc discharge one can see the increase of the sputtering rate in the short pulse region. This increase is more pronounced at 1200V. Such behaviour correlates well with the observed high current peak at the beginning of the pulse, which is more pronounced at high voltages. The shorter is the pulse the greater is the impact of the current peak into the average current value within the pulse. Therefore high average currents (see *Fig. 4-13*) and thus faster sputtering are characteristic for the short dc pulses.

In contrast to the dc mode in rf case the sputtering rate strongly falls when short pulses are applied. At 10 and 20 µs nearly no sputtering occurred and therefore the corresponding points are missing in the plot (see *Fig. 4-25* (b)). The high current peak at the beginning of the pulse, which boosts the dc sputtering at short pulses, is also found in the rf pulse (*Fig. 4-10*). Nevertheless the main reason of the sputtering rate fall at short pulses is that the rf voltage needs about 50 µs to reach its prescribed value (see *Fig. 4-7*).

For both dc and rf pulsed discharges the sputtering rate of Cu is higher than that of Si. Important is that the sputtering rates of both Cu and Si for dc and rf discharges are nearly identical at pulse lengths greater than 200 µs. So it can be concluded that with the exception of the effects at the beginning of the pulse (10-200 µs), the dc and rf discharges are the same in terms of sputtering rates.

### 4.1.4.2 Investigation of the sputtered crater shapes

In this part the influence of voltage, current, duty cycle and pulse duration on crater shapes is studied. As in the previous paragraph, parameters of the PGD are sequentially considered.

**Influence of voltage and current on crater shapes** The dependence of the crater shapes on voltages and current is also well known for continuous mode. The rise of voltage or current causes a typical change of the sputtered crater curvature from concave to convex. In this work an identical behaviour is found also for the pulsed dc discharge (see *Fig. 4-26*). The craters in a Cu sample are sputtered at different voltages and total input currents, but at constant pulse parameters and changing pressures. In *Fig. 4-26* the depth of all craters is normalized to the maximum and
Results and discussion

minimum depth values of each crater. As in continuous mode the crater shape changes from convex to concave, when voltage or current increase, being almost flat at 1000 V and 5 mA. Surprisingly, a high voltage (1200 V) and high current (10 mA) also cause a nearly flat crater. Nevertheless the high power conditions are not optimal for depth profiling because of the high sputtering rate and sample heating.

![Graph showing crater shapes measured at different voltages and total input currents](image)

**Fig. 4-26** Sputtered crater shapes measured at different voltages and total input currents of the dc generator (duty cycle 0.2, pulse length 200 µs, frequency 2 kHz). Black curves – Cu, red curves – Al.

There are numerous theories explaining the often observed crater behaviour. It is reported that the GD constriction by the anode tube plays an important role at the crater formation. The reason is that the potential distribution and particle density differs in the regions close to the anode tube and in the middle of the crater. At defined electrical conditions this provokes uneven sputtering over the sample surface. The assumption about the potential distribution can be an explanation of the observation that the anode geometry has a strong impact on the sputtered crater formation. Some authors suppose that pressure is the crucial parameter for the crater shape, because it determines such an important plasma parameter as the
particles mean free path.\textsuperscript{188,189} Because the pressure variation is directly related to the current change, it is difficult to conclude whether the observed effect is caused by pressure or current. Therefore, Rose\textsuperscript{195} measured the crater shapes using different discharge gases. Changing the discharge gas one can achieve different pressures keeping the electrical parameters constant. Indeed the crater shapes were observed to be different for different discharge gases. This effect was also mentioned in the work of Hartenstein et al..\textsuperscript{220} Nevertheless the result obtained in the present work argues against the hypothesis of high pressure impact. One more way to change the pressure keeping the electrical parameters constant is to vary the sample, for example Cu and Al. Al has a higher secondary electron emission coefficient than Cu. Therefore the resistance of the discharge is lower when operated with an Al sample. Thus at the same voltage and current for Al the pressure is lower than that for Cu. In this way the influence of pressure can be seen. So the crater matrix presented in Fig. 4-26 is measured also for an Al sample. Despite a different pressure, no significant difference between Cu and Al matrix can be seen. This result indicates that the pressure change of ca. 2 hPa has no influence on the crater shape.

**Influence of duty cycle and pulse duration on crater shapes** Fig. 4-24 demonstrates that the duty cycle has no influence on the crater shape, if the pulse length is kept constant. The duty cycle defines the power introduced into the discharge and therefore it is responsible for both, sputtering rate and heat. Bogaerts et al. suppose that the crater profile is not affected by the discharge gas temperature, because the computational studies have shown that the discharge gas temperature profile varies mainly in the axial direction.\textsuperscript{45,122}

However, the duty cycle has no influence on the crater form only when the pulse duration is constant. In the Fig. 4-27 the shapes of the craters sputtered with pulsed dc discharge at three different duty cycles (0.05, 0.2 and 0.4) and various pulse durations (10-1000 µs) are presented. For the comparison the craters of the continuous discharge are also measured. All the craters of pulsed mode are sputtered the same time. The craters of the continuous mode are sputtered within the time which is equivalent to the corresponding duty cycle. For example for the duty
cycle 0.05 the sputtering time is 20 minutes, thus for the continuous mode the sputtering time should be 20 minutes × 0.05 duty cycle = 1 minute.

![Fig. 4-27 Shapes of craters sputtered with pulsed dc discharge at three different duty cycles (0.05, 0.2 and 0.4) and various pulse durations (10-1000 µs) (800 V 7 hPa). Orange craters are from the Cu sample, grey – from the Si.](image)

The rows in the Fig. 4-27 correspond to the different duty cycles, the columns – to the pulse durations. In each row the y-axis scale is the crater depth. This scale is the same for different pulse durations within the row (but different for Cu and Si). So, one can compare not only the crater shape but the crater depth when the pulse duration is changed. The depth scale for different duty cycles is different, but it is not important here because the dependence of the sputtering rate on the duty cycle has already been discussed in the previous section (see 4.1.4.1). It is observed that the pulse length is a crucial parameter for the crater formation: for both Cu and Si sample the crater shape changes from convex to concave with increasing of the pulse length, being nearly flat at 200 µs (see Fig. 4-27). It is important to emphasize that the longer the pulse the closer the crater shape to that of the continuous mode. Finally at 1000 µs pulse the crater shape is the same as in continuous mode. This observation is in agreement with the previously discussed effect that application of pulses longer than 1 ms causes a discharge gas heating close to that of the continuous discharge (see 4.1.1).

From the Fig. 4-27 it can be also seen that the applied frequency and duty cycle are not affecting the sputtered crater shape. Therefore in the next figures only one duty cycle (0.05) is considered and frequencies are not shown.
In the Fig. 4-28 one can see the shapes of the craters sputtered with pulsed dc discharge at 0.05 duty cycle, 800 V voltage and different pulse lengths. The crater depth doesn’t change dramatically when the pulse duration is changed.

Nevertheless at higher voltage (1200 V) the crater depth decreases with pulse length (see Fig. 4-29). This is in agreement with the sputtering rate studies for the pulsed dc case: at high voltage the sputtering rates are greater when short pulses are applied (see Fig. 4-25 (a)). In addition at higher voltage the impact of the voltage on the crater shape (see Fig. 4-26) predominates over the pulse duration impact. Therefore all craters in Fig. 4-29 are convex.

The crater shapes observed for the pulsed rf discharge behave similar to the dc case: at constant duty cycle (0.05) they change from convex to concave with increasing pulse length (see Fig. 4-30).
This result is in agreement with the work of Präßler et al.\textsuperscript{113} who concluded that the intensity-time profiles, the shape of the sputtering craters and the resulting depth resolution are very similar for dc and rf modes. However the crater depth shows the opposite of the dc discharge behavior. At 10 and 20 $\mu$s the sputtering was so slow that it was impossible to get measurable crater. Sputtering rate measurements have shown the same effect (see Fig. 4-25 (b)). Hence in the rf case the application of short pulses dramatically suppresses the sputtering. The minimal pulse length which provides appropriate sputtering depends on the applied experimental setup and should be established for each system individually. In the present work this threshold pulse length value, or the time of the rf voltage bias formation (see Fig. 4-7), is 50 $\mu$s.

In this part the crater shape effects which are important for the optimization of the GD OES depth profiling with PGD are shown. Analogous to the sputtering rate studies (4.1.4.1), it can be concluded that dc and rf pulsed discharges are similar in terms of sputtered crater shapes, except the effects at the beginning of the pulse.

**4.1.4.3 Correlation of the observed crater formation effects with the GD OES depth profiles**

The effects described in the previous part are essential for the GD OES depth profiling with application of pulsed discharge. Therefore in this part the observed sputtering rate and crater shape behaviour is correlated with the GD OES depth profiles of layered sample. To be sure that the profile behaviour is subjected to the pulsing parameters and caused not by sample inhomogeneity, it is important to consider a sample, containing flat and reproducible layers. Hence in the present work for the systematic study CrNi/Cu (9*100nm/8*100nm) periodic multilayer samples on a Si substrate are used. Such layered systems, which are known from electronic applications,\textsuperscript{221} are characterized by reproducible, well defined metal/metal interfaces and thus are suitable for the depth profile studies.\textsuperscript{65,66,222,223} They can be effectively used even for the accurate depth calibration.\textsuperscript{224}

For depth profiling with pulsed discharge the rf mode is mostly used. Rf discharge allows measuring insulators, but is also widely applied for the analysis of conductive samples,\textsuperscript{83,225,226} because it is less affected by nonconductive inclusions or surface oxides. Moreover, there is no commercial instrument with a dc pulser
existing but most rf generators are able to run in pulsed mode. Thus the depth profile studies in the current work are done with pulsed rf discharge.

The multilayered samples are measured several times at different pulsing conditions (the electrical conditions are immutable 500 V and 3.5 hPa): at various duty cycles and constant pulse length (Fig. 4-31) and at various pulse length and constant duty cycle (Fig. 4-32). Fig. 4-31 demonstrates three depth profiles measured at 0.05, 0.2 and 0.4 duty cycles.

![Fig. 4-31](image)

**Fig. 4-31** Rf GD OES depth profiles of a CrNi/Cu (9*100nm/8*100nm) periodic multilayer sample on a Si substrate measured at three different duty cycles – 0.05, 0.2 and 0.4 (pulse duration 200 µs, voltage 500 V, pressure 3.5 hPa).

Besides the well known degradation of depth resolution with depth, one can see that the sputtering time of the layers decreases proportionally to the duty cycle. This behaviour correlates with the previously described sputtering rate studies (see 4.1.4.1).

The depth profiles measured with three different pulse lengths at constant duty cycle are depicted in Fig. 4-32.

![Fig. 4-32](image)

**Fig. 4-32** Rf GD OES depth profiles of a CrNi/Cu (9*100nm/8*100nm) periodic multilayer sample on a Si substrate measured at three different pulse durations – 50, 200 and 1000 µs (duty cycle 0.4, voltage 500 V, pressure 3.5 hPa).
In this case the sputtering time changes as well - the application of short pulse length strongly retards the sputtering processes. As the profiles were measured with rf discharge, such sputtering degradation is attributed to the slow bias voltage setting at the beginning of the pulse (see Fig. 4-7) and is in agreement with sputtering rate and crater studies. It should be mentioned here that a different pulse length in the Fig. 4-32 causes not only a sputtering rate variation but also a significant change of the depth profile shape. Therefore it is worthwhile to check how the depth resolution is affected by the pulsing parameters.

There are several approaches of defining the depth resolution. The most common one is: the depth resolution is a depth interval where the intensity of the measured profile drops from 84 % to 16 % of the maximum. From this definition it is clear that the slope of the intensity change at the interface is directly connected with the depth resolution: a steeper slope means a better resolution and a flatter crater. Therefore to evaluate the influence of pulsing parameters on the multilayer depth profiles the slopes of Cr and Si signals at the interface multilayer/substrate are considered (see Fig. 4-33).

The original Cr and Si signal intensities are normalized to 1. The sputtering times of different profiles are normalized as well such to bring the beginning of Si signal growth to one point. Thereby the evaluated depth profiles indicate that the duty cycle
Results and discussion

has no influence on the depth resolution, because the Cr and Si signal slopes in Fig. 4-33 (a) are identical. Also the calculated relative depth resolution of the Cr profiles is not strongly changed with duty cycle (the relative depth resolution is calculated using the inverse maximum slope method\textsuperscript{38}). This is in agreement with the previous founding that the duty cycle has no influence on the crater shape (see Fig. 4-24).

In contrast to the duty cycle, the pulse length evidently affects the slopes of Cr and Si signals and consequently the relative depth resolution (see Fig. 4-33 (b)). The smallest slope and thus the worst depth resolution correspond to the 50 µs pulse. At this pulse duration the sputtered crater is observed to be convex (see Fig. 4-30). At 200, 400 and 1000 µs the slopes are steeper which is again in agreement with the crater shape behavior in Fig. 4-30: with increasing pulse duration the craters are getting flatter. The emission signals measured at 400 µs, 1000 µs and with continuous mode are congruent probably because there is no significant difference in the corresponding crater shapes (see Fig. 4-30). On the other hand, the relative depth resolution of the continuous mode is slightly better than that of pulsed mode (see Fig. 4-33 (b) 6% versus 7 %).

![Optimised GD OES depth profiles of CrNi/Cu (9*100nm/8*100nm) periodic multilayer sample on a Si substrate measured (a) with continuous rf discharge (500 V, 3,5 hPa) and (b) pulsed rf discharge (duty cycle 0,4, pulse duration 400 µs, 500 V, 3,5 hPa).](image)

However the pulsed discharge is found to be optimal for the analysis of CrNi/Cu multilayer samples at optimal discharge conditions: duty cycle 0,4, pulse duration 400 µs, 500 V, 3,5 hPa (see Fig. 4-34 (b)). The application of pulsed discharge gives
an opportunity to reduce the sputtering rate and thus to get more data points for each layer. In addition the profile measured with mild pulsed discharge is not strongly affected by the plasma ignition at the beginning of measurement. The profile measured with continuous discharge has an artificial emission peak at the beginning of the profile due to the plasma ignition (Fig. 4-34 (a)).

In this part the depth profile behavior at different pulsing parameters is explained by the crater formation effects described in the 4.1.4.1 and 4.1.4.2. Such knowledge and connection between the pulsing parameters and depth profiles is helpful for the optimization of the GD OES depth profiling.

4.1.4.4 Sputter-induced surface topography formation

It is well known that the depth resolution of GD OES depth profiling depends not only on the shape of the sputtered crater, but also on its roughness. The roughness of the crater can be caused by different sputtering rates of structural components present in the sample matrix. The surface changes induced by the ion bombardment attracted the attention of scientists already several tens of years ago. Formation of the fanciful structures on the surface which was exposed to the ion beam provoked a number of studies and attempts to explain and systematize the observed effects. Boris Navinsek summarized in his review paper the results of the recent investigations on this topic. He described the observed surface changes induced by the ion bombardment on various materials using ions with energies from 500 eV to a few tens of keV. Around hundred articles which deal with sputtering effects were cited. It was shown that different groups working with ion beam observed similar surface changes. The comparison of the sputtering conditions used by these groups allowed to classify and sometimes to explain the topographical changes of the surface.\textsuperscript{227}

GD is a sputtering tool which opposed to the other techniques provides softer (because of the low energy of bombarding ions) and homogeneous (because of the random bombarding ions incidence) sputtering (see 2.1.2). There are very few publications where the surface modification due to the GD sputtering is considered.\textsuperscript{214,215} Nevertheless the sputter-induced effects found for the GD are very similar to those observed with other, more energetic, ion sources. For example
Dessenne et al. mentioned the formation of cones on the surface of a sputtered Al alloy sample. A similar effect is described by several authors who studied the ion beam sputtering with energies in the keV region. Thus also in case of GD more attention should be paid to the sputter-induced surface topography formation.

The reason why in the present work the surface topography is considered is that particular depth profiles don’t correlate with the previously discussed sputtered crater effects. In Fig. 4-35 there are depth profiles of SAW (a) and solar cell (b) samples. Both samples are measured at two different duty cycles. For a better comparison the time scale of the profiles is normalized to the duty cycle and the intensity is normalized to 1. Hence the normalized profiles measured at different duty cycles should be congruent (because according to the previous observations the sputtering time is inversely proportional to the duty cycle).

While the depth profiles of the SAW sample are indeed congruent, the depth profiles of the solar cell sample show another behaviour. In case of the solar cell sample measured at two duty cycles not only the sputtering time, but also the shape of the Cu profile differs. This contradicts the results about the sputtering rates and sputtered crater shapes. In sections 4.1.4.1 and 4.1.4.3 it is shown that the sputtering rate decreases proportionally with increasing duty cycle. It is also found that the duty cycle has no influence on the crater shape; therefore the duty cycle should not influence the shape of the depth profiles. Thus the behaviour of the depth profiles of the solar cell samples in Fig. 4-35 (b) cannot be explained by the crater shape.
results and discussion

Another possible reason of the observed effect is the crater roughness which can differ when various duty cycles are applied. To verify this suggestion the solar cell sample is sputtered using three different duty cycles. The sputtering time is set such to remove the half of the CIGSe layer. The images of the sputtered craters are acquired at a SEM microscope. In Fig. 4-36 one can see the images of the non sputtered CIGSe surface and of the crater bottoms sputtered in the CIGSe layer at 7, 20 and 40% duty cycle.

From Fig. 4-36 it can be seen that sputtering in the GD causes a formation of cones on the surface of the CIGSe layer. The density of the cones depends on the duty cycle: the higher the duty cycle, the denser the cones.
For a better comparison of the cones the surfaces in Fig. 4-36 are cut by a focused ion beam (FIB) (see Fig. 4-37). The FIB-cuts confirm that at higher duty cycles the cones are closer. Also the height of the cones is greater. Hence it can be concluded that the overall sputtered crater roughness increases when high duty cycles are applied. This phenomenon explains the change of the shape of the Cu depth profile in Fig. 4-35 (b) at 20 % duty cycle. Sputter-induced crater roughness strongly affects the depth profile.

**Fig. 4-37** SEM images (Crossbeam 1540 XB, Zeiss, 5 kV) of the FIB-cuts (FIB Crossbeam 1540 XB, Zeiss, sputtered with Ga⁺ ions 50-500 pA) of the (a) not sputtered CIGSe surface (b) surface sputtered at 7 % duty cycle (Spectruma GDA 650, 500 V 3,5 hPa, frequency 350 Hz, pulse length 200 µs, sputtering time 150 s), (c) 20 % duty cycle (1000 Hz, 75 s), (d) 40 % duty cycle (2000 Hz, 13 s). Scale is 1 µm. The sputtering time is set such to remove the half of the CIGSe layer.

In addition in Fig. 4-35 can be seen that the sputtering rate at 20 % duty cycle is much slower than it should be (it should decrease proportional to the duty cycle). This effect can be explained by a heating of the sample surface when a high duty cycle is applied: when the sputtered surface is heated, the sputtering rate decreases.
According to the “theory of momentum” the transfer of momentum from the particle bombarding the surface is similar to a billiards push. If a surface atom achieves a sufficiently large momentum, it will be removed from the atomic bond. The efficiency of the momentum transfer and thus the sputtering yield decrease when the temperature increases.\textsuperscript{81,82}

To get deeper insight into the mechanism of the cone formation, an EDX scan across one of the cones is made. Apparently the cones contain an excess of Cu (see Fig. 4-38). EDX measurements made on the lamella which is cut from the crater sputtered at 40 % duty cycle showed that the element distribution in the cones is not uniform (see Fig. 4-39).

From Fig. 4-39 one can see that the elemental composition on top of the cone differs from that in its foot. In particular the top of the cone (point 2 in Fig. 4-39) consists mainly of Cu and Ga and nearly no Se and In are found. In contrast to the cone top the foot of the cone (point 1 in Fig. 4-39) contains also Se and In but less Ga. The EDX scan along the neighboring cone (arrow 3 in Fig. 4-39) confirms the observations: on the top only Ga and Cu are found and deeper in the cone Se and In appear, while the Cu and Ga content sharply decay. The high Ga content on the top of the cone very probably comes from the FIB cut preparation procedure: for the
imaging of the sample during the FIB exposure Ga⁺ ions are used. Therefore the sample surface around the FIB cut is covered by a thin Ga layer.

Summarizing, the EDX and SEM measurements indicate that there are some inclusions in the CIGSe layer which consist mainly of Cu and are sputtered slower than the surrounding material. This way the cones are formed. In Fig. 4-36 and Fig. 4-37 one can see that the number and the size of the inclusions (cones) depend on the sputtering conditions. Therefore it is obvious that the inclusions appear due to the sputtering procedure.

One of the possible mechanisms of the cones formation is the diffusion of Cu on the sputtered surface due to the energy impact caused by sputtering. The higher the duty cycle, the greater the energy impact into the sputtered surface and thus more Cu agglomerates are formed. This explains why at 20 and 40 % duty cycles the cone density on the sputtered surface strongly increased in comparison to 7 % (see Fig. 4-36).

Fig. 4-39 TEM image of the lamella which is cut from the solar cell sample sputtered at 40 % duty cycle (see Fig. 4-37 (d)) and zoomed STEM image of the same lamella. The EDX measurements are done at the points 1 and 2. The EDX-scan is done along arrow 3.
Results and discussion

In contrast to the solar cell sample in case of the SAW sample the structure of the sputtered surface doesn't vary at different duty cycles. In Fig. 4-40 it is seen that the SEM images of the SAW sample surfaces sputtered at 10 and 30 % duty cycles are nearly identical. Therefore also the normalized depth profiles of this sample measured at two different duty cycles are congruent.

![Fig. 4-40 SEM (Crossbeam 1540 XB, Zeiss, 5 kV) images of the (a) not sputtered SAW sample (Al10nm/Cu100nm/Al10nm/Ti5nm/LiNbO$_3$ substrate) surface, (b) surface sputtered at 10 % duty cycle (Spectruma GDA 750, 700 V, 2.5 hPa, frequency 3700 Hz, pulse length 27 µs, sputtering time 3 s), (c) at 30 % duty cycle (frequency 9950 Hz, pulse length 30 µs, sputtering time 10 s). The sputtering time is set such to remove around half of the Cu layer.]

4.1.5 Light emission and spectra of the PGD

Besides the electrical properties, sputtering features and temperature of the discharge gas, the light emission of the PGD is crucial for the analytical applications. Light emission of the PGD attracted great attention of scientists and provoked numerous studies.\textsuperscript{92-94,101,184,199,200,228,229} The majority of the works are undertaken on the spatial and temporal behavior of the characteristic emission lines within the pulse. These studies provide essential information about the plasma processes and chemistry.

The time resolved measurements may be useful for the analytical applications as well. It is known that during the pulse there are regions with different excitation and ionization mechanisms.\textsuperscript{230} By recording of the emission at a certain time of the pulse one can either suppress or intensify the signal of the plasma species. For example, it is found that the signal-to-background ratio is improved with application of time-gated detection.\textsuperscript{101} Another advantageous feature of the gated detection is the
Results and discussion

reduced curvature of the calibration curves when the emission signal only at the beginning of the pulse is acquired and used as analytical signal.\textsuperscript{84,184,229} This phenomenon is explained by the reduced reabsorption of the emitted light during the first microseconds of the discharge when the sputtered material is not yet completely diffused.\textsuperscript{101} Hence the time-gated detection in GD OES devices is proved to be useful. However it adds complexity, and cost to the instrumentation and thereby is not implemented at the commercial scale till nowadays.

In the works which deal with gated emission only some defined, mostly atomic emission lines are considered.\textsuperscript{92-94,228,229} There is no systematic investigation of the correlation between the pulsing parameters and the spectrum of the PGD. Therefore in the present work the influence of the duty cycle and pulse duration on the spectra of both dc and rf pulsed discharges is studied by means of a commercial GD OES spectrometer with CCD detection.

At this point two types of light detection should be briefly compared – PMT (Photomultiplier tube) and CCD (Charge-coupled Device). The spectrometers applied in the present studies measure the emission signal with PMT detectors every 500 µs or acquire the overall emission every 10 ms (min.) with CCD arrays. On the one hand the PMT detection is faster and necessary for the analysis of thin layers (10 nm and less as in SAW samples). But on the other hand PMTs measure at some moments irrespective to that if they are within the pulse or between the pulses. Therefore PMT signals may contain measurement artifacts like in Fig. 4-41. In contrast to the PMT, the CCD signal in Fig. 4-41 is immutable, because the CCD detector averages the emission signal over the pulses. Furthermore CCDs are able to record the continuous spectrum simultaneously. In Fig. 4-41 the depth profile of a solar cell sample (Cu(In,Ga)Se\textsubscript{2}/Mo) measured in the 100-700 nm spectral range is shown. So in the present studies the CCD detection is used for the investigation of the emission spectra and the PMT is applied for fast time resolved measurements.
Results and discussion

Spectra measured at different duty cycles (0,1, 0,2 and 0,4) but the same pulse duration of 200 µs have shown that the emission intensity of all lines increases proportionally to the duty cycle (see Fig. 4-42). This is valid for both dc and rf pulsed discharges. In Fig. 4-42 the emission lines of Cu atoms (CuI 324,754 nm) and Ar ions (ArII 434,806) measured at different duty cycles in pulsed dc ((a) and (b)) and rf ((c) and (d)) modes are presented. It is seen that the emission intensities in the dc and rf mode are nearly identical.

In Fig. 4-42 one more attention worthy effect can be seen: the intensity of atomic Cu line measured at continuous discharge is less than it should be relative to the pulsed mode (see Fig. 4-42 (a) and (c)). In the case of the ionic Ar line this effect is not so pronounced, however the intensity at continuous mode is only 2 times higher (instead of 2,5) than that at 0,4 duty cycle.
Results and discussion

To examine the influence of the pulse length on the light emission of PGD emission spectra are measured at different pulse durations (20-1000 µs) but at constant duty cycle of 0.2. These measurements have shown that even at constant duty cycle, which is responsible for the power introduced into the discharge source, the pulse duration significantly affects the emission intensity. Furthermore this influence differs for various emission lines. Detailed examination of the spectra revealed that in case of pulsed dc discharge the intensity of atomic lines rises with decrease of the pulse length (see Fig. 4-43). The important feature is that at a pulse length of 20 µs the emission intensity of the pulsed dc discharge reaches the same intensity level as the continuous discharge (see Fig. 4-43 (a) and (c)). In contrast to the atomic emission lines, the intensity of ionic lines of pulsed dc discharge is weaker than that of continuous mode and approximately proportional to the duty cycle (see Fig. 4-43 (b))
Results and discussion

and (d)). The pulse length doesn’t have significant influence on the emission intensity of the ionic emission lines (see Fig. 4-43) (b) and (d)).

![Fig. 4-43 Characteristic emission lines of (a) atomic Cu, (b) ionic Cu, (c) atomic Ar, (d) ionic Ar measured at different pulse durations but the same duty cycle of 0,2 with pulsed dc discharge.](image)

The phenomena observed for the pulsed dc mode are found also in case of the pulsed rf mode (see Fig. 4-44). The line intensities of pulsed rf and dc discharges are similar as well. The only difference between dc and rf discharges is that in case of the rf mode the emission intensity is strongly suppressed when short pulses (20 or 50 µs) are applied (see Fig. 4-44). This effect is partly explained by the previously discussed bias formation procedure at the beginning of the pulse (see part 4.1.2.2). The rf voltage needs around 50 µs after the pulse ignition to reach its prescribed value. Therefore the light emission as well as the sputtering rate is found to be reduced when pulses shorter than 50 µs are applied.
Results and discussion

To understand the different behavior of the atomic and ionic spectral lines fast time resolved measurements of the emission within the pulse are undertaken using a PMT detector. For this experiment two atomic (CuI 324,754 nm and ArI 415,859 nm) and two ionic (CuII 224,700 nm and ArII 434,806 nm) spectral lines are selected (Fig. 4-45). It is found that for both pulsed dc and rf modes the atomic lines show a strong enhanced emission intensity in the first 50 µs of the pulse (see Fig. 4-45 (a) and (b)), whereas the ionic lines have only a small emission peak at the beginning of the pulse (see Fig. 4-45 (c) and (d)), which is most probably caused by the acoustical waves generation. The intensified emission of atomic lines when short pulses are applied is already mentioned in the literature. On the other hand in case of rf discharge the observed emission peak of the atomic lines at the beginning of the pulse (see Fig. 4-45 (a) and (b)) is in contradiction with Fig. 4-44 (a) and (c) where those line intensities are strongly reduced when short pulses are applied.
It must be mentioned that time resolved intensity measurements were done only for 1000 µs long pulses and 0.2 duty cycle. Therefore changes of the intensity as function of time are possible and must be expected, if other pulse lengths and duty cycles are used. Furthermore, for the measurements the upper limit of the current amplifier bandwidth (1 MHz @ 1 mA/V, see 3.3) is applied. This means that there may be e.g. a light emission in the first µs, which cannot be resolved with the used equipment. Last but not least there are small differences between the instrumentation used for the time resolved PMT and the CCD measurements (e.g. another but very similar rf generator).

It can be concluded that in case of pulsed dc discharge the emission intensity of ions is not much influenced by the pulse duration. In contrast, the emission intensity of the atomic lines is higher at short pulses due to the observed emission prepeak. This
Results and discussion

Prepeak can be caused either by the sharp current rise at the beginning of the pulse (see 4.1.2.2) or by the reduced selfabsorption and was only observed at atomic lines.\textsuperscript{84,184,229} In case of pulsed rf discharge the same tendencies are found. However, the emission intensity at 20 and 50 µs pulses is strongly suppressed for atoms and ions.

Within the studies of the time resolved light emission during the pulse the high emission peak after the pulse termination (afterglow) is found for some lines (e.g. \textsuperscript{228}). The reason of the afterglow and its dependence on the discharge parameters is fairly complex and could be a topic of another dissertation.\textsuperscript{228} Therefore the afterglow is not considered in this work.

The effects observed in this part should be taken into account at the GD OES analysis with application of pulsed discharge. It is important to know that not only the duty cycle, but also the pulse duration influences the emission intensity. Moreover this influence is different for the atomic and ionic emission lines. This is confirmed at the comparison of atomic and ionic lines of other elements (e.g. Al I \textsuperscript{396,152}nm and Al II \textsuperscript{167,079}nm, Fe I \textsuperscript{371,994} and Fe II \textsuperscript{238,204}).

4.1.6 Quantification of the GD OES depth profiles measured with PGD

The application of pulsed GD in commercial spectrometers for the quantitative analysis has some limitations, because existing quantification principles are established for continuous discharge. In the previous chapters it is shown that in order to optimize the measurement with pulsed GD, not only the optimal voltage and current have to be found (as in the case of continuous discharge), but also a suitable duty cycle, pulse duration and frequency. It is not clear how these three extra parameters fit into the existing quantification model. Furthermore, usually heat-sensitive samples are insulators or semiconductors; therefore the application of rf PGD is necessary. In the case of rf discharge it is difficult to measure and control the electrical parameters of the discharge, although this is crucial for the quantification. Because of the complications mentioned above, PGD is applied in modern commercial devices mostly for qualitative analysis.

Before quantification it is essential to optimise the qualitative analysis, i.e. to find such sputtering conditions at which the measured depth profile reliably
Results and discussion

represents the real element distribution in the sample. The solar cell samples are thermally sensitive due to the glass substrate; the SAW samples contain very thin layers in nm range. Therefore the main criteria which are important for a successful depth profiling of these samples are: flat sputtered crater, minimal thermal stress and moderate sputtering rates. Taking into account these criteria and the observed influence of the PGD parameters on the crater shapes, sputtering rates, plasma heating and surface topography, the optimal analysis conditions are found. In Fig. 4-46 one can see the optimised GD OES depth profiles of solar cell and SAW samples.

![Fig. 4-46 Rf GD OES depth profile of the (a) solar cell sample (Spectruma GDA 650, CCD detection, 500 V, 3.5 hPa, pulse length 200 µs, frequency 350 Hz, duty cycle 0.07) and (b) SAW sample (Spectruma GDA 750, PMT detection, 700 V, 2.5 hPa, pulse length 200 µs, frequency 500 Hz, duty cycle 0.1).](image)

In the following sections the quantitative GD OES analysis of the solar cell and SAW samples measured with pulsed GD is presented. The validity of both quantification algorithms, described in the introduction, is checked for pulsed rf discharge.

As the pulsing parameters (duty cycle, pulse length and frequency) are found to have a strong influence on the crater shapes, sputtering rates, plasma heating and surface topography, for quantification they are not changed.

Regarding the electrical parameters of the PGD - the significance of the GD voltage and current for the quantitative GD OES analysis is already mentioned in the introduction. It is important to keep these parameters constant while measuring standard and unknown samples, because according to the Boumans law the
sputtering rate depends on voltage and current. It is found that Boumans law is valid not only for continuous but also for pulsed glow discharge (dc and rf modes see 4.1.4.1). In addition the emission yield is strongly affected by the electrical conditions of the GD plasma. Therefore in the present work voltage and current are kept constant, where possible.

4.1.6.1 Matrix specific calibration – solar cell samples

Quantitative depth profiling of the Cu(In,Ga)Se$_2$ layers on the Mo layer and glass substrate is done using a set of solar cell samples with different Ga/(Ga+In) concentration ratio (see Table 4-1). The ratio of the Ga and (Ga+In) contents in the samples is determined by XRF measurements. The CuInSe$_2$ and CuGaSe$_2$ samples have no element gradients in the absorber layer. In addition the density and the thickness of these layers are known. Hence CuInSe$_2$ and CuGaSe$_2$ samples can be used as standards for the quantification of the other samples in the Table 4-1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ga/(Ga+In) XRF</th>
<th>Cu m %</th>
<th>In m %</th>
<th>Ga m %</th>
<th>Se m %</th>
<th>Thickness μm</th>
<th>Density g/cm$^3$</th>
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<tr>
<td>CuInSe$_2$</td>
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<td>17.2</td>
<td>36.4</td>
<td>46.4</td>
<td>2.05</td>
<td>5.803</td>
<td></td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu(In,Ga)Se$_2$</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu(In,Ga)Se$_2$</td>
<td>0.76</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<td>CuGaSe$_2$</td>
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<td>20</td>
<td>24.8</td>
<td>55.2</td>
<td>1.89</td>
<td>5.613</td>
<td></td>
</tr>
</tbody>
</table>

*Table 4-1 The list of the solar cell samples containing CIGSe layers with different concentration ratios - Ga/(Ga+In) on the 0.5 μm Mo layer and soda-lime glass substrate.*

First of all the depth profiles of two standard samples are measured using the optimal analytical conditions – CCD detection, 500 V, 3.5 hPa, pulse length 200 μs, frequency 350 Hz, duty cycle 7% (see Fig. 4-47).
Results and discussion

Fig. 4-47 GD OES depth profile of the (a) CuInSe$_2$ standard sample and (b) CuGaSe$_2$ standard sample from Table 4-1 (Spectruma GDA 650, CCD detection, 500 V, 3,5 hPa, pulse length 200 µs, frequency 350 Hz, duty cycle 0,07).

Using the measured depth profiles of the standard samples calibration plots are made: the emission intensity is plotted versus the corresponding concentrations. In Fig. 4-48 the calibration plot for Cu is shown. For the zero point of the calibration plot a pure Mo sample is measured.

One can see that all points in Fig. 4-48 are on one line. Hence the dependence of concentration $c$ on intensity $I$ is described by the simple equation $I=constant\cdot c$, where the constant is the same for all samples. According to equation 2-1 this means that the sputtering rate $q$ and emission yield $R_i$ are the same for all samples in the calibration. Such calibration is called matrix specific, because only samples with very similar matrix can have the same sputtering rate. The emission yield $R_i$ is independent of the sample matrix. To get the same emission yield all standards and
unknown samples should be sputtered at identical electrical conditions (voltage and current). The CuInSe$_2$ and CuGaSe$_2$ standards are sputtered at constant voltage and pressure and due to the similar matrixes of these two samples the current doesn’t significantly vary. However to determine the depth, the absolute sputtering rates must be used for calibration ($c^*q = f(intensity)$, see equation 2-1). Therefore the sputtering rates of the standard samples are determined and used for the quantification: CuGaSe$_2$ 0,098 µg/s, CuInSe$_2$ 0,081 µg/s and Mo 0,308 µg/s. One can see that the sputtering rates of CuGaSe$_2$ and CuInSe$_2$ are very similar.

To check the correctness of the calibration the depth profiles of the standard samples from Fig. 4-47 are quantified. The GD OES quantification results show a good agreement with the element concentration values measured by XRF (see Fig. 4-49 and Table 4-3). Also the calculation of the layer thickness from the measured masses of the elements corresponds very well to the given data (2,05 µm and 2,48 µm). This means that the known density values of the ternary compounds (CuInSe$_2$ 5.803 g/cm$^3$ and CuGaSe$_2$ 5.613 g/cm$^3$) are correct. Therefore it can be concluded that the layers are dense and don’t contain any pores.

Further the depth profiles of the unknown solar cell samples (with different Ga/(Ga+In) concentration ratios 0,33, 0,45 and 0,76) are measured and quantified using the above described matrix specific calibration. In Fig. 4-50 the measured and quantified depth profiles of these samples are presented. One can see that the Ar intensity in the profiles of both standard and unknown samples doesn’t change,
indicating that the electrical conditions (voltage and current) are identical for all samples. This is essential for the matrix specific calibration where sputtering rates and emission yields of different samples should be the same.

Fig. 4-50 Measured and quantified GD OES depth profiles of the solar cell samples with different Ga/(Ga+In) concentration ratio: (a) 0.33 (b) 0.45 (c) 0.76 (Spectruma GDA 650, CCD detection, 500 V, 3.5 hPa, pulse length 200 µs, frequency 350 Hz, duty cycle 0.07).
Results and discussion

From the quantified depth profiles in Fig. 4-50 the average Ga and In concentrations in the CIGSe layers are determined. Afterwards the Ga/(Ga+In) concentration ratios are calculated for each sample and plotted versus XRF data (see Fig. 4-51). It is clearly seen that the XRF and GD OES quantification results are identical.

The quantitative GD OES depth profile is also compared with an AES depth profile of the same sample (see Fig. 4-52). Both depth profiling techniques indicated In and Ga gradients in the CIGSe layer and a nearly homogeneous distribution of the Cu and Se contents. The layer thickness and the absolute concentrations of GD OES and AES measurements are in a good agreement as well.
Hence, it can be concluded that the matrix specific quantification principle described in the introduction (see 2.2.2) is valid also for the pulsed discharge. Similarly to the continuous discharge mode in case of the pulsed mode the standards and the samples should be measured at the same electrical conditions. The described quantification procedure of the CIGSe solar cell samples can be simply performed at any commercial GD OES device which has a pulsed rf generator.

4.1.6.2 Matrix independent calibration – SAW samples

The quantitative GD OES analysis of SAW samples requires the matrix independent quantification algorithm (see 2.2.2), because these samples contain two different matrixes – Cu and Al (see 2.5.2). It is well known that the sputtering rate of Cu is higher than that of Al (SR factor of Cu is 1,15 and of Al is 0,12). Therefore in the calibration plot (m %- Intensity) the points which correspond to the samples with Cu and Al matrixes will not fit the line, if the sputtering rate or the relative sputtering rate (RSR) is not taken into account (see also 2.2.2). The multiplication of the element concentration by the RSR (m %*RSR) compensates the difference in the sputtering rates and brings the points of the calibration plot on one line. Therefore this quantification principle is called matrix independent.

As already said, the important condition of a successful quantification is that all standard and unknown samples are sputtered at the same voltage and current. In the case of solar cell samples the measurements are done at constant voltage and pressure, but because of the same matrix the current does not change. In the case when the calibration plot contains samples with different matrixes and the unknown sample itself consists of different matrixes, voltage and current must be kept constant. The problem is that in case of pulsed discharge it is technically not possible to keep the current and voltage constant.

Therefore the following quantification procedure is proposed:

1. Measure the standard samples for the calibration plots in continuous rf mode at fixed effective voltage and “true power” (this control mode provides the requested power to the plasma by compensating for the power losses that occur as the power is delivered to the GD): 700 V 2,74 W;
2. Measure the SAW sample (10nmAl/100nmCu/10nmAl/5nmTi/LiNbO₃) in pulsed rf mode at fixed effective voltage and pressure - 700 V, 9.1 hPa (the pressure 9.1 hPa corresponds to the 2.74 W when measuring the Cu sample). As the power (and thus the current) is not fixed, it deviates from the power used for the calibration (by about 20%). The power fluctuations in the measured depth profile of the SAW sample cause deviations of the emission yields from those of the standard samples.

3. The emission yield fluctuations must be compensated. Therefore the measured intensities are corrected to a standard set of excitation conditions (voltage and current) according to the method developed by Arne Bengtson (see 2.2.2).

The quantification procedure described above is performed using the commercial GD OES device (LECO GDS 850A) at Swerea KIMAB – a leading institute within corrosion and metals research in Stockholm. The list of standard samples used for the quantification includes samples with various matrices, such as Cu, Al, Ti, Zn, Fe and Nb (see Experimental details Table 3-2). In Fig. 4-53 the calibration plot for Al without (a) and with (b) sputtering rate correction is presented. One can see that the multiplication of the concentration by the RSR of the corresponding standard shifts the points to the one line. This phenomenon appears for both low and high concentration regions.

Fig. 4-53 Al calibration plots for the matrix independent quantification of the SAW samples: (a) without and (b) with sputtering rate correction.
The 2\textsuperscript{nd} step of the proposed quantification procedure is to measure the depth profile of the SAW sample using pulsed rf discharge. Afterwards, according to the 3\textsuperscript{rd} quantification step, the measured intensities should be corrected to a standard set of excitation conditions (to compensate the current fluctuations). To perform this correction one needs to know the effective voltage and power within the pulses. It is found that to be able to record the electrical parameters within the pulse, minimum 10 ms pulse length can be used for the depth profiling. According to the previous investigations (see Fig. 4-46 (b)) the optimal duty cycle for the SAW samples is 0,1. Hence the SAW sample is measured at 700 V, 9,1 hPa, 10 Hz, 0,1 duty cycle and 10 ms pulse length (see Fig. 4-54).

In Fig. 4-54 one can see (a) the measured depth profile of the SAW sample (10nmAl/100nmCu/10nmAl/5nmTi/LiNbO\textsubscript{3}) and (b) the zoomed in image of two pulses within the Cu layer. The effective voltage and true power values are subsequently used for the intensity correction. Further the corrected intensities are recalculated into concentrations by means of the calibration plots. The sputtering time is recalculated into depth according to the equations 2-8 and 2-9 (see introduction 2.2.2). The time periods between the pulses where no emission appears coalesce in the depth scale. Therefore the derived concentration-depth profile of the SAW sample doesn’t show any pulsed structure (see Fig. 4-55).
From the quantified depth profile of the SAW sample one can conclude that the thickness of the Cu layer is around 100 nm. This result is in agreement with the given value of the Cu layer thickness. On the other hand, the Al layers thickness can be hardly estimated from the quantified depth profile. The Al concentrations even don’t reach the 100 % concentration value although it is known that there are pure Al layers in the sample. Apparently these layers are too thin to be resolved in the GD OES depth profile. However the thickness of the Al layers can be derived from the measured intensity-time profiles of the SAW sample. The integral of the intensity-time profile gives the total sputtered mass of the corresponding element pro crater surface – g/m$^2$. With known mass and density of the layer the layer thickness can be calculated. So the integral of the Al intensity which corresponds to the first and second Al layers is 0,025 g/m$^2$ and 0,027 g/m$^2$, correspondingly. Dividing these values by the Al density (2,699 g/cm$^3$) gives the depths of the Al layers – 9,263 nm and 10,004 nm. Analogous the depth of the Cu layer is determined: (0,994 g/m$^2$)/(8,920 g/cm$^3$)=111,435 nm. The calculated depth values are in a very good agreement with the given layer thicknesses - 10nmAl/100nmCu/10nmAl.

Analogous with the matrix specific calibration it can be concluded that the matrix independent quantification principle, as well as the intensity correction developed by Arne Bengtson (see 2.2.2), is valid also for the pulsed discharge. The proposed quantification procedure is performed at the commercial GD OES device and can be used for the analysis with application of pulsed rf discharge.
4.2 Application of PGD in GD OES analysis

The studies of the PGD described in the previous chapters are relevant for the application of the GD OES analysis in materials science. In the present chapter some examples are shown where pulsed GD OES measurements are helpful at the investigation of the thin film solar cells (TFSC – see 2.5.1) and SAW devices (see 2.5.2).

4.2.1 Layer stacks of CIGSe thin film solar cells

4.2.1.1 Comparison of GD OES with other depth profiling techniques

The layer, which has the greatest influence on the efficiency of TFSC, is the sunlight absorbing layer CIGSe. The elements in this layer are often distributed inhomogeneously. As already discussed in the introduction (see 2.5.1) the composition of the absorber layer may affect the electrical and optoelectrical properties of thin film devices. Hence the analysis of the elemental distributions in the thin films is essential for both research and industry. To find the most suitable depth profiling method for the thin film solar cells several techniques are compared in terms of their spatial and lateral resolution, speed of measurement, accuracy and availability. This comparative study is the result of the collaborative work of the research groups from various European and American institutes, universities and companies. For the depth profiling analysis all research groups used identical samples with a 2 µm thick CIGSe layer on a Mo/soda-lime glass substrate with solar-conversion efficiency of up to 20.1 %. The work is mainly focused on the elemental distributions of the matrix elements, in particular Cu, In, Ga and Se. The sample preparation procedure, methods used and results are comprehensively described in a joint article and book.\textsuperscript{231,232}
The methods which were compared are:
- X-ray photoelectron spectrometry (XPS);
- Auger electron spectrometry (AES);
- Glow discharge optical emission spectrometry (GD OES);
- Glow discharge mass spectrometry (GD MS);
- Secondary ion mass spectrometry (SIMS);
- Secondary neutral mass spectrometry (SNMS);
- Raman depth profiling;
- Raman mapping;
- Rutherford backscattering spectrometry (RBS);
- Elastic recoil detection analysis (ERDA);
- Grazing-incidence X-ray backscatter diffraction (GI-XRD);
- Angle-dependent soft X-ray emission (AXES);
- Energy-dispersive X-ray spectrometry in a transmission electron microscope (TEM-EDX);
- Ellipsometry;
- Wavelength-dispersive X-ray spectrometry in a scanning electron microscope (SEM-WDX);
- Energy-dispersive X-ray spectrometry in a scanning electron microscope (SEM-EDX);
- Scanning AES;
- Time-of-flight secondary ion mass spectrometry (TOF-SIMS).

In Fig. 4-56 the Ga distributions across the absorber layer measured by various techniques are presented.
Fig. 4-56 Ga distributions in the 2.2 µm thick Cu(In,Ga)Se$_2$ layer measured by various techniques.\textsuperscript{231}
Nearly all depth profiling techniques show a similar Ga gradient in the CIGSe layer with rise of the Ga content close to the absorber/Mo interface. However the question which technique is the best for depth profiling of solar cells cannot be answered. It is concluded that there is no method which provides satisfactory quantitative elemental distributions across the CIGSe layer, because all applied measurement techniques have their advantages and disadvantages. To select the measurement technique one needs to specify the requirements to the method and result, such as: destructive or nondestructive method, matrix or trace elements should be measured, what should be the depth and spatial resolution, measurement time, cost and availability. To avoid any ambiguous results it is better to use two or several measurement techniques.

In the joint article of D. Abou-Ras et al. all applied methods are discussed with respect to their strengths. GD OES along with GD MS are described as methods which provide the fastest acquisitions (2 µm thick CIGSe layer is analyzed within 5-7 min) and have the possibility to measure the distributions of trace elements. So GD OES is a technique which can be used in an industrial scale, for example to control the manufacturing process.

4.2.1.2 The role of an Al$_2$O$_3$ barrier layer in achieving high efficiency solar cells on flexible steel substrates

This work belongs to the investigations of the research group from HZB and is published in the joint paper of Sophie E. Gledhill et al.. Flexible substrate materials are attractive for the possibility to make lightweight flexible solar cell devices with advantages for certain applications, e.g. in space. In addition flexible substrates give the possibility to deposit the thin-film materials in roll-to-roll processes, which are potentially cost advantageous. One of the substrate materials that has shown promising results is steel. However to guarantee a good solar cell performance, the diffusion of Fe from the steel into the CIGSe absorber layer should be prevented, i.e. a barrier layer between the solar cell stack and the steel substrate is necessary. The requirements for a good barrier layer are: it should electronically and chemically isolate the CIGSe and Mo layers from the steel; it should be easily and homogeneously deposited and cheap. The Al$_2$O$_3$ used in the present work meets these criteria. GD OES and SIMS depth profiles indicate the efficiency of Al$_2$O$_3$ as
Results and discussion

barrier as well as its relation to the Na distribution in the solar cell and to the solar cell performance. In Fig. 4-57 one can see the measured GD OES and SIMS depth profiles of two CIGSe samples on steel substrates prepared with and without the Al₂O₃ barrier layer.

![Fig. 4-57 GD OES and SIMS depth profiles of the solar cell samples without (a) - GD OES (c) - SIMS and with (b) - GD OES (d) - SIMS 400 nm Al₂O₃ barrier layer.](image)

It is concluded that the results of the SIMS and GD OES depth profiling are complementary because GD OES shows the Na profile in the Mo layer free of artifacts, whereas SIMS is more sensitive and indicates the Fe and Na traces in the CIGSe layer. SIMS measurements confirm that the diffusion of Fe into the CIGSe layer is hindered by the Al₂O₃ barrier, because the observed Fe signal in the sample (in CIGSe layer) without barrier is an order of magnitude higher than in the sample without Al₂O₃. The reduction of Fe in the CIGSe layer improves the solar cell device efficiency. It is observed that the devices with the barrier layer have higher values of...
Results and discussion

short circuit current $I_{SC}$, open circuit voltage $U_{OC}$ and filling factor $FF$. In addition the quantum efficiencies $QE$ of the solar cells with the $\text{Al}_2\text{O}_3$ barrier are improved.

However, even with the barrier layer the solar cells on the steel substrate have lower $V_{OC}$ and $FF$ than the devices grown on soda-lime glass. The most probable explanation of this phenomenon is the reduced Na content in the CIGSe layer. It is known that Na has a positive influence on the solar cell performance. The chalcopyrite phase field $\alpha$ (see Fig. 2-11) is increased by the addition of Na. There is a theory that Na replaces the donor lattice defects and thus suppresses the formation of the ordered defect compounds.\textsuperscript{163} It is mentioned in the introduction (see 2.5.1) that in case of glass substrate during the layer growth at high temperatures Na diffuses through the Mo layer into the CIGSe. In case of the steel substrate the Mo is coated by an 8 nm evaporated NaF layer to provide the Na source. Afterwards the CIGSe is deposited. The SIMS measurements indicated that the sample with barrier contains 3 times less Na in the CIGSe than the sample without aluminum oxide. So the amorphous $\text{Al}_2\text{O}_3$ acts not only as a barrier for the Fe but also as a trap for Na. The GD OES profiles show that Na is accumulated at the Mo/$\text{Al}_2\text{O}_3$ interface, when the barrier layer is present, leading to a decrease of the Na amount in the chalcopyrite.

In summary, the $\text{Al}_2\text{O}_3$ barrier layer is found to slow down the Fe diffusion from the steel substrate. However the Na trapping by $\text{Al}_2\text{O}_3$ worsens the ultimate device performance. Therefore the optimization of the Na content in the CIGSe layer is necessary.\textsuperscript{233}

4.2.1.3 Investigation of the growth procedure of the Cu(In,Ga)Se\textsubscript{2}-films

This work is a part of the studies performed by the research group from HZB and is published in the joint paper of Thorsten Rissom et al..\textsuperscript{234} The aim of these studies is to gain better understanding regarding the spontaneous diffusion of In and Ga during the CIGSe film growth. The In and Ga distributions in the chalcopyrite layer have an impact on the optoelectronic properties of the solar cell devices. It is known that the band-gap energy of CuInSe\textsubscript{2} (1.04 eV) is smaller than that of CuGaSe\textsubscript{2} (1.68 eV). Hence the In and Ga distributions affect the light absorption behavior of the CIGSe layer in its volume.
In present work two types of solar cell samples with CIGSe layer are studied: Cu-poor and Cu-rich. For the preparation of these samples the chalcopyrite layer deposition process is interrupted before (Cu-pure) and shortly after (Cu-rich) the stoichiometry point. Thereafter the samples are heated in the in situ processing chamber attached to the EDDI (Beamline for Energy Dispersive Diffraction) synchrotron beamline at BESSY II. To record the structural changes of the samples during the annealing process the synchrotron radiation energy dispersive X-ray diffractometry is used. To control the in-depth element distributions within the CIGSe layers the GD OES depth profiles of the samples before and after the annealing process are measured. The in situ energy dispersive XRD (ED XRD) has shown that at the beginning of the annealing process for both Cu-rich and Cu-poor samples there are two distinct phases with a different Ga content. However in case of the Cu-rich sample at a temperature of about 470°C the diffraction peaks which correspond to these phases start to merge. For the Cu-poor sample the double peak remains intact through the annealing process. The GD OES depth profiles helped to explain the observed reflections in the ED XRD spectrum. In Fig. 4-58 the depth profiles for In and Ga for the Cu-poor and Cu-rich samples before and after annealing are presented. The double diffraction peak is explained by the strong In and Ga gradients in the CIGSe layer. The depth profiles of the Cu-poor sample before and after annealing remain nearly unchanged, whereas the Cu-rich sample is clearly more homogeneous after the annealing process.

**Fig. 4-58** In and Ga GD OES depth profiles of the solar cell samples with (a) Cu-poor and (b) Cu-rich CIGSe layer measured before and after annealing.234
Thus it is concluded that for temperatures of up to 530 °C the leveling of the In and Ga gradients in the absorber layer is strongly enhanced for Cu-rich solar cell samples. This may be attributed to the formation of the Cu_{2-x}Se phase when a Cu excess exists. This phase initiates an internal recrystallization and thus a large grain size and an enhanced interdiffusion of In and Ga within the chalcopyrite film.234

4.2.1.4 Study of Zn incorporation into CuInS$_2$ solar cell absorbers

This work is a part of the studies performed by the research group from HZB and is comprehensively described in the diploma thesis of Jens Dietrich.235 Earlier studies have shown that Zn incorporation into CuInS$_2$ film leads to an increase of the open circuit voltage $V_{OC}$ but decrease the short circuit current $I_{SC}$. However the underlying mechanisms are not yet understood. Also the diffusion of Zn into the CuInS$_2$ layer has never been investigated. In the present studies the prefactor $D_0$ of Zn diffusion into the CuInS$_2$ layer is determined from the measured GD OES depth profiles of the solar cell samples. For this the 3 µm thick CuInS$_2$ layers are covered by 200 nm ZnS. Hereafter the samples are heated up to various temperatures from 200 to 500 °C. In Fig. 4-59 one can see the measured depth profiles of two samples annealed at 350 °C and 425 °C. The Zn depth profile clearly indicates the diffusion of Zn into the absorber layer at higher temperature.

![Fig. 4-59 GD OES depth profiles of the solar cell samples measured after 1 h annealing at 350 °C (left) and 425 °C (right).]
Results and discussion

The diffusion coefficients $D$ of Zn into the CuInS$_2$ are determined for each applied temperature from the corresponding Zn depth profiles using equation 4-1, where $c$ is Zn concentration; $x$ the depth; $t$ the annealing time and $M$ the molar mass:

$$\ln(c(x,t)) = \ln\left(\frac{M}{\sqrt{2\pi Dt}}\right) + \left(-\frac{1}{4Dt}\right)x^2$$

Instead of the logarithm of the concentration the logarithm of the emission intensity can be applied, because the concentration is linearly proportional to the emission intensity, when the sputtering rate does not change (see Fig. 4-59 time scale). The depth $x$ is estimated using the known thicknesses of ZnS and CuInS$_2$ layers. Hence for the determination of the diffusion coefficients the logarithm of the Zn emission intensity from the depth profiles measured at different temperatures is plotted versus the square of the depth (see Fig. 4-60).

According to equation 4-1 the diffusion coefficient $D$ can be calculated from the slope of linear regions of these plots. In this way the $D$ values are deduced and used for
the Arrhenius plot: \( \ln(D(T)) \) versus 1000/T. Taking into account that \( D(T)=D_0 \exp(-E_A/kT) \) the prefactor \( D_0 \) and the activation energy \( E_A \) are determined from the Arrhenius plot: \( D_0=(1.9 \pm 0.2) \times 10^{-7} \) cm²/s and \( E_A=(0.83 \pm 0.01) \) eV.

With known \( D_0 \) and \( E_A \) the diffusion depth of Zn \( L_D \) can be controlled by varying the annealing time \( t \) and temperature \( T \): \( L_D=(D*t)^{1/2} \). This helped to study the influence of the Zn diffusion depth on the \( V_{OC}, I_{SC} \) and \( QE \) of the solar cell devices with CuInS₂ absorber layer.²³⁵

### 4.2.2 Electrode metallizations of SAW devices

GD OES depth profiling proved to be a proper method for the determination of the Al and Cu layer thickness. In section 4.1.6.2, where the quantification of the SAW sample (10nmAl/100nmCu/10nmAl/5nmTi/LiNbO₃) is described, the depth of both, Al and Cu layer, is deduced from the intensity-time profile. The derived depth values are in a very good agreement with the depths determined by TEM.

In this part it is shown that GD OES depth profiling allows controlling the element distributions in the electrodes which is important for the study and development of the new high performance SAW devices. More detailed description of the work and additional studies with application of GD OES analysis can be found in the dissertation of M. Spindler.²³⁶

### 4.2.2.1 The role of Al in high performance Cu-based SAW devices

In the introduction it is mentioned that the addition of a small amount of Al to the Cu-based electrodes reduces the diffusion of Cu to the electrode surface and along the Cu grain boundaries (see 2.5.2). In this way the damage of Cu electrodes due to the power load is reduced and the lifetime of the SAW device is extended. However it is essential to find an optimal Al content in the Cu electrode which provides both reduced Cu diffusion and oxidation and low electrical resistivity of the electrodes (see 2.5.2). This task is a part of the comprehensive studies performed by the research group of Dr. Thomas Gemming at IFW Dresden.

Three types of electrode preparation are studied: co-evaporation of pure Cu and Al, evaporation of a Cu (5 at. % Al) ingot and preparation of Cu/Al layer stacks. The first two preparation methods are found to be not suitable for the reproducible
Results and discussion

Cu-Al electrode manufacture. The GD OES depth profiling confirmed that the co-evaporation process of Cu and Al can not be properly controlled. In Fig 4-61 the quantified depth profile of a co-evaporated Cu-Al metallization is shown. One can see that the Al concentration strongly exceeds the nominal Al concentration in Cu (1-5 at. % Al).

![Figure 4-61 GD OES depth profile of a Cu-Al metallization prepared by the co-evaporation of Cu and Al (Spectruma GDA 750, PMT detection, continuous dc discharge, 1100 V, 1,4 hPa).](image)

Evaporation of the Cu-Al ingot also doesn’t provide the expected Cu to Al concentration ratio in the target. Fig. 4-62 demonstrates the huge difference between the Al content in the evaporated ingot and in the resulting electrode material: Cu/Al ingot - 5 at.% Al, electrode material – ca. 0,11 at% Al.

![Figure 4-62 GD OES depth profile of the (a) Cu (5 at.% Al) ingot and (b) Cu-Al metallization prepared by the evaporation of Cu (5 at.% Al) ingot (Spectruma GDA 750, PMT detection, continuous dc discharge, 1100 V, 1,4 hPa).](image)
Results and discussion

Therefore for the further studies the sequential evaporation of Al and Cu is selected. This preparation method provides reproducible Cu/Al layer stacks. The thicknesses of the layers can be precisely controlled by the variation of the power of electron beam and evaporation time.

Investigations of Spindler et al. have shown that Al layers < 10 nm on top and under the Cu electrode significantly improve the TTF values compared to pure Cu electrodes. It is also known that an annealing of the Cu/Al layer stacks leads to a further extension of the SAW electrode lifetime. To understand the impact of Al at the Al-Cu interface, TEM investigation of the annealed sample is done. The EDX scan across the lamella of the Al2nm/Cu100nm/Al2nm/Ti5nm/LiNbO3 interface of the annealed SAW sample indicates that there is an increase of oxygen simultaneously with Al and Ti layer towards the substrate. The Cu layer is observed to be nearly unaffected by oxygen (see Fig. 4-63).

![Fig. 4-63](a) TEM image of the Al2nm/Cu100nm/Al2nm/Ti5nm/LiNbO3 layer stack after annealing up to 450°C and power treatment and (b) EDX line scan on the Cu/Al/Ti/LiNbO3 interface of this sample.

XPS measurements have shown that the Ti layer gets oxidized while the Al layer contains metallic Al. That means that there is the possibility for Al atoms to diffuse into the Cu-film (grain boundaries and grains) and block the fast diffusion paths of Cu along its interfaces and grain boundaries. However from the TEM-EDX line scan one can not definitely conclude that Al diffuses into the Cu layer, because it is done
locally along the narrow line which is 2 nm thick. To get a reliable result about the average Al diffusion a bigger measurement area should be considered. For this purpose GD OES depth profiling is a suitable method because the sputtering area is in the mm region. For depth profiling of the SAW samples the 2,5 mm anode is used. In Fig. 4-64 GD OES depth profiles of the SAW sample (Cu20nm/Al2nm/Ti5nm/LiNbO$_3$ substrate) before and after the annealing processes are presented.

![Graphs showing GD OES depth profiles before and after annealing](image)

**Fig. 4-64** GD OES depth profiles of a Cu/Al/Ti/LiNbO$_3$ SAW sample (a) before and (b) after 2 h annealing at 320 °C (Spectruma GDA 750, PMT detection, 700 V, 2,5 hPa, duty cycle 0,03, 1100 Hz, 27 µs).

The comparison of the Al signals clearly indicates greater Al diffusion into the Cu layer in the case of the annealed sample. This result along with the measurements of the electrode lifetime indicates that the stuffing of Cu grain boundaries with Al atoms could be a mechanism to stabilize interfaces and to increase the power durability and lifetime of the SAW devices.
5 Conclusions

This dissertation covers the features of pulsed glow discharge (PGD), which are crucial for both understanding of the discharge plasma processes and analytical applications. In the present work the influence of the duty cycle, pulse duration and frequency on the PGD is investigated and compared for direct current and radio frequency discharges. In the research attention is firstly paid on the electrical parameters of PGD, then on the crater shapes, sputtering rates and finally on the light emission. According to the studies carried out, the measurement of depth profiles of thermally fragile (Cu(In,Ga)Se₂ (CIGSe) solar cells on a glass substrate) and thin layered samples (electrode metallizations of SAW devices) with pulsed rf GD OES are optimized. A quantification procedure is adapted for the pulsed mode and applied to the measured depth profiles. Finally it is shown that the optimized pulsed GD OES measurements are relevant to the investigation of the thin film solar cells and SAW devices.

The main conclusions of the dissertation are given below:

- The influence of the PGD parameters (pulse duration, pulse frequency and duty cycle) on the voltage–current (U-I) characteristics and current and voltage signal shapes is ascertained. The U–I plots indicate heating of the discharge gas when operating at high duty cycles.

It is found, that the current signal is not constant during the pulse. Thus the pulse duration is an important parameter of the PGD. At fixed duty cycle the average discharge current depends on the pulse duration: the shorter the dc pulse the higher the average current.
The voltage signal shape is rectangular and not influenced by the pulse parameters. However, with the experimental setup used in this work the rf voltage needs around 50 µs to reach its prescribed value because of the bias voltage formation. Hence, in case of rf discharge, in contrast to the dc mode, the use of very short pulses leads to a decrease of the sputtering rate.

- The influence of the pulsing parameters on the shape of the sputtered crater as well as on the sputtering rate is revealed. The observed effects correlate with the current signal within the pulse. The sputtered crater shape is strongly affected by the duration of the applied pulses even when the duty cycle is fixed. The depth profile behaviour at various pulsing parameters is explained by the crater formation effects. Such knowledge and relation between the pulsing parameters and depth profiles is helpful for the optimization of GD OES depth profiling.

It is noteworthy that the Boumans equation, originally deduced for continuous dc discharge, is found to be valid also for pulsed rf and dc mode. The effect of sputtering on the CIGSe layer surface of the solar cells is described for the first time. Investigations of the CIGSe layer of the solar cells by SEM have shown that sputter induced effects can be reduced by variation of the pulsing parameters.

- The influence of the pulsing parameters on the spectra of both pulsed dc and rf discharges is studied. The effects observed in this part should be taken into account at the GD OES analysis with application of pulsed discharge. It is important to know that not only the duty cycle, but also the pulse duration influences the emission intensity. Moreover this influence differs for the atomic and ionic emission lines: the emission intensity of ions is not much influenced by the pulse duration (at fixed duty cycle). In contrast, the emission intensity of the atomic lines is higher at short pulses due to the observed emission peak at the beginning of the pulse.

- A new method for the estimation of the gas temperature (from U-I characteristics of PGD) in the glow discharge is developed. The calculated temperature values are compared with another temperature measurement technique (from the rotational spectra of nitrogen species). The temperature difference between pulsed and
Conclusions

continuous mode calculated from the spectra of the second positive system of nitrogen is 78 K and from the spectra of first negative system – 90 K. These values are also close to the temperature difference deduced from the U-I plots of the pulsed and continuous discharges - 100 K. Hence there are three different temperature estimation procedures (U-I plots, rotational spectra of N\textsubscript{2} and N\textsubscript{2}\textsuperscript{+}) which indicate that the discharge gas temperature can be reduced by around 100 K when pulsed glow discharge is applied. However the study of the discharge gas temperature is not completed. More attention should be paid to the absolute value of the discharge gas temperature and to the cathode (sample) temperature as well.

• With regard to the question whether direct current (dc) and radio frequency (rf) pulsed discharges behave similarly it can be concluded that the pulsed rf and dc discharges are very similar in terms of the electrical properties, sputtered crater formation, light emission and temperature. Nearly all phenomena found with dc discharges also appear in the rf case. The only feature which makes pulsed rf discharge different from the dc one is that in contrast to the dc mode at the beginning of the rf pulse the voltage reaches its prescribed value with a delay of around 50 µs (the delay value depends on the capacitance of the experimental system).

• Concerning the quantification of GD OES depth profiles measured with PGD it can be concluded that matrix specific, as well as matrix independent quantification principles and the intensity correction developed by Arne Bengtson are valid also for the pulsed discharge. Similarly to the continuous discharge mode in case of the pulsed mode the standards and the samples should be measured at the same electrical conditions. The CIGSe solar cell samples on a glass substrate and thin layered electrode metallizations of SAW devices are measured and quantified with application of PGD. The proposed quantification procedures are implemented at the commercial GD OES devices and can be used for the analysis with application of pulsed rf discharge.

• The studies of the pulsed glow discharge performed in this dissertation are relevant for the application of the GD OES analysis in materials science. During the
collaborative work with Helmholtz-Zentrum Berlin für Materialien und Energie and with the research group of Dr. Thomas Gemming at IFW Dresden the optimized pulsed GD OES measurements could be successfully applied at the investigation of thin film solar cells with CIGSe light absorbing layer and electrode metallizations of SAW devices. In case of the solar cell samples pulsed GD OES depth profiling along with SIMS measurements reveal the role of the Al$_2$O$_3$ barrier layer in high efficiency solar cells consisting of a CIGSe/Mo layer stack on a flexible steel substrate (the barrier layer is between the Mo and steel substrate to prevent the Fe diffusion). The features of the CIGSe film growth are studied with help of pulsed GD OES and in situ synchrotron XRD measurements. The diffusion coefficient of Zn into the CuInS$_2$ layer is determined for the first time from the measured GD OES depth profiles of the corresponding solar cell samples. In case of SAW samples pulsed GD OES measurements helped to evaluate the different SAW electrode preparation procedures and to choose the most suitable one. In addition pulsed GD OES depth profiling along with XPS, TEM-EDX and electrode lifetime measurements indicates the possible mechanism of power durability and lifetime improvement of the SAW devices when small amount of Al is added to the Cu-based electrodes.

The GD OES depth profiling of the solar cell samples is compared with various depth profiling techniques. It is concluded that there is no perfect depth profiling method which provides satisfactory elemental distributions across the CIGSe layer because all applied measurement techniques have their advantages and disadvantages. However with the knowledge earned in the course of the present dissertation the pulsed GD OES depth profiling became a useful method complementing the other analytical techniques.
Bibliography


Bibliography


Bibliography


Bibliography


Acknowledgements

I would like to thank all those who contributed to the work in this dissertation.

I am grateful that I could get the financial support from the MC RTN GLADNET (No. MRTN-CT-2006-035459). It was an unforgettable experience for me to be a member of the international project GLADNET. I appreciate the opportunities I got to learn the outstanding researchers and meet good friends all over the world, to travel a lot, see the foreign cultures as well as to present and discuss the scientific results at the conferences and internal project meetings.

My sincere thanks to Prof. Dr. Jürgen Eckert for accepting me to carry out the work at IFW Dresden in the Institute for Complex Materials where I had excellent conditions for the research, a lot of friendly colleagues and competent people around me.

I am infinitely thankful to my supervisor Dr. Volker Hoffmann for his permanent support, valuable suggestions, discussions, inspiration and for the extra working hours answering all my questions, correcting errors and suggesting new experiments. I would also like to thank him for the patient reading of this dissertation and giving me useful comments.

I want to thank Dr. Denis Klemm, Dr. Maxim Voronov and Dr. Petr Šmíd for their kind help especially at the beginning of my work, and answering my numerous questions. I am particularly grateful to Ingrid Wetzig, Romy Keller, Günther Pietzsch, Matthias Uhlemann, Ekaterina Kleisz and Steffi Kaschube for their friendly support in the lab and measurements. Dankeschön für die Unterstützung!

I would like to extend my sincerest thanks to the following people for the successful and fruitful collaboration: Prof. Dr. Edward B. M. Steers and Dr. Tamara Gusarova from London Metropolitan University; Prof. Dr. Arne Bengtson, Simone Weyler and other colleagues from Corrosion and Metals Research Institute in Stockholm; Dr. Daniel Abou-Ras, Dr. Raquel Caballero, Dr. Thorsten Rissom et al. from Helmholtz-
Acknowledgements

Zentrum Berlin für Materialien und Energie; Mario Spindler, Dr. Siegfried Menzel et al. from the research group of Dr. Thomas Gemming at IFW Dresden; Dr. Zoltan Donkó and Aranka Derzsi from Research Institute for Solid State Physics and Optics in Budapest; Michael Analytis, Rüdiger Meihsner and Rüdiger Brünner from Spectruma company; Michael Köster and Thomas Asam from TAZ company; Zdeněk Weiss from LECO company; Dr. Steffen Oswald from IFW Dresden and Dr. Thomas Wirth from Federal Institute for Materials Research and Testing.

I thank all my colleagues and friends from the IFW and GADNET for the great time we spent together.

A special thank to my partner for his patience, friendship and enormous support. Finally deepest thanks to my dear family for their love and support. Большое спасибо!:)