Transparent rectifying contacts on wide-band gap oxide semiconductors

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Dipl.-Phys. Alexander Lajn

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Gutachter: Prof. Dr. Marius Grundmann (Universität Leipzig)

Prof. Dr. Thomas Riedl (Universität Wuppertal)

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1 Introduction

The major driving force for entering the age of information technology was the massive spread of microelectronics and especially of the personal computer into the society in the last decades of the past century. In the following, with the global connection of computers via the Internet, information transfer was significantly simplified and accelerated. Advances in device miniaturization and software technology, recently resulting for example in smart phones and tablet computers, yielded even further integration of information retrieval and exchange into daily life. As a consequence of this ongoing process, electronic devices and their handling take a back seat providing more and more attention to the information itself.

Pursuing this trend is very demanding for software development, but also requires new hardware concepts to be involved. Transparent electronics (TE) is such a concept, as it permits to fabricate see-through devices, e.g. displays. Thus, the information and the environment are visible for the user at the same time. In combination with appropriate sensor devices, information may even be selected according to the user’s location and view, which is referred to as augmented reality [Azu97]. In order to realize TE-devices, all components of the latter have to exhibit a negligible light absorption in the visible spectral range, which severely affects both, the material selection and the device design. Neither the common semiconductors for thin-film transistors or light-emitting diodes (e.g. Si, GaAs, InGaAs), nor the common metallic conductors can in consequence be applied.

A promising material class for the realization of the functional components of TE are metal oxides. Aside from the already more common representatives of very high (transparent conductive oxides (TCO), e.g. InSnO, ZnO:Al) or low (insulators, e.g. SiO$_2$, Al$_2$O$_3$) conductivity, semiconducting wide band-gap oxides (e.g. ZnO) complete the available conductivity range. The first fully transparent transistor, reported by Hoffmann et al. in 2003 [HNW03], was an all-oxidic device with ZnO-channel, AlTiO gate dielectric and ITO electrodes. In later works, the channel material ZnO, which crystallizes even at room temperature, was mixed with other oxides to form amorphous oxide semiconductors (ZnSnO [Gör+06], InGaZnO [Nom+04]). Furthermore, reduced and therefore cost-beneficial growth temperatures as low as room temperature for all components of the TFTs are feasible [For+05]. Therefore, devices can be even fabricated on flexible substrates like plastic foils, which limits growth temperatures to be below about 200°C [Nom+04] but enables new fields of application.

All previously cited reports demonstrate metal-insulator-semiconductor field-effect transistors (MISFETs). It has been shown that highly rectifying, but opaque metal-oxide contacts can
be fabricated on ZnO [ADM07; Laj+09]. By applying them, metal-semiconductor field-effect transistors (MESFETs) can be fabricated, which exhibit at least similar or even better electrical performance compared to MISFETs [Fre+08; Gru+10].

The aim of this work was to fabricate and characterize fully transparent MESFETs (TMES-FET). Therefore, fully transparent rectifying contacts (TRC) [Fre+11], based on the metal-oxide contact concept, and optimized transparent Ohmic TCO electrodes were developed and combined.

From the most promising candidates of opaque metal-oxide contact materials, platinum oxide and silver oxide were selected and their deposition conditions were optimized to maximize transmittance in the visible under the constraint of maintaining the electrical performance. A depth-resolved study of the oxidational state of the TRC metal-oxide was conducted in order to gain insight into the physical origin of the observed rectification. Moreover, the robustness of the TRC potential barrier formation to semiconductor crystallinity ranging from single crystalline to amorphous and the lateral homogeneity of the potential barrier was investigated.

The applicability of the TRC as UV-photodetectors is demonstrated.

The growth parameter dependency of the optical and electrical performance of room-temperature grown TCO films was studied, permitting to chose optimal conditions for the Ohmic electrodes of the TMESFETs. Additionally, the contact resistance of the electrodes was investigated.

Finally, the previous results were combined and TMESFETs were successfully fabricated using a high-temperature pulsed-laser-deposition-grown MgZnO channel layer on sapphire substrates. Their electrical performance was studied, namely in terms of their on-off current ratio, the field-effect mobility and the subthreshold slope. A special focus was drawn on device reproducibility, long-term degradation and stability towards visible light illumination, elevated temperatures and bias stress. Aside from static characteristics, also the effect of pulsed bias was investigated. The TMESFET concept was then transferred to low-temperature-grown amorphous InGaZnO channel layers on glass and flexible substrates, respectively.

By integrating TMESFETs, transparent inverter circuits were fabricated and studied with respect to their electrical performance, also under visible light illumination and elevated temperatures.

As a practical application, a MESFET-based chip for the detection of neuronal action potentials was developed and the applicability of the MESFETs for small signal sensing in wet environments was demonstrated.

This work was carried out in the semiconductor physics group at Universität Leipzig. Sample growth was conducted here and in cooperation with P. Barquinha from CENIMAT in Portugal. Structural, morphological, optical and electrical measurements were conducted at facilities of Universität Leipzig. Photoelectron spectroscopy was carried out in cooperation with the

\[1\text{If not otherwise stated, all individuals named in the following are members of Universität Leipzig}\]
physical chemistry workgroup of Prof. R. Denecke at Universität Leipzig and in cooperation with J. Rubio-Zuazo and G. Castro at the Spanish CRG BM25 beamline (SLine) at the European synchrotron radiation facility (ESRF) in Grenoble, France. The development of the chip for the measurements of neuronal cells and related measurements were carried out in cooperation with the soft matter physics division at Universität Leipzig.

The pulsed-laser deposition (PLD) was carried out by Holger Hochmuth. Contact sputtering was carried out in cooperation with Holger Hochmuth, Monika Hahn and Hannes Münch. The sputtering of the InGaZnO channel layers was conducted by Pedro Barquihna at CENIMAT in Portugal. The sample preparation, namely the photolithography, was carried out in cooperation with Gisela Biehne and Monika Hahn. Ellipsometric measurements were carried out by the ellipsometry workgroup within the semiconductor physics group at Universität Leipzig, namely Helena Franke, Tammo Böntgen and Jan Lorbeer. Hall effect measurements were carried out in cooperation with Tobias Diez, Kerstin Brachwitz, Matthias Brandt and Robert Heinold. SEM images, cross sections, TEM-lamella preparation and EDX-analysis was carried out by Jörg Lenzner, TEM was performed by Gerald Wagner. AFM and XRD were performed in cooperation with Michael Lorenz, Tammo Böntgen, Fabian J. Klüpfel, Friedrich L. Schein and Kerstin Brachwitz. Photoelectron spectroscopy was carried out in cooperation with Juan Rubio-Zuazo and German Castro (both ESRF) and Sandra Wickert, Friedrich L. Schein and Michael Lorenz. The transmission measurements were carried out in cooperation with Tobias Diez and Fabian J. Klüpfel. The electrical measurements were carried out in cooperation with Tobias Diez, Heiko Frenzel and Fabian J. Klüpfel. The photocurrent measurements were carried out in cooperation with Matthias Schmidt. The development of the cell-potential sensor chip and related measurements were carried out in collaboration with Fabian J. Klüpfel and Sebastian Schmidt.
2 Material and device background

2.1 Transparent oxide (semi)conductors

2.1.1 Zinc oxide

Zinc oxide is a binary, ionic, direct semiconductor, which typically crystallizes in wurtzite structure, only under pressure a transition to rocksalt structure is observed. The lattice constants are $a = 3.249 \text{ Å}$ and $c = 5.2042 \text{ Å}$ [Lan+84]. The zinc is tetragonally coordinated to four oxygen atoms in the lattice. The O- and Zn-sub-lattices are shifted by $0.345 \times c$ along the c-axis [Lan+84], yielding the formation of positive and negative surface net charges on (0001) and (000$\bar{1}$) surface planes. Zinc oxide single crystals, grown by different methods including melt growth, hydrothermal growth and vapor phase growth, are commercially available and are applicable for homoepitaxial growth. ZnO has also been grown heteroepitaxially on a multitude of substrates including Si, CaF$_2$, GaAs, ScAlMgO$_4$, nevertheless most of the studies on heteroepitaxial growth use sapphire substrates [Oez+05]. The primary advantages of this material are the affordable price, the availability of large wafers (e.g. 2-inch or $50 \times 50 \text{ mm}^2$ as used in this work), the insulating properties and the high optical transmittance. While a-sapphire ([11$\bar{2}$0]) permits almost perfectly lattice matched growth of (0001)-ZnO (the c-lattice constant of sapphire is with 12.991 Å almost exactly four times the a-lattice constant of ZnO), for c-sapphire a lattice mismatch as high as 18.4% yields significant defect formation and performance reduction. The optical band gap of ZnO is 3.37 eV at room temperature. Therefore, no fundamental absorption occurs in the visible spectral range. The band gap can be increased or decreased by alloying ZnO with Mg and Cd, respectively. ZnO exhibits intrinsically n-type conduction. While a large number of deep and shallow defects were observed in ZnO, for only few of them the exact origin is known [Laj+10; San+07; Wen+07a]. Moreover, until now reports on reliable p-type doping and related devices are lacking. Nevertheless, the application of ZnO in unipolar or hetero-bipolar devices is promising. Aside from being investigated and potentially applied as semiconductor, Zinc oxide is already being applied e.g. in solar cells as highly doped front electrode (cmp. sec. 5).

2.1.2 Amorphous oxide semiconductors

A prominent example for amorphous semiconductors is hydrogenated silicon (a-Si:H) [SLC75]. While the majority of current highly-integrated circuitry is based on poly-Si, highly uni-
form and stable TFTs based on a-Si:H were the prerequisite for the revolution of the LC-displays [LCSG79]. Being a covalent semiconductor, highly directional sp\(^3\)-hybridized orbitals mainly form the conduction band minimum in Si as indicated in fig. 2.1 (a). While in a periodic arrangement of a large number of atoms, the energy levels of the electrons form a continuum or in other words a band. Therefore, electron transport is not hindered by energetic barriers and the electrons are delocalized. The introduction of disorder upon amorphization yields the formation of localized energy states (tail states) of varying energy. Therefore, transport transforms into hopping conduction between the localized states. In succession, the mobility decreases significantly. While polycrystalline Si exhibits mobilities of several hundreds of cm\(^2\)/Vs, for a-Si:H only about 0.5 cm\(^2\)/Vs are reached.

A different behavior is observed for post-transition-metal oxide semiconductors as e.g. InGaZnO. While single-crystalline material exhibits mobilities in the range of 100 cm\(^2\)/Vs [Nom+03], amorphous material is reported to reach mobilities in excess of 10 cm\(^2\)/Vs [Nom+04; KNH09]. Generally, for these ionic materials the conduction band is predominantly composed of metal s-orbitals [Hos06] (cmp. fig. 2.1 (b)). During amorphization, predominately angular disorder is introduced as the inter-atomic distances remain almost constant [Nom+07]. In consequence, the overlap between neighboring metal s-orbitals does not significantly change, electrons remain at least partly delocalized and therefore mobility is only weakly affected [Nom+04; Hos06]. As it turned out, the binary compounds e.g. ZnO or SnO, which have been in the focus of early transparent transistor research [HNW03; Pre+04], tend to crystallize even at low temperatures yielding decreased mobility due to grain boundary scattering. Alloying compounds of different crystal structures allows to suppress the crystallization, even for temperatures up to about 500\(^\circ\)C [Nom+08], and to fabricate excellent transparent devices [Nom+04; For+05; Gör+06]. The carrier concentration can be efficiently controlled in the ternary and quaternary com-
pounds via controlling the valence of the constituents (chemical doping) by oxygen pressure variation during growth [Tak+05; Hos06]. The optical band gaps of these alloys are in excess of 3 eV, such that they are well suited for application in transparent electronics.

### 2.2 Schottky diodes and transport processes

One of the first investigated semiconductor devices is the rectifying metal-semiconductor contact, which is named in honor to Walter Schottky. Comprising of a metal and a semiconductor in intimate contact, the current rectifying effect is the major feature of this device. Physically, this effect is based the formation of a space charge layer and hence the occurrence of a potential barrier at the interface [SN07]. In abrupt approximation, the extension of the space charge layer is given by:

\[
 w = \sqrt{\frac{2 \varepsilon_s \varepsilon_0}{\varepsilon (N_D - N_A)} \left( V_{bi} - V - \frac{k_B T}{e} \right)}. \tag{2.1}
\]

Here, \( \varepsilon_s \) is the semiconductor’s relative permittivity, \( \varepsilon_0 \) is the vacuum permittivity, \( e \) the elementary charge, \( (N_D - N_A) \) the net doping density. \( V_{bi} \) denotes the built-in voltage, \( V \) external bias, \( k_B \) the Boltzmann constant and \( T \) the temperature. The capacitance of the space-charge layer assuming a parallel-plate capacitor is then given by

\[
 C = \frac{\varepsilon_s \varepsilon_0 S}{w}, \tag{2.2}
\]

with \( S \) denoting the contact area.

Two different models were proposed for the description of the current flow for sufficiently low net doping densities, based on:

- Thermionic emission (TE) (proposed by Bethe [Bet42])
- Diffusion (DF) (proposed by Schottky [Sch38])

Both of these models yield in principle the same exponential relation between current and voltage as given in equation 2.3:

\[
 I = I_S \left[ \exp \left\{ \frac{e(V - IR_S)}{n k_B T} \right\} - 1 \right] - \frac{V - IR_S}{R_P}. \tag{2.3}
\]

---

1 Ferdinand Braun, (1850-1918), discovered rectifying behavior in metal sulfides in 1874 while teaching at St. Thomas School, Leipzig.
2 Walter Hermann Schottky, (1886–1976), German physicist
3 The charge density is given by \( e(N_D - N_A) \) in the space charge layer and zero outside.
4 Additionally, field emission and thermionic field emission may occur for high doping densities and also recombination currents may contribute to the diode current [SN07].
5 The following considerations assume an n-type semiconductor.
In order to account for real diodes, the parallel and the series resistance, $R_P$ and $R_S$, respectively, are considered. The ideality factor $n$ is introduced to account for the voltage dependence of the potential barrier. Finally, $I_S$ denotes the saturation current and here both previously mentioned transport mechanisms differ significantly:

- The saturation current considering **thermionic emission** is given by:

\[
I_S = S A^* T^2 \exp \left\{ -\frac{e \Phi_{B,\text{eff}}}{k_B T} \right\},
\]

with $\Phi_{B,\text{eff}}$ being the effective barrier height. $A^* = \frac{4\pi e m^* k^2}{\hbar^3}$ is the effective Richardson constant, $m^*$ denotes the effective electron mass and $h$ is the Planck constant. For ZnO, $A^*$ is $32 \frac{A}{cm^2K^2}$ and for InGaZnO $A^* = 41 \frac{A}{cm^2K^2}$, using $m^*_{e,ZnO} = 0.27 m_e$ and $m^*_{e,\text{GaInZnO}} = 0.34 m_e$, respectively [SN07; Tak+05].

- The saturation current considering **diffusion** is given by:

\[
I_S = S e \mu N_C \sqrt{\frac{2e(N_D - N_A)(V_{bd} - V)}{e_0 \varepsilon_s}} \exp \left\{ -\frac{e \Phi_{B,\text{eff}}}{k_B T} \right\},
\]

with $\mu$ being the electron mobility, $N_C$ the density of states at the conduction band edge. Obviously, both terms are dominated by the exponential dependence on the barrier height, but the dependence on temperature and external bias is different. This originates in the different physical approaches each valid in a specific non congruent parameter range. While charge carriers are assumed to propagate scatter-free within the space charge region for TE theory, DF explicitly considers scattering to occur. Conclusively, the ratio between the electron mean free path and the extension of the space charge layer is crucial for the applicability of the respective model [Bet42]. Transferred to material parameters, TE applies for high net doping densities and high mobilities. A unified model, which considers both transport mechanisms in series was proposed by Crowell and Sze [CS66].

- The saturation current of the combined **thermionic emission / diffusion** model is given by:

\[
I_{S,\text{TED}} = S A^{**} T^2 \exp \left\{ -\frac{e \Phi_{B,\text{eff}}}{k_B T} \right\},
\]

with the effective Richardson number $A^{**}$ given by

\[
A^{**} = \frac{f_p f_q A^*}{1 + \frac{f_p f_q A^*}{e_m}}.
\]

The criterion to differentiate between TE and DF is introduced by the velocity ratio between
\( v_r \) and \( v_d \). The recombination velocity at the top of the barrier \( v_r \), given by

\[
v_r = \sqrt{\frac{kT}{2\pi m^*}},
\]

is based on the assumption that the electron flux from the semiconductor to the metal equals the flux in the opposite direction. The diffusion velocity \( v_d \) is given by

\[
v_d = \left[ \frac{e}{kT} \exp\left(\frac{-e\Phi_{B,\text{eff}}}{kT}\right) \int_0^w \exp\left(\frac{eE_c(x)}{kT}\right) dx \right]^{-1}.
\]

Here, \( E_c(x) \) describes the band bending of the conduction band. The probability of an electron reaching the metal from the semiconductor without being scattered back is denominated \( f_p \); \( f_p \) is a factor permitting to consider current deviations due to tunneling and quantum mechanical reflection at the barrier in the following \( f_q = 1 \) is assumed. The distance \( x_{m,E} \) between the point of maximal electrical field and the interface is given by

\[
x_{m,E} = \frac{e}{8\pi \sqrt{\frac{(N_D - N_A)(V_{bi} - kT/\epsilon)}{e^2 \epsilon_0}}}.
\]

The mean free path \( l \) is given by \( l = \frac{v_r \mu m^*}{e} \).

### 2.2.1 Applicability of the respective theory for oxide semiconductors

The practically occurring mobilities and net doping densities of the oxide semiconductors, which are in focus of this work, are sometimes already at the edge of the applicability of TE theory. In this section the validity range for the respective models is investigated in more detail.

For a given barrier height \( \Phi \), the saturation current according to the TED model is calculated and a pseudo barrier height \( \Phi_{P,TE} \) is extracted from this using the TE model and equation 2.4. The difference between both barrier heights, assuming \( I_{S,TED}(\Phi) = I_{S,TE}(\Phi_{P,TE}) \), yields an indication of the practical limit of TE theory and is given by:

\[
\Phi_{P,TE} - \Phi = \frac{kT}{e} \ln \left( \frac{A^{**}}{A^*} \right).
\]

For a practically relevant range of electron mobilities \( \mu (1 - 1000 \text{ cm}^2/\text{Vs}) \), net doping densities \( N_D - N_A (10^{14} - 10^{18} \text{ cm}^{-3}) \) and temperatures \( T (100 - 450 \text{ K}) \), the calculated barrier height difference is depicted in figure 2.2 (calculated for \( \Phi = 1 \text{ V} \)). As expected, for large \( N_D - N_A \) and \( \mu \), TE and TED model reveal identical barrier heights, as thermionic emission is dominant in this regime. For lower \( N_D - N_A \) and \( \mu \), the pseudo barrier height extracted using TE model becomes larger than the true barrier height. The overestimation of the barrier height by the TE model is equivalent to the fact that transport is no more limited by thermionic emission.
Figure 2.2: Calculated difference of pseudo barrier height \( \Phi_{P,TE} \) and model barrier height (for \( \Phi = 1 \) V). The solid white contour line denotes a difference of 0.02 V. The dotted (dashed) contour line shows the variation of the latter contour line for \( \Phi \) of 1.2 (0.8) V.

but by diffusion. The magnitude of the overestimation increases significantly with increasing temperature. At 100 K, for almost the entire \((N_D - N_A) - \mu\)-range of practical relevance, thermionic emission yields a barrier height difference of less than 0.02 V, which is considered to be of the order of the uncertainty of the barrier height extracted from the current-voltage characteristic [RW88]. At room temperature, the maximum of the overestimation reaches for the investigated \((N_D - N_A) - \mu\)-range more than 0.1 V, requiring to consider diffusion currents in a much wider parameter range than at low temperatures. At elevated temperatures above room temperature, this effect is even more pronounced. As a rule of thumbs for the validity of TE theory in ZnO and related materials, one can state: “For each order of magnitude, the net doping density is below \(10^{18} \) cm\(^{-3}\), then majority carrier mobility has to be one order of magnitude larger than 1 cm\(^2\)/Vs”. By varying \( \Phi \) between 0.8 and 1.2 V, which is the range of the best reported barrier heights on zinc oxide and related materials [ADM07; Laj+09; Fre+10a; LWG11; Lee+11; Wen+06], only the difference of the barrier heights changes only weakly as indicated by the dashed and dotted contour lines in figure 2.2. Changes of the effective electron mass and the relative dielectric constant within the typical range of oxide semiconductors, only weakly affect the difference of the barrier heights, keeping the trend as depicted in figure 2.2.
Conclusively, the dominating transport process of Schottky diodes on zinc oxide and related oxide semiconductors crucially depends on the net doping density and the majority carrier mobility. Thermionic emission theory does not apply in general. Nevertheless, for single crystalline material, which typically exhibits higher mobilities of the order of 100 cm$^2$/Vs or more at room temperature, TE model is expected to be applicable in the practically relevant temperature range (except for highly compensated material). For samples of poor crystalline quality and low mobility the applicability of the TE model has be carefully checked each time.

2.2.1.1 Barrier inhomogeneity

In the previous paragraphs a perfectly homogeneous interface yielding a spatially constant barrier height was implicitly assumed. For real samples, this is in most cases not fulfilled. Lateral barrier fluctuations significantly affect the charge transport, especially the respective temperature dependence. Those fluctuations might originate for example from surface imperfections, process-induced damage of the surface, termination-dependent variation of the ionization potential [ADM07; Hoh+11] and are observed for a large number of different semiconductor materials [Laj+09; SM99; Wen+06; WG91; Jia+02] (cmp. also sec. 4.3).

Inhomogeneous barriers and thermionic emission  Werner and Gütter proposed a simple analytical model to describe current-voltage characteristics and their temperature dependence affected by barrier inhomogeneities [WG91]. A Gaussian distribution of the barrier heights is assumed:

\[
P(\Phi_B)(V) = \frac{1}{\sigma(V)\sqrt{2\pi}} \exp\left(-\frac{(\Phi_{B,m}(V) - \Phi_B)^2}{2\sigma^2(V)}\right),
\]

characterized by a standard deviation $\sigma$ and a mean barrier height $\Phi_{B,m}$. The integral of the thermionic current over all barrier heights of the distribution is identical to the current flow over an effective, possibly temperature dependent barrier height.

\[
j(\Phi_{B,\text{eff}}) = \int_{-\infty}^{\infty} j(\Phi_B) P(\Phi_B) d\Phi_B
\]

Due to $j_{\text{TE}}(\Phi) \propto \exp(\Phi)$, this integral can be analytically solved yielding the temperature dependence of the effective barrier height [WG91]:

\[
\Phi_{B,\text{eff}} = \Phi_{B,m} - \frac{\sigma^2}{2k_BT/e}.
\]

\(^a\)As mobility increases with decreasing temperature for many materials, TE theory is often applicable to an even wider parameter range at low temperatures.
Material and device background

Figure 2.3: Calculated difference between effective barrier heights of TED and TE theory using numerical approximation of equation 2.15 for $\Phi_{B,m} = 1.2$ V and $\sigma = 0.12$ V.

The latter equation corresponds to the fact that current flows preferentially over the lower barrier paths; the effective barrier height is lower than the mean barrier height and the deviation increases for decreasing temperature. In order to extend the model to include the deformation of the barrier distribution for applied bias, a linear voltage dependence of $\sigma$ and $\Phi_{B,m}$ is introduced:

$$\Phi_{B,m}(V) = \Phi_{B,m}(V = 0) + \rho_{\Phi} V$$

$$\sigma(V) = \sigma(V = 0) + \rho_{\sigma} V$$

The respective voltage coefficients $\rho_{\sigma}$ and $\rho_{\Phi}$ are assumed to be independent of temperature. In succession, the ideality factor, previously introduced to account for the voltage-dependence of the barrier height, can be written as:

$$n = \frac{1}{1 - \rho_{\Phi} + e \rho_{\sigma} / (2 k_B T)}.$$ 

(2.19)
Figure 2.4: Maximal deviation of effective barrier height for $1 < \mu [cm^2/Vs] < 1000$ and $10^{14} < (N_D - N_A) [cm^{-3}] < 10^{18}$ in dependence of mean barrier height and barrier distribution width. The shaded area of the 100 K-plot indicates the range, where, at least for part of the investigated mobility/net doping density range, numerical calculation fails.

**Extension of barrier inhomogeneity model to TED-theory** As already indicated in section 2.2.1, TE theory is not generally applicable, depending on the material parameters of the semiconductor used. Nevertheless, also for the case of diffusion currents dominating the charge transport over the barrier, perfectly homogeneous barriers are unlikely to occur, or at least difficult to prepare experimentally. Therefore, the theory of a Gaussian distributed barrier height is derived in the following for TED theory. First, the relation between effective and mean barrier height has to be derived analogue to equation 2.15 in section 2.2.1.1. The required integration of $j_{TED}(\Phi) \propto \exp(\Phi)/(1 + \frac{\Phi}{\Phi_d(\Phi)})$ over all possible barrier heights of the Gaussian distribution not analytically solvable. The interval for numeric integration is constrained, at least for low barriers, by the validity limits of the applied models. The potential barrier and the space charge layer only exist for $(V_{bi} - V - \frac{kT}{e}) > 0$.

The consideration of the Schottky-effect yields an even stronger constraint of $(V_{bi} - V - \frac{kT}{e}) > \frac{9e}{32\pi} \sqrt{\frac{N_D}{\pi e^2}} = V_{min}$ (cmp. section 8). In this work, the integration was carried out between $2V_{min}$ and $\Phi_{B,m} + 10\sigma$.

In order to verify the deviation induced by the finite integration, also for thermionic emission

---

1Barrier height and built-in voltage are related by $\Phi_{B} = V_{bi} + kT/e(1 + \ln(N_C/N_D))$ (approximated for the non-degenerated case; up to about $10^{18} \text{ cm}^{-3}$ the deviation is < 5 mV for ZnO.)
the effective barrier heights were calculated and compared to the known result of the infinite integration. It is remarkable, that typically for lower temperatures (below about 200 K), the deviation between finite and infinite integration increases (up to several hundreds of millivolts). But both effective barrier heights (TE and TED model) calculated by finite integration deviate only weakly (in the order of a few tens of millivolts). Therefore, the difference between finitely and infinitely integrated TE effective barrier heights was used to rescale $\Phi_{\text{B,eff,TED}}$ in order to minimize its error due to the finite integration. Nevertheless, due to the different integrands for TE and TED model, the rescaling is only an approximation. The difference between the numerically determined and rescaled effective barrier height for the TED-model and the effective barrier height calculated using formula \ref{eq:2.15} for the TE-model is depicted for zero bias in figure 2.3 (for $\Phi_{\text{B,m}} = 1.2$ V and $\sigma = 0.12$ V). As the difference is positive, the effective barrier height derived using TED theory is slightly larger than for TE theory. The maximum deviation is only few tens of millivolts at low temperatures and very low electron mobilities. For most cases, the maximum deviation is below the previously mentioned accuracy of the barrier height extracted from an IV-curve. This also holds for a wide range of different barrier height distributions. For further verification, the maximum of the effective barrier height de-
violation, calculated for $1 < \mu [cm^2/V\ s] < 1000$ and $10^{14} < (N_D - N_A) < 10^{18}$, was determined for various $\Phi_{B,m}$ and $\sigma$ (cmp. figure 2.4). In general, the deviation is small compared to the accuracy of the barrier height for not too large distribution width and not too small mean barrier heights. The application of the numerical calculation is limited for low temperatures, as expected by equation 2.15, which yields negative values of $\Phi_{B,\text{eff}}$.

Conclusively, the relation between effective barrier height and mean barrier height derived for TE theory (equation 2.15) is in good approximation also valid for TED theory.

Finally, the observable deviations of the effective barrier heights for a spatially inhomogeneous barrier have to be calculated. Therefore, both the minor difference in the relation of mean and effective barrier heights and the major differences between effective barrier heights extracted from the saturation current have to be considered. The resulting deviation between full-TED and TE-only to is depicted exemplarily for zero bias for a mean barrier height of 1.2 V and a barrier distribution width of 120 mV in figure 2.5.

Due to the comparably weak effect of barrier height changes (as indicated by the dashed and dotted contour lines in fig. 2.2) the range for which TED theory has to be considered is rather similar to the homogeneous case. This is obvious from the comparison of fig. 2.2 and 2.5. Thus, the conclusions previously drawn for homogeneous barriers for applicability of TE and TED theory are generally also valid for inhomogeneous barriers.
2.3 Metal-semiconductor field-effect transistor

The general principle of a normally-on metal-semiconductor field-effect transistor (MESFET) is depicted in fig. 2.6 (a-i) in absence of any bias. By fabricating a gate electrode, consisting of a Schottky contact with a space charge layer extending into the channel, the current between source and drain electrode becomes controllable. The edge of the space charge layer, initially located somewhere within the channel, can be tuned by the gate potential to reach both interfaces of the channel layer. While reaching the substrate surface is equal to full depletion of the channel, the opposite case reflects a fully conductive channel.

The current between source and drain electrode is driven by $V_{SD}$. For low $V_{SD}$, in absence of full depletion, an increase of this potential yields a linear current increase according to Ohm’s law (cmp. fig. 2.6 (b) except the dash-dotted line). As indicated in fig. 2.6 (a-ii), the respective electrical field due to $V_{SD}$ vertically extends the space charge layer increasingly with decreasing lateral distance to the drain contact. For a certain $V_{SD} = V_{SD, sat}$, the space charge layer extends at the drain side over the whole channel, which is called pinch-off (dashed line in fig. 2.6 (b)).

In the following, an n-type semiconductor will be considered with respect of the content of this work.
For further increased $V_{SD} = V_{SD} + \Delta V$, the pinch-off point shifts towards the drain electrode and the additional voltage $\Delta V$ drops across the extended space-charge layer. Conclusively, the diffusive source-drain current remains constant at $I_{SD,\text{sat}}$ due to the constant voltage drop along the remaining channel. Further increase of $V_{SD}$ ultimately causes breakdown of the barrier and impact ionization yields excessive increase of $I_{SD}$. For increasing gate bias, both $I_{SD,\text{sat}}$ and $V_{SD,\text{sat}}$ increase, as the smaller extension of the space-charge layer (for $V_{SD} = 0 \text{ V}$) requires a larger electrical field to be pinched-off, which yields at the same time a higher current. Conclusively, the MESFET exhibits a set of characteristic curves in dependence of $V_{SD}$ and $V_{G}$ as depicted in fig. 2.7. For practical reasons, only slices of the field are considered. The dependence of $I_{SD}$ on $V_{G}$ for constant $V_{SD}$ is denominated transfer curve and the set of $I_{SD}$ on $V_{SD}$ for several steps of $V_{G}$ represents the output characteristic.

In order to derive the ideal current-voltage characteristic of the MESFET, the following assumptions are applied:

- axis orientation and channel dimensions as indicated in fig. 2.6 (a-i)
- homogeneous doping density ($N_D - N_A$)
- long channel approximation ($L \gg d$)
- abrupt approximation valid for space-charge layer
- gradual channel approximation ($\mathcal{E}_x \ll \mathcal{E}_z$)
- constant electron mobility ($v = \mu \mathcal{E}_x$)
- gate currents are negligible

The current between source and drain is then given by [Gru06]:

$$I_{SD} = I_P \left[ \frac{3V_D}{V_P} - 2 \frac{(V_{bi} + V_G + V_D)^{3/2} - (V_{bi} + V_G)^{3/2}}{V_P^{3/2}} \right]$$  \hspace{1cm} (2.20)

and the saturation current for $V_{bi} + V_G + V_D = V_P$ is given by:

$$I_{SD,\text{sat}} = I_P \left[ 1 - 3 \frac{V_{bi} + V_G}{V_P} + 2 \left( \frac{V_{bi} + V_G}{V_P} \right)^{3/2} \right].$$  \hspace{1cm} (2.21)

$V_P$ and $I_P$ are the pinch-off voltage and current, respectively:

$$V_P = \frac{ed^2(N_D - N_A)}{2\varepsilon_s\varepsilon_0}$$  \hspace{1cm} (2.22)

$$I_P = \frac{e^2}{6\varepsilon_0} \frac{\mu(N_D - N_A)WD^3}{\varepsilon_s L}.$$  \hspace{1cm} (2.23)
The pinch-off current is affected by both, material parameters, namely the mobility, and the geometry of the device. Using the derivative of either the current or the saturation current, which is denominated transconductance and extracted either from the output characteristic or the transfer curve, the field-effect mobility can be determined. The dominant sources of uncertainty for the latter calculation are the uncertainty for the channel thickness and the doping density.

\[ g|_{V_{SD} \to 0} = \frac{\partial I_{SD}}{\partial V_{SD}}|_{V_{SD} \to 0} = g_{\max} \left[ 1 - \sqrt{\frac{V_{bi} + V_G}{V_P}} \right] = \frac{\partial I_{SD}}{\partial V_G} = g_{m, sat} \] (2.24)

\[ g_{\max} = \frac{e(N_D - N_A)d\mu_{FE}W}{L} \] (2.25)

In real devices, gate leakage current is not zero and affects both, on- and off-regime. Conclusively, according to Kirchhoff’s law source and drain current are no more equal. In the off-regime, with typically \( V_G \ll 0 \) and \( V_{SD} \gg 0 \), a large potential difference exists between gate and drain and thus \( |I_D| \approx |I_G| \). In the on-regime, the gate current increases quickly for positive gate bias and as soon as \( V_G \approx V_{bi} \), the space charge layer vanishes and the leakage current will be of the order of the channel current yielding a decrease of \( I_D \). For low \( V_{SD} \), even a sign change of \( I_D \) occurs. Conclusively, MESFETs can only be tuned in a limited range between normally-on and normally-off mode. A normally-off device will suffer from leakage currents. Accumulation mode similar to MISFETs cannot be achieved, therefore a MESFET channel layer is required to exhibit high conductivity prior to the formation of the space charge layer by the gate contact deposition and the substrate is preferentially highly insulating to suppress shunt currents. The switching regime of the transistor is mainly characterized by the slope the current increases with increasing gate potential:

\[ S = \frac{\partial V_G}{\partial \log I_{DS}} \] (2.26)

which is a measure of the effectiveness of a gate potential change on the channel current. An important figure of merit is the minimal slope, which is denominated subthreshold slope \( SS \) and theoretically reaches [Lia+91]:

\[ SS_{\text{min, theo}} = \ln(10) \times \frac{k_B T}{e} \approx 60 \text{ meV/dec@300 K} \] (2.27)

For MISFETs, \( SS \) may be significantly increased by the voltage drop among the insulator. Lower \( SS \) yields an increased transistor and device performance, e.g. noise-margin [Lia+91]. Furthermore, in real field-effect transistors \( J_{SD, sat} \) increases with increasing \( V_{SD} \), e.g. due to channel length being modulated by the source-drain potential [Zeg12]. The latter effect is

\[ \text{This value may differ from the Hall mobility. MISFET may suffer from scattering at the semiconductor-insulator interface, while this is inhibited in MESFET.} \]
predominantly important for short channel devices.
3 Fabrication and characterization

3.1 Fabrication methods

3.1.1 Pulsed laser deposition

The primarily applied method for the growth of conducting, semiconducting and insulating films in this work is pulsed-laser deposition (PLD). PLD is a non-equilibrium deposition technique based on high energy laser pulses ablating material from a target onto a substrate under vacuum conditions.

The working principle is sketched in fig. 3.1. In this work, the nanosecond short light pulses of a KrF excimer laser operating at a wavelength of 248 nm with a pulse energy of 600 mJ were focused on the target mounted on a rotatable holder in the vacuum growth chamber. The repetition rate of the laser (1 – 25 Hz) permits to adjust the growth rate. The targets were
prepared by G. Ramm (Universität Leipzig) by mixing powders containing the desired film components and successive pressing and baking. The laser pulses are absorbed in the surface layer of the target, yielding melting, evaporation and ionization of the latter. Finally, a plasma plume is formed, transporting the target material to the substrate. The transported material consists primarily of ions and atoms, but may also contain in lower densities larger particles. At the substrate, which was mounted in a distance of 10 cm from the target in this work, condensation and conclusively film growth takes place. The substrate temperature, which is crucial for the dissipation of the energy during condensation and thus for crystallization, is controlled by a heater attached to the rotatable substrate holder. Temperatures between room temperature and 700°C can be adjusted by the heater power of up to 500 W. The pressure of the background gas, e.g. oxygen, affects growth kinetics and stoichiometry and can be controlled between $3 \times 10^{-4}$ mbar and 0.1 mbar. The samples investigated in this work were grown by H. Hochmuth (Universität Leipzig).

As PLD maintains the stoichiometry of the target composition, it is ideally suited for the growth and the investigation of multi-component compounds, namely for oxides. Especially, by repetitively using the same targets, growth parameters can be optimized while maintaining an almost constant film composition. Moreover, the film thickness can be easily controlled via the number of applied laser pulses. Of the order of ten pulses are required for the growth of one monolayer.

A major constraint of PLD is the difficult scalability, as the plasma plume extension limits the maximal substrate size. Off-axis deposition, which introduces an offset between the rotating axis of the target (and thus the plasma) and the substrate, permits to extend the maximal substrate size [Lor+10a]. Additionally, droplet formation in the grown film due to the larger particles occasionally emitted from the target, may crucially affect device performance [Miil+11]. Using an eclipse, which blocks the direct path between target and substrate, this can be overcome at the cost of massive decrease of the deposition rate. Furthermore, PLD is subjected to limited reproducibility due to several effects. The growth rate is affected by the coating of the laser entry window, which reduces the pulse energy on the target, and by the history of the target. Film contamination may take place due to target contamination occurring during fabrication and storage in and outside of the growth chamber. Furthermore, contaminants in the growth chamber introduced in previous growth runs or due to the evaporation of the substrate heater materials affect the films. To overcome at least part of the latter issues in this work, the target surface was cleaned with some laser pulses prior to the first film growth and a specific target was reserved to be only used for the growth of the transistor channel layers. Additionally, the use of large area substrates containing multiple samples increases the comparability.
3.1.2 Sputtering

Sputtering denotes a physical vapor deposition method, which uses for the generation of a plasma an electrical field instead of light as in the previous section. A sketch of a sputtering setup is depicted in fig. 3.2. Generally, by applying a high voltage between the target and the substrate electrode, a plasma is generated by impact ionization of the inert gas introduced into the chamber (e.g. argon). The gas ions of the plasma erode the target and the eroded, mostly neutral particles condensate on the substrate to form a film.

Several types of sputtering can be differentiated:

**DC-sputtering** denotes the case depicted in fig. 3.2, where a constant electrical field is applied between the target cathode and the substrate-carrying anode. Due to the continuous charge transfer onto the target, insulating targets would charge up, which yields the formation of an opposing electrical field inhibiting the erosion process. Thus, only conductive materials can be sputtered using this method.

**HF-sputtering** or rf-sputtering names the process, where an alternating electrical field is applied between the electrodes ($f_{\text{typ.}} = 13.56$ MHz). In succession, also semiconducting or insulating materials can be deposited. By additional biasing of the substrate, the kinetic energy of the impacting particles can be tuned.
**Magnetron-sputtering** denotes the previously described setups, which additionally contain a magnetic field among the target increasing the ionization rate and thus the sputter rate.

**Reactive sputtering** includes the addition of reactive components, e.g. oxygen, to the atmosphere in the sputter chamber. Accordingly, the material eroded from the target reacts and the film consists of the reaction product. Furthermore, the ionization of the reactive gas and successive acceleration yields to negative sputtering or etching of the substrate.

In this work, metallic Ohmic contacts and TRC were always deposited using (reactive) DC-magnetron sputtering. The distance between anode and cathode was fixed at 4 cm. The pressure was controlled via the mass flow of the introduced gases. While 100 sccm of argon yielded a base pressure of about 0.024 mbar for all non-reactive sputter runs, a base pressure of 0.028 mbar used for a mixture of 50 sccm of argon and 50 sccm of oxygen for the reactive runs. The details of the sputter time and power setting are given in the respective sections. The amorphous InGaZnO channel layers, as investigated in sec. 6.1.2, were grown using a HF-magnetron sputtering setup at room temperature by P. Barquinha (CENIMAT, Portugal).

### 3.1.3 Photolithography and device fabrication

While the previous paragraphs of this section described the undefined fabrication of layers, this paragraph is dedicated to the structuring of the latter in order to finally obtain devices. The main method used for this purpose is photolithography. The general work flow is sketched in fig. 3.3.

1. **Mask fabrication:** After surface cleaning of the sample using acetone and isopropanol, the positive\(^1\) photoresist (AZ 1514H) is applied to the sample by spin coating (4000 min\(^{-1}\),

\(^{1}\) *Positive* resists become *more* soluble to the developer solution by light exposure.
3 Fabrication and characterization

2. Subsequently, the resist is dried in the oven for 5 min at 90°C.

2. **Mask manipulation:** The sample is aligned with the photolithographic mask, which consists of a glass plate with absorbing chromium areas, using a *SÜSS MJB3 mask aligner* in contact mode. The achievable diffraction limited spatial resolution of the latter device is below 2 μm. After exposure for 5 – 7 s using a mercury-vapor lamp, the resist is developed in NaOH (6.64 g/l), washed in distilled water and dried in the oven for 5 min at 90°C.

3. **Surface manipulation:** Depending on the desired type of structure, either additive (e.g. PLD, sputtering; branch (a) in fig. 3.3) or subtractive (wet etching; branch (b) in fig. 3.3) processes are applied.

4. **Mask removal:** Using acetone, the mask is removed. After an initial exposure of about one minute to acetone only, the process can be further enhanced using an ultrasonic bath. With that, the exact definition of the desired structures can be assured.

Exemplarily, the fabrication steps for a simple TFT are depicted in fig. 3.4. With the first subtractive step, the channel mesa is defined (fig. 3.4 (i)). For the case of TFTs based on MgZnO channel layers (cmp. sec. 6.1.1) the channel layer is exposed to phosphoric acid (1:80, room temperature) for 20 – 25 s. For the TFTs based on InGaZnO channel layers (cmp. sec. 6.1.2), the concentration and the etching time has to be increased. The etch process is stopped by rinsing the sample with distilled water. Subsequently, the Ohmic source and drain contacts consisting of a TCO (cmp. sec. 5) are defined. In a last step, the gate electrode is fabricated using reactive dc-magnetronspattering.

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2Most of the samples were prior to the spin coating mounted onto a GaAs or Si substrate using colophony in order to increase manageability and surface for the mask aligner suction table.
3.2 Characterization methods

**Current-voltage** measurements (IV) were carried out using *Agilent 4156C/4155C Precision Semiconductor Parameter Analyzers*. The measurements were controlled by matlab-programs written by H. von Wenckstern, M. Brandt and F. J. Klüpfel (all Universität Leipzig). The integration time was $\geq 20$ ms in order to minimize noise, except for the pulse measurements. The samples were, if not otherwise stated, kept in the dark at room temperature. Socketed samples were measured in the *Agilent Test Fixture 16442A*, while for the measurement of unsocketed samples a semi-automatic wafer prober *Süss MicroTec PA 200* was used. The latter device was controlled by a matlab-program written by F. J. Klüpfel. The chuck temperature of the wafer prober can be adjusted between room temperature and $150^\circ$C by a *Huber Unichiller*. The low temperature measurements were conducted in a self-built nitrogen flow cryostat.

**Photocurrent** measurements were carried out on socketed samples using a 100 W halogen lamp served as light source. The wave length of the light was controlled by a *Zeiss SPM 2* monochromator using a LiF-prism. The slit width of the monochromator was 0.5 mm. The photo-current was amplified by a *Stanford Research Systems SR510* Lock-In amplifier with a sensitivity of $10^6$ A/V. The wave length-dependent photon flux reaching the diode was determined using a calibrated pyrodetector *Oriel 70128*. The photo current measurements were carried out on the socketed diodes in photo-voltaic mode (bias 0 V).

**Conductivity and Hall-effect** measurements were carried out using a self-built setup with a magnetic field of 0.43 T. A *Keithley 220* current source, with a current range between 1 nA and 1 A was used. The different contact configurations are scanned by a *Keithley 7065* Hall-measurement card. The signal is detected with a *Keithley 2000* multimeter. All measurements were conducted in van-der-Pauw geometry. The measurements were controlled by a matlab program written by H. von Wenckstern and M. Brandt.

**Capacitance-voltage** measurements (CV) were recorded using an *Agilent 4294A Precision Impedance Analyzer* or, in case of quasi-static CV (QSCV) with the respective measurement mode of the *Agilent 4156C/4155C Precision Semiconductor Parameter Analyzers*. The measurements were controlled by matlab-programs written by H. von Wenckstern, F. Schmidt and F. J. Klüpfel (all Universität Leipzig). The samples were, if not otherwise stated, kept in the dark at room temperature. Socketed samples were measured in the test fixture or the nitrogen flow cryostat, while for the measurement of unsocketed samples the wafer prober *Süss MicroTec PA 200* was used.

**Optical transmission** spectra were recorded using a *Perkin Elmer Lambda 40* UV/VIS spectrometer, which permits to investigate the spectral range between 200 nm and 1200 nm.
The spatially resolved, spectrally integral transmission in the visible spectral range of selected devices was measured using a setup built by F. J. Klüpfel (Universität Leipzig). A Canon EOS 450D with a macroscopic lens combined with an extension tube was mounted on a tripod, facing a backside-illuminated frosted glass serving as light diffuser and sample holder. From the grey value difference between an image of the sample and an image without the sample, the transmission is extracted. The spatial resolution of the respective images reaches 5 \( \mu \text{m/pixel} \).

**Atomic force microscopy** was carried out in non-contact mode using a Park Systems XE-150.

**Transmission electron microscopy** was carried out on lamellas, which were prepared by focused ion beam milling (Ga) by J. Lenzner (Universität Leipzig) and subsequent polishing with Ar\(^+\) ions in a Gatan Duo-Mill device. The TEM images were recorded using a Philips CM-200 STEM equipped with a super twin objective lens (point resolution 2.3 nm) by G. Wagner (Universität Leipzig).

**X-ray diffraction** patterns were recorded using a Philips X-pert device with open detector using CuK\(_{\alpha,1}\)–radiation.

**X-ray photoelectron-spectroscopy** (XPS) was carried out at branch B of the Spanish CRG BM25 beamline (SpLine)[Cas98] at the European Synchrotron Radiation Facility (ESRF), Grenoble, France. The photon energy can be tuned in the range of 5 – 45 keV, with a photon flux up to \(10^{13} \text{s}^{-1}\). The monochromator resolution is given by \(\Delta_{\text{mono}} = (1.5...2) \times 10^{-4} \times h\nu\). The electrostatic analyzer (FOCUS HV-CSA300) permits the detection of electrons with kinetic energies up to 15 keV. A pass energy of 100 eV was used for all measurements, yielding an analyzer resolution of \(\Delta_{\text{analyz}} = 1.5 \text{ eV}\). Within this setup, also X-ray reflectivity measurements (XRR) can be conducted.
4 Transparent rectifying contacts

The concept of oxidized metal contacts to zinc oxide has been proven in previous works to exhibit superior electrical performance compared to purely metallic contacts [ADM07; All+09]. In this chapter, the extension of the latter concept to contacts transparent for visible light is presented. Silver and platinum based contacts exhibit the highest electrical performance [Laj+09; Fre+08; All+09; ADM07] and are conclusively selected for the investigation. In the first section, the optimization of the deposition conditions in dependence on the optical and electrical properties is demonstrated. Afterwards, a study on the interfacial oxidational state of the contact material conducted using hard X-ray photoelectron spectroscopy is presented. In the third section, the homogeneity of the potential barrier is studied and the applicability of the TRC concept to semiconductors of reduced crystallinity is investigated. In the last section, the TRC are applied as UV-photodetectors.

4.1 Optimization of the deposition conditions

The reliable preparation of rectifying contacts on zinc oxide is still a challenge, yielding to a wide range of applied surface pretreatments including chemical and/or physical methods (Reviews on Schottky contacts on ZnO: [Oez+05; BL11]). Nevertheless, results obtained by different groups for similar contact materials still vary significantly indicating the dominant influence of the zinc oxide sample on the contact properties. Therefore, in order to exclude sample effects for the optimization of the barrier properties, all contacts used for optimization were deposited on pieces cleaved from one and the same sample. It consists of an about 200 nm thick Al-doped ZnO film, serving as back side contact [Wen+06] and a 1 \( \mu \)m thick ZnO film, both grown by PLD on an as-received circular 2 inch in diameter a-plane sapphire substrate. The oxygen partial pressure and the growth temperature were 0.02 mbar and 670°C, respectively.

In order to increase the contact transmittance, the contact material’s thickness has to be reduced, which requires the deposition conditions of the DC magnetron sputtering setup to be adapted accordingly. As previous investigations revealed, the parameter window for the ignition of the plasma is comparably narrow for the DC-sputtering setup used in this work. Therefore, the total gas pressure \(^1\) and the sputtering voltage were not varied. Further-

\(^1\) Approximately realized by keeping the sum of the argon and the oxygen mass flow constant at 100 sccm.
more, XPS-investigations of reactively sputtered silver deposited with different oxygen flow rates showed, that the metallic silver species are detectable up to an oxygen flow rate of 30 sccm [Hei09]. Therefore, an oxygen mass flow of 50 sccm was chosen in order to establish an oxidized metal contact. The desired thickness reduction requires to reduce the deposition rate compared to previously deposited opaque contacts, in order to avoid too short deposition times and with that hardly controllable irregularities during the plasma ignition significantly affecting the device reproducibility. Thus, using a sputtering power of 5 W, which is a factor of 6 lower compared to the opaque contact conditions, permits to reliably deposit contacts of reduced thickness. Previous investigations [Laj+09] showed, that it is necessary to cover the contact layer with a conductive layer in order to form an equipotential surface, therefore contacts were covered with an about 1-3 nm thin layer ($P = 5 \, \text{W}$, $t = 10 \, \text{s}$) of gold for the case of $\text{Ag}_x\text{O}$ and platinum for $\text{PtO}_y$, respectively. The circular shape of the contacts was defined using molybdenum steel shadow masks. The contact thickness was determined using scanning electron microscopic images of cross sections fabricated by focused ion beam milling.

While the absorption decreases with thickness, the rate of failure of the contacts is expected to increase, namely due to the increasing effect of surface roughness, voids and short-circuits. Therefore, the contact thickness was varied in multiple steps via variable deposition time between 7 and 60 seconds. For each sample, the current–voltage characteristics of typically 8 to 12 TRCs were recorded. Using thermionic emission theory only, the $IV$-characteristics of the diodes were fitted (cmp. section 2.2), accordingly with a net doping density of $\approx 3 \times 10^{16} \, \text{cm}^{-3}$ and a mobility, which is typically $> 50 \, \text{cm}^2/\text{Vs}$ for similarly grown samples \(^2\). The median of the determined parameters, namely $\Phi_{B,\text{eff}}$ and $n$, are depicted for both contact materials in fig. 4.1. The error bars denote the standard deviation. For both contact materials, the ideality factor generally decreases slightly with decreasing thickness from about 1.7 to about 1.4. The behavior of the effective barrier height differs for both materials. For $\text{Ag}_x\text{O}$-contacts, $\Phi_{B,\text{eff}}$ continuously decreases with decreasing contact thickness and the parallel resistance (not shown here) also decreases as expected. In contrast, for $\text{PtO}_y$-contacts, $\Phi_{B,\text{eff}}$ unexpectedly first increases with decreasing thickness and decreases only for thicknesses below 10 nm as expected. The unexpected behavior for high thicknesses might be related to edge effects, as for the same samples, also a comparably low parallel resistance was extracted from the fit. In order to relate the electrical performance and the absorbance, the average visible transmittance of the contacts was determined using a self-built setup (cmp. sec. 3.2). It permits to determine the spatially resolved, spectrally integrated transmittance of the samples and therefore, in contrast to spatially integrating transmittance measurements, to differ contact and substrate transmittance. The extracted mean visible transmission in dependence of the overall TRC thickness $d_{\text{TRC}}$ (including the capping layer) is depicted in fig. 4.2 (a). It is

\(^2\)The highly conductive back-side contact layer inhibits reliable Hall effect measurements of the nominally undoped zinc oxide layer.
Figure 4.1: Thickness dependence of the contact parameters extracted from fitting using thermionic emission theory for (a) Ag\textsubscript{x}O- and (b) PtO\textsubscript{y}-based contacts.

important to note, that \( T_{\text{vis}} \) includes the absorbance of the zinc oxide layer and the sapphire substrate. \( T_{\text{vis}} \) decreases with increasing thickness for both materials as expected. Using Beer’s law \( (I/I_0 = \exp(-\alpha d)) \), where \( I \) and \( I_0 \) denote the transmitted and the incident intensity, respectively, \( \alpha \) the absorption coefficient and \( d \) the absorbing film thickness, the thickness dependence can be fitted. The extracted absorption coefficients are similar for both materials with \( \alpha_{\text{Ag}_xO} = (2.2\pm0.5) \times 10^5 \text{ cm}^{-1} \) and \( \alpha_{\text{PtO}_y} = (2.2\pm0.3) \times 10^5 \text{ cm}^{-1} \). Previous investigations of the optical properties of silver oxide and platinum oxide layers revealed comparable values of the absorption coefficients [Nef+96; Kum+03; Gao+04]. The transmission of the TRC layers with an overall thickness of 10 nm, which yield the best compromise between optical and electrical properties, are depicted in fig. 4.2 (b). The TRC were deposited on ZnO, which was grown on an \( a \)-sapphire substrate exhibiting a mean transmittance of about 88%. The mean visible transmittance reaches 70% (60%) for the Ag-(Pt-)based TRC.

The microscopic structure of an Ag-based TRC, as revealed by TEM (cmp. sec. 3.2), is depicted in fig. 4.3. The TRC was fabricated on an about 20 – 25 nm thin ZnO-layer deposited on \( a \)-sapphire. The thickness of the TRC film can be determined to be about 10 nm. The silver oxide layer is compact and without voids, a clear indication of the gold capping layer is not observed. The latter indicates the gold to probably form a net like structure. The silver oxide is nano-crystalline. Part of the interface region is amorphous, which is possibly induced by the negative sputtering in the initial phase of the contact deposition.

In order to determine the optical constants of the TRC contact material and especially to further investigate the contact material’s absorption, films of reactively sputtered Ag\textsubscript{x}O and
PtO\textsubscript{y} with a large thickness of \( \approx 760 \) nm and \( 500 \) nm, respectively, were deposited on silicon and on sapphire substrates \(^3\). The wave-length dependent ellipsometric parameters \( \Psi \) and \( \Delta \) were determined by spectroscopic ellipsometry, conducted by H. Franke (Universität Leipzig). Using an effective medium approximation (EMA) two layer model, the optical constants \( n \) and \( k \) of Ag\textsubscript{x}O and PtO\textsubscript{y} were extracted. From the extinction coefficient \( k \), the absorption coefficient was calculated according to \( \alpha = 4\pi k/\lambda \). The spectra of the absorption coefficients are depicted in fig. 4.4. Generally, the absorption coefficient increases for increasing photon energy. While for platinum oxide, no specific features are observed, for silver oxide a steep increase of absorption in the visible spectral range is observed. The onset of this absorption edge is located at \( 2.5 \pm 0.2 \) eV, explaining the yellow-greenish color of the silver-based TRC samples. This feature is also reproduced in the transmission spectrum of the Ag-based TRC as depicted in fig. 4.2 (b).

The mean absorption coefficients in the visible spectral range are \( \alpha_{\text{vis,Ag}\textsubscript{x}O} = 2.8 \times 10^4 \) cm\(^{-1}\) and \( \alpha_{\text{vis,PtO}\textsubscript{y}} = 2.6 \times 10^5 \) cm\(^{-1}\). For platinum oxide, this value coincides fairly well with the absorption coefficients extracted from the transmission measurements. In contrast, for silver

\(^3\)The oxygen flow was with 50 sccm identical to the optimal conditions for TRC, but the sputtering power was increased to 30 W in order to adapt the deposition rate to the larger thickness required for reliable determination of the optical constants.
oxide the ellipsometrically determined absorption coefficient is about one order of magnitude lower than the value extracted from the transmission measurements. If the ellipsometrically determined absorption coefficient was correct also for the TRC contacts, the devices would be much more transparent. Therefore, probably the optical constants of thick silver oxide layers are not similar to their thin counterparts indicating a microscopic difference e.g. of the stoichiometry, the structure, the density of the two different types of films. Nevertheless, it is promising to further investigate the optical properties of the silver oxide in dependence of the growth conditions in order to potentially transfer the advantageously low absorption of the thicker films to device-applicable thin contact layers.

4.1.1 Further optimization and outlook

Another mean to further optimize the transmittance of the TRC, is to use capping layers of sufficiently high conductivity but lower absorbance compared to the used metal layers. These requirements are fulfilled by transparent conductive oxides (cmp. sec. 5), e.g. ZnO doped with aluminium (AZO). In a first experiment, the metal layer was replaced gradually by the AZO. While the first sample exhibited the standard TRC structure, the second sample consisted of a half-in-thickness metallic capping layer and an additional AZO layer (grown by PLD at room temperature, 3 wt% - Al2O3 in ZnO-target, pO2 = 0.016 mbar, ≈ 100 nm thick). For the third sample, the silver oxide was capped only with AZO (identical growth conditions as for the second sample). Please note, that in order to deposit the AZO layer, the samples had to be transferred from the sputtering chamber to the PLD chamber, which includes exposure to air. The average values of the ΦB,eff and n as extracted from the IV-characteristics using thermionic emission theory are depicted in fig. 4.5. Obviously, the rectification degrades massively if AZO is used for the capping, as ΦB,eff drops by almost 0.3 V. Furthermore, the ideality factors reach
comparably large values, which further substantiates the contact performance degradation. The decrease by several orders of magnitude of the parallel resistance points towards the potential origin of the barrier lowering. As reported recently by Müller et al., droplet formation during growth of AZO potentially yields low barrier regions [Mül+11]. For the case of the ultra-thin TRC layers, these droplets probably penetrate the contact layer yielding a multitude of shunts. Therefore, in order to overcome this issue, other growth techniques, which avoid the droplet formation are required, e.g. eclipse-PLD or rf-magnetron sputtering. Especially, the subsequent growth of both, the silver oxide or platinum oxide contact layer and the TCO capping layer without vacuum break in a rf-magnetron sputter chamber appears worth further investigations.

Conclusively, by combining a silver oxide or platinum oxide layer with a capping layer consisting of gold or platinum, respectively, highly transparent rectifying contacts can be fabricated. While the achievable barrier heights are comparably similar, the transmittance of the Ag-based TRC exceeds that of the Pt-based counterpart. The typical mean transmittance (deposited on ZnO grown on sapphire substrate) in the visible spectral range is 70% (60%) for the Ag-based (Pt-based) TRC. The overall thickness for optimal performance of these combined layers is about 10 nm.

Figure 4.4: Absorption coefficient spectra of reactively sputtered Ag\textsubscript{x}O and PtO\textsubscript{y}.
Figure 4.5: Effective barrier height, ideality factor and parallel resistance of AgₓO-contacts for gradual capping replacement of Au by AZO. The error bars reflect the standard deviation.
4.2 Chemical analysis of the contact material

From the first report on oxidic high performance Schottky contacts to ZnO [ADM07] until today, several groups have continued this approach and demonstrated for different contact materials high rectification ratios and quite ideal behavior—at least compared to previous reports on zinc oxide based Schottky diodes [All+09; Fre+08; Laj+11; KKK10]. Previous investigations of the oxidational state of several contact materials using X-ray photo-electron spectroscopy (XPS), indicated the Pt- and Ag-based contacts to be predominantly oxidized [Laj08; Laj+09]. Nevertheless, only the surface oxidational state was accessible in these measurements, as the probing depth of common XPS-systems using Cu or Al X-ray tubes is typically below 3 nm for vertical photon emission. Unfortunately, the commonly applied method of sputter-etching in order to gain depth resolved information for thicker films is not applicable for these samples. The etching rate of oxygen is higher compared to the metal species yielding an apparent reduction of the contact material with increased probing depth [Laj08]. Nevertheless, in order to permit a deeper understanding of the functionality of these contacts, it is important to know whether the contact material is also oxidic in the vicinity of the interface. Therefore, further XPS experiments using hard X-ray radiation, which permits to investigate core level binding energies of atoms located several tens of nanometers below the sample surface [Rub+11], were conducted. A summary of the experimentally observed chemical shifts of silver and platinum containing samples is given in table 4.1.

Table 4.1: Binding energies, FWHM and chemical shifts of the different oxidational states of Ag and Pt. FO = foil, BU = bulk, SF = sputtered film, TD = thermal decomposition, SCA = surface corrosion in air.

<table>
<thead>
<tr>
<th>element</th>
<th>oxidation state</th>
<th>core level</th>
<th>$E_{\text{bind}}$ (eV)</th>
<th>FWHM (eV)</th>
<th>$\Delta E_{\text{bind}}$ (eV)</th>
<th>fabrication method / type</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>$^7\text{Ag}$</td>
<td>Ag ($3d_{5/2}$)</td>
<td>368.2</td>
<td>367.7</td>
<td>0.5</td>
<td>SF</td>
<td>[Abe+04]</td>
</tr>
<tr>
<td></td>
<td>$^2\text{Ag}^+$</td>
<td>368.9</td>
<td>1.15</td>
<td></td>
<td></td>
<td>TD</td>
<td>[WH94]</td>
</tr>
<tr>
<td></td>
<td>$^2\text{Ag}^+$</td>
<td>367.7</td>
<td>1.5</td>
<td>0.3</td>
<td></td>
<td>TD</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$^2\text{Ag}^+$</td>
<td>367.3</td>
<td>1.75</td>
<td>0.7</td>
<td></td>
<td>TD</td>
<td></td>
</tr>
<tr>
<td>Pt</td>
<td>$^7\text{Pt}$</td>
<td>Pt ($4f_{7/2}$)</td>
<td>70.98</td>
<td>72.25</td>
<td>1.27</td>
<td>SCA</td>
<td>[Bar78]</td>
</tr>
<tr>
<td></td>
<td>$^4\text{Pt}^+$</td>
<td>74</td>
<td>3.02</td>
<td></td>
<td></td>
<td>SCA</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$^0\text{Pt}$</td>
<td>71.2</td>
<td>2.2</td>
<td></td>
<td></td>
<td>TD</td>
<td>[PB84]</td>
</tr>
<tr>
<td></td>
<td>$^2\text{Pt}^+$</td>
<td>74.1</td>
<td>1.9</td>
<td>2.9</td>
<td></td>
<td>BU</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$^4\text{Pt}^+$</td>
<td>71.3</td>
<td>1.5</td>
<td></td>
<td></td>
<td>SF</td>
<td>[Ban+75]</td>
</tr>
<tr>
<td></td>
<td>$^2\text{Pt}^+$</td>
<td>72.25</td>
<td>0.95</td>
<td></td>
<td></td>
<td>SF</td>
<td></td>
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<tr>
<td></td>
<td>$^4\text{Pt}^+$</td>
<td>74</td>
<td>2.7</td>
<td></td>
<td></td>
<td>SF</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$^0\text{Pt}$</td>
<td>71.2</td>
<td>1.2</td>
<td></td>
<td></td>
<td>SF</td>
<td>[Hec+79]</td>
</tr>
<tr>
<td></td>
<td>$^2\text{Pt}^+$</td>
<td>72.4</td>
<td>2.4</td>
<td></td>
<td></td>
<td>SF</td>
<td></td>
</tr>
</tbody>
</table>

The chemical shift of silver core levels due to the oxidation is with $< 1$ eV comparably small (cmp. table 4.1). In order to verify this for the case of the contact material used in this
work, two samples are compared. The first one consists of a potentially metallic silver film sputtered in pure argon atmosphere and the second one comprises of a reactively sputtered potentially oxidized film. The respective spectra of both Ag $2p_{3/2}$ core levels are compared in fig. 4.6 (a), revealing no difference within the noise margin. It is noteworthy, that the spectra were recorded with a photon energy of 10 keV, yielding an integrated information of the entire deposited film (nominal thickness for these samples $\approx 5$ nm). Also, the investigation of Auger electrons as applied previously [Laj08] is inappropriate due to insufficient peak intensity. Thus, the acquisition of a depth profile of the oxidational state of silver oxide-based contacts is not possible. In contrast to silver oxide, for oxidized platinum a chemical shift of the core levels up to 3 eV is reported (cmp. table 4.1). This is confirmed in a similar experiment as previously described for silver (cmp. fig. 4.6 (b)), rendering this material promising for recording a depth profile of the oxidational state. Consequently, in the following only the Pt-based contact material is investigated in detail.

4.2.1 Preparation

For the investigations, hydrothermally grown zinc oxide single crystals (oxygen terminated, purchased from Crystec GmbH) were chosen. After annealing, these substrates exhibit a smooth surface as depicted in figure 4.7. Steps of half a c-lattice constant of zinc oxide can be observed. The rms-roughness is $\leq 0.15$ nm, which permits the formation of a reasonably
sharp interface in order to distinguish contact layer and zinc oxide with respect to the length scale of the XPS probing depth.

A layer of Pt was reactively sputtered with similar conditions as used for the TRC (cmp. sec. 4.1), except that the thickness of the oxidic layer was increased, which will be explained in the following. The samples were afterwards transferred in dry conditions to the ESRF in Grenoble, France. The experiments were carried out at the Spanish CRG X-ray beamline (BM 25B) in cooperation with J. Rubio-Zuazo and G. R. Castro. The samples were mounted on a molybdenum steel sample holder using silver conductive paste. The electrical connection of the sample surface and the sample holder was checked.

4.2.2 General considerations

Electrons created by incident X-ray photons are subjected to elastic and inelastic scattering. While elastic scattering events only change the trajectory of the electrons, inelastic scattering events cause the involved electrons to be "lost" for photoelectron-spectroscopy, as their initial kinetic energy is changed. The respective length scale is denoted inelastic mean free path $\lambda_{\text{IMFP}}$ and defined as: "The average of distances, measured along the trajectories, that particles with a given energy travel between inelastic collisions in a substance." [RC11]. The photoemission intensity is proportional to $\exp(-d/(\lambda_{\text{IMFP}} \cos(\theta)))$, where $d$ denotes the depth within the probed layer and $\theta$ the angle between recorded electron emission and surface normal (here: $\theta = 15^\circ$). Due to the significant dependence of $\lambda_{\text{IMFP}}$ on the kinetic energy of the electrons, depth resolved measurements can be realized if the beam energy can be tuned in a sufficiently wide range. While for some materials experimental data on $\lambda_{\text{IMFP}}$ is available (e.g. for Au [RC11]), for the majority of substances predictive equations as proposed by Tanuma et al. [TPP94] or Gries [Gri96] have to be applied. According to the TPP-2M formula, which is given for energies

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\*The effect of elastic scattering on the mean free path was neglected. Especially for lower kinetic energies, the effective attenuation length (EAL) would have to be considered.
Figure 4.8: X-ray reflectivity measurement for film thickness determination at a beam energy of 9 keV ($\lambda = 1.38\text{Å}$). The inset depicts the assumed layer stack model and the resulting fit parameters.

$E$ (in eV) by [TPP03]:

$$\lambda_{\text{IMFP}} = \frac{E}{E_p^2[\beta \ln(E) - (C/E) + (D/E^2)]} \text{ (in Å)}$$

with:

$\beta = -0.10 + 0.944 \left( E_p^2 + E_g^2 \right)^{-1/2} + 0.069 \rho^{0.1}$

$\gamma = 0.191 \rho^{-1/2}$

$C = 1.97 - 0.91U$

$D = 53.4 - 20.8U$

$U = N_v \rho / M = E_p^2 / 829.4$

$E_p = 28.8 \sqrt{N_v \rho / M}$

$\lambda_{\text{IMFP}}$ can be calculated with decent accuracy for kinetic energies up to 30 keV, as recently reported [TPP11]. Here, $N_v$ is the number of valence electrons per molecule, $M$ is the molecular weight (in g/mol), $\rho$ is the density (in g/cm$^3$) and $E_g$ denotes the band gap (in eV). As the density of the layer is not well known yet, we will consider first X-ray reflectivity measure-
ments which allows to determine this parameter aside from other values related to the sample structure. The respective data is depicted in fig. 4.8, recorded at a beam energy of 9 keV, which corresponds to a wavelength of $\lambda = 1.3776 \, \text{Å}$. The reflectance oscillations indicate the presence of the thin film on the ZnO substrate, as expected. The absence of overtones in the oscillations indicates the thin film to consist more or less of only a single layer. Thus, the occurrence of a sharply separated metallic layer of sufficient purity and thickness ($> \approx 2 \text{ nm}$) at the interface to the zinc oxide can be excluded at this point. Nevertheless, a metallic Pt layer of about 1 nm thickness was additionally simulated and the data could be described adequately. But as the number of parameters is increased significantly, it is considered to contain ambiguity and thus not shown. From the angular period of the intensity modulations, the film thickness can be deduced. At first order, Bragg’s law can be applied. Using a more elaborated approach including a layer stack model, as implemented in the freely available IMD extension of the XOP (X-ray Oriented Programs) software package, more parameters become accessible [RD04; RD11; Win98]. The optical constants of the overlayer, assumed to consist of PtO$_2$ only, are modeled using the density as free parameter. The ZnO optical constants are taken from the database of the software. Both interfaces are modeled using error functions and the roughness is modeled by a single fit parameter $\sigma$ for each interface. Furthermore, the thickness of the overlayer is used for fitting. The layer stack model yielding the best fit to the measured data is visualized in the inset of fig. 4.8. The interface roughness between substrate and overlayer is in good accordance with the previously measured rms-roughness of the ZnO substrates. The roughness of the TRC contact layer is increased compared to the substrate. The thickness of the contact layer is determined to be about $18 \pm 0.2 \text{ nm}$. The best fit is obtained for a density of the overlayer of 11.8 g/cm$^3$, which is similar to the literature value of hexagonal PtO$_2$ [Dep12a]. Nevertheless, a lower density of 10.2 g/cm$^3$ is also reported for PtO$_2$ [Dep12b]. Thus, in case of the validity of the lower density value, the increased density might indicate the presence of metallic Pt in the overlayer ($\rho_{\text{Pt}} = 21.4 \text{ g/cm}^3$ [Dep12c]).

Reconsidering now the calculation of the IMFP, the contact material is assumed to consist only of PtO$_2$. Hence, $N_\nu = 22$ [TPP03], $M = 227 \text{ g/mol}$, $\rho = 11.8 \text{ g/cm}^3$ and $E_g = 1.2 \text{ eV}$ [Nef+96] are used. The resulting spectrum of $\lambda_{\text{IMFP}}$ is depicted in the inset of fig. 4.9. Within the experimentally accessible kinetic energy range (for a binding energy of about 2 keV e.g. Pt 3d$_{3/2}$ core level), $\lambda_{\text{IMFP}}$ increases from about 6 nm to about 12 nm. The respective exponential characteristic of the contribution of different sample depths are depicted in fig. 4.9 for the extrema of the accessible kinetic energies $^5$. Thus, according to the determined thickness of the overlayer of about 18 nm, it is obvious that the contribution of the interfacial region can be changed by about a factor of three within the accessible kinetic energy range. At the same time, the substrate reference signal, which is urgently required for energy normalization, can still be recorded as a sufficient part of the signal originates from there. At this point it is worth

$^5$Here, only a homogeneous material is considered.
Figure 4.9: Depth dependence of the contribution to the elastic peak intensity for the highest and the lowest kinetic energy used in this work. The dashed line indicates the thickness of the platinum oxide film. The inset depicts the calculated inelastic mean free path within PtO$_2$ for different kinetic energies.

mentioning, that XRR and XPS measurements were conducted within the same setup at the same position of the sample assuring similar sample conditions to apply for both measurements.

4.2.3 Depth profiling of the oxidational state

For photon energies between 9 and 16 keV, varied in steps of 1 keV, the overlayer-related Pt 3d$_{3/2}$ core level and the substrate-related Zn 2s core level were recorded. While the overlayer level is required for the depth profiling itself, the substrate level permits to calibrate the beam energy. Moreover, the ratio of both peak areas permits to validate the previously postulated interface sensitivity and to determine the overlayer thickness, independently. The latter relation is depicted in fig. 4.10. The depicted ratios are calculated from the recorded spectra, which were normalized by the mean beam current during the measurement, Scofield’s photoionization cross sections [Sco73] ($\sigma_X$ for a core level X) and the analyzer transmission function $\Gamma$ [Rub12]. As expected, the contribution from the substrate increases with increasing photon energy. The ratio between the substrate and the overlayer peak area can be modeled using the theoretical peak intensity, e.g. as given in [RFC10], assuming identical angular
Figure 4.10: Beam energy dependence of the peak area of the substrate Zn 2s level with respect to the overlayer Pt 3d_{3/2} level. The dashed line is a fit using equation 4.2.

anisotropy for both photoemission processes:

\[
R = \frac{\sigma_{\text{Zn 2s}}(\hbar\nu)\Gamma(\hbar\nu - E_{\text{bind}}, \text{Zn 2s})E\text{AL}_{\text{ZnO}}(\hbar\nu - E_{\text{bind}}, \text{Zn 2s})}{\sigma_{\text{Pt 3d}_{3/2}}(\hbar\nu)\Gamma(\hbar\nu - E_{\text{bind}}, \text{Pt 3d}_{3/2})E\text{AL}_{\text{PtO}_2}(\hbar\nu - E_{\text{bind}}, \text{Pt 3d}_{3/2})} \times \\
\times \exp\left(\frac{E\text{AL}_{\text{PtO}_2}(\hbar\nu - E_{\text{bind}}, \text{Zn 2s})\cos\theta}{E\text{AL}_{\text{PtO}_2}(\hbar\nu - E_{\text{bind}}, \text{Pt 3d}_{3/2})\cos\theta}\right) \\
\times \left[1 - \exp\left(\frac{-d_{\text{PtO}_2}}{E\text{AL}_{\text{PtO}_2}(\hbar\nu - E_{\text{bind}}, \text{Pt 3d}_{3/2})}\cos\theta\right)\right].
\]  

(4.2)

Here, EAL_Y denotes the effective attenuation length of electrons within a substance Y, which is approximated in the following by \(\lambda_{\text{IMFP}}\) calculated using equation 4.1. The binding energy of the core level X is given by \(E_{\text{bind},X}\). By fitting equation 4.2 to the determined peak area ratios, an overlayer thickness of \(d = 17 \pm 2\) nm was extracted, which is in good accordance to the XRR value of 18 nm. This indicates, that no significant diffusion of Pt into the ZnO occurs, which is consistent with previous Auger measurements [HRe08].

The zinc core level spectral position was used to determine the photon energy and to correct eventual charging of the sample. Therefore, the zinc level was assumed to consist of only a single component, which is a good approximation due to the very low chemical shifts (< 0.5 eV) reported for zinc [Sch73]. The accordingly shifted Pt spectra are depicted in fig. 4.11 (a). Obviously, the peak center is still neither constant nor at least monotonically changing for changing photon energy, thus a remaining uncertainty of the photon energy e.g. due to
charging of the sample has to be considered. The depth profile of the oxidational state of the contact material is generated by fitting the spectra for each photon energy. As for Pt, three oxidational states (involving Pt and O only) are commonly reported (cmp. table 4.1). Thus, each spectrum is generally fitted by the sum of three Voigt profiles. Each profile contains four parameters: peak height, energetic position, Gauss FWHM, Lorenz FWHM. Aside to these twelve parameters, the background due to inelastic scattering has to be parametrized as well, requiring another three parameters (constant offset, Shirley-parameter and parabolic contribution to account for downward kink of background for increasing binding energy). Therefore, in order to avoid ambiguity the following constraints were included for reducing the number of free fitting parameters:

- the FWHM is similar for all oxidational states
- the Gauss FWHM is given by \( \Delta_{\text{Gauss}} = \sqrt{\Delta_{\text{mono}}^2 + \Delta_{\text{analyz}}^2} \), with a monochromator resolution of \( \Delta_{\text{mono}} = (1.5 \ldots 2) \times 10^{-4} \times h\nu \) and an analyzer resolution of \( \Delta_{\text{analyz}} = 1.5 \text{ eV} \) [Rub12].
- the Lorentz FWHM of the Pt 3d\(_{3/2}\) core level is fixed at 2.65 eV, which was the lower
Figure 4.12: Beam energy dependence of the relative areas of the Pt\(^0\) and the Pt\(^{2+}\) component of the Pt 3d\(_{3/2}\) core level. The dashed line is a linear fit.

bound observed in multiple measurements of metallic Pt layers on zinc oxide.

- the chemical shift for the Pt\(^{2+}\) and Pt\(^{4+}\) state is fixed at +1 eV and +3 eV, respectively (cmp. table 4.1)

Thus, for each spectrum only the background parameters, the energetic position of the Pt\(^0\) level and the intensities of all three components was left variable for fitting. The resulting energetic position of the Pt\(^0\) core level is depicted in fig. 4.11, reproducing the already mentioned uncertainty in the calibration of the photon energy. Remarkably, the mean value is increased by about 1 eV compared to the literature value of 2202 eV for the Pt 3d\(_{3/2}\) level [TV12]. This can be due to aging-related changes of the analyzer work function [Rub12] or to a contact formation related shift of the zinc core level [Cop+05]. For all spectra, the respective contribution of the Pt\(^{2+}\) state is vanishing. The relative areas of the remaining Pt\(^0\) and Pt\(^{4+}\) state are depicted in fig. 4.12, revealing a significant increase of the metallic state for increasing photon energy. The peak area is proportional to the concentration of the respective component in the sample.

Conclusively, the contact layer consists predominantly of platinum oxide. Nevertheless, a small volume fraction of the contact material is metallic platinum. This fraction is inhomogeneously distributed—the concentration of metallic platinum increases towards the zinc oxide interface.
Possibly, the zinc at the surface is oxidized, while the Pt is reduced. Such an effect will probably only occur in the vicinity of the interface, while the rest of the contact material will remain oxidic as deposited. This effect is a possible explanation for the compliance of oxidic contact behavior with thermionic emission theory [All+09].
4.3 From single crystals to amorphous thin films

In the following section, the physical properties of the potential barrier being the origin of the TRC functionality are investigated using the example of silver based TRC. At the same time, it is demonstrated that TRC are also applicable to amorphous semiconductors.

4.3.1 Sample preparation

Four sets of samples were prepared. They consist of amorphous, room-temperature sputtered gallium-indium-zinc oxide on glass substrates, high temperature grown zinc oxide on sapphire substrates and hydrothermally grown zinc oxide single crystals (sc) (Zn- and O-face). Hydrothermally grown, oxygen-terminated and zinc-terminated ZnO single crystals (purchased from Crystech GmbH) were processed in the as-received state and in an annealed state suitable for epitaxy (850°C, 700 mbar O₂, 60 min) [Wen+07b]. For the heteroepitaxial sample, an about 200 nm thick ZnO:Al (3 wt% Al in target) film, serving as back-contact layer [Wen+06] and subsequently an about 1 µm thick nominally undoped ZnO film was deposited on an as-received 2 inch in diameter a-plane sapphire substrate by PLD. The oxygen partial pressure and the growth temperature were 0.04 mbar and 600°C, respectively. The amorphous 225 nm thick GaInZnO layer was deposited at room temperature using radio-frequency magnetron sputtering (fabricated by P. Barquinha at CENIMAT, FCT-UNL, Caparica, Portugal); prior to the contact deposition the film was annealed for one hour in air at 150°C. The circular Schottky contacts (diameter between 450 and 750 µm) and the surrounding Ohmic contacts were defined by standard photo-lithography. The Ohmic gold contacts were deposited by DC-sputtering at room temperature, for the hetero-epitaxial sample the direct connection to the ZnO:Al back-contact layer was ensured (cmp. (i) of fig. 4.14 (b)). The Ag-based TRC were deposited according to the previously determined optimal conditions (cmp. sec. 4.1). The samples were mounted and contacted on TO-18 sockets, including an 90°C - 45 minute annealing step in air to harden the epoxy resin used for bonding the connecting wires.

4.3.1.1 Sample structure and morphology

The surface morphologies of the investigated samples, as revealed by AFM, are depicted in fig. 4.13. The Zn-terminated single crystal exhibits a comparably rough topology in the as-received state, which is probably due to surface adsorbates and polishing damage (fig. 4.13 a). After annealing the surface recovers and terraces are formed, separated by steps of typically one c-lattice constant (fig. 4.13 b). The oxygen-terminated single crystal exhibits in the as-received state a flat surface (RMS-roughness= 0.13 nm) (fig. 4.13 c); the scratches stem from the polishing process. After annealing, the surface of the O-face terminated ZnO single crystal also exhibits terraces with a step-height of typically half of the c-lattice constant of ZnO (fig. 4.13 d). Similar results have been obtained previously [Wen+07b; Gra+07]. The hetero-epitaxially
grown ZnO-film exhibits a grainy surface with a RMS-roughness of 3.4 nm (fig. 4.13 e). The GaInZnO exhibits a flat and granular surface with a RMS-roughness of 0.31 nm (fig. 4.13 f). The RMS-roughness values are summarized in table 4.2.

The XRD rocking-curves of the ZnO (002)-reflex are depicted in fig. 4.14 (a). As expected, the single crystalline substrates exhibit FWHM-values around 100 arc-seconds in the as-received state, compared to 850 arc-seconds of the hetero-epitaxial ZnO film (see table 4.2). The annealing of the ZnO substrates reduces the FWHM significantly to about 30 arc-seconds, indicating that both the distribution of the c-lattice constants in the sample and the tilt-distribution of the crystallites narrow. Previous investigations showed, that the chemo-mechanical polishing of the substrates causes a surface layer of deteriorated crystalline quality, which is removed by the annealing [Cho+05]. Thus, the bulk is probably not significantly affected by the annealing. In contrast, for the GaInZnO-sample no X-ray reflex was detected (also in the wide angle scan, not shown here), which indicates at least X-ray amorphous phase.
Table 4.2: RMS-roughness determined by AFM, FWHM of the rocking curve obtained by XRD, net doping density for zero bias calculated from CV-measurements and free electron density and mobility extracted from room temperature Hall-effect measurements.

<table>
<thead>
<tr>
<th>Sample</th>
<th>ZnO Sc (nm)</th>
<th>ZnO O-face (nm)</th>
<th>ZnO thin film (nm)</th>
<th>GaInZnO (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn-face</td>
<td>2.3</td>
<td>0.25</td>
<td>0.13</td>
<td>0.17</td>
</tr>
<tr>
<td>annealed</td>
<td>0.17</td>
<td>0.17</td>
<td>3.4</td>
<td>0.31</td>
</tr>
<tr>
<td>O-face</td>
<td>0.13</td>
<td>0.17</td>
<td>3.4</td>
<td>0.31</td>
</tr>
<tr>
<td>annealed</td>
<td>0.17</td>
<td>0.17</td>
<td>3.4</td>
<td>0.31</td>
</tr>
</tbody>
</table>

Figure 4.14: (a) XRD rocking-curve of the samples; the FWHM-values are summarized in table 4.2. (b) Contact geometry applied for the hetero-epitaxial sample (i) and for all other samples (ii).

4.3.2 Electrical Characteristics

4.3.2.1 Room temperature characteristics

The room temperature IV-characteristics, measured under atmospheric conditions, are depicted in fig. 4.15; the forward currents for large positive bias differ significantly indicating different series resistances of the contacts. On the one hand, the current path is different for the investigated samples. For the hetero-epitaxial sample, the ZnO:Al back-contact layer serves as Ohmic contact (cmp. fig. 4.14(b) (i)). Hence, the series resistance is low, as the Ohmic contact layer (ZnO:Al) is separated only by the about 1 µm thin zinc oxide layer from all positions of the Schottky contact. For all other samples both Schottky contact and Ohmic contact lie on the top (cmp. fig. 4.14 (b) ii)) and are separated by about 25 µm, as defined by the photolithographic masks. Thus, the mean current path through the semiconductor between both electrodes, taking into account the contact diameter of several hundred microns, is about two orders of magnitude longer compared to the hetero-epitaxial sample.

On the other hand, the conductivities of the semiconductor materials are different, as room-
temperature Hall-effect measurements reveal (cmp. table 4.2). Due to the annealing, the conductivity of the single crystals drops, which might originate in a reduction of shallow defect levels like $\text{ZnI}^{[\text{Laj+10}]}$. Furthermore Li is omnipresent in hydrothermally grown ZnO single crystals and acts as compensating defect $[\text{Vin+10}]$; the annealing might affect the local Li concentration. The net doping density extracted from $CV$-measurements is given in table 4.2. The Zn-terminated samples are a good example for annealing induced compensation. The free electron density decreases due to the annealing by about four orders of magnitude, whereas the net doping density at zero bias remains almost unchanged. For the annealed O-face ZnO sample only an upper limit of the net doping density can be extracted from $CV$ measurements, the lower limit being given by the electron density extracted from Hall-effect.

The contact parameters were extracted by fitting the forward $IV$ characteristics with equation 2.3 and 2.6 are summarized in table 4.2. The mobility measured by Hall-effect and the net doping density calculated from $CV$-measurements were used. For the hetero-epitaxial sample, due to the highly conductive back contact layer, a Hall-effect measurement of the ZnO-layer is not possible. Here, according to measurements on ZnO-layers on sapphire fabricated under similar conditions in the semiconductor physics group of Universität Leipzig a mobility of $100 \text{ cm}^2/\text{Vs}$ was assumed. The effective barrier heights at room temperature for all diodes range between 0.87 V and 0.94 V. For both crystal terminations, the effective barrier heights of the Schottky contacts on bulk ZnO are almost similar in the as-received state and increase significantly due the annealing process.

![Figure 4.15: Current-voltage characteristics of the TRC at room temperature.](image-url)
The ideality factors of all samples range at room temperature between 1.2 and 2.2. Such values indicate already a significant inhomogeneity of the barrier, as the ideality factor describes the voltage dependency of the barrier height [WG91]. Both the Schottky effect and the consideration of thermionic emission/ diffusion theory alone only weakly increase the ideality factor, depending on the net doping concentration, to less than 1.1 for an ideal contact.

The mean barrier height at room temperature, extracted from CV-measurements, is given also in table 4.3 for the hetero-epitaxial sample and the as-received Zn-face sample. For all other samples, the extracted barrier heights depended significantly on the applied measuring frequency due to high series resistance-related cut-off or freeze-out of dominating donor levels in the accessible frequency range. As expected for Schottky contacts with an inhomogeneous barrier, the mean barrier heights of more than 1.2 V are larger than the effective barrier heights. Similar values for the mean barrier heights of opaque Ag$_x$O Schottky contacts on ZnO were reported [Laj+09; ADM07]. Using equation 2.15, the width of the barrier height distribution was determined to be 125 mV and 154 mV, which is in the same range as for opaque contacts, consisting of the same and of different contact materials [Wen+06; Laj+09].

4.3.2.2 Temperature dependent characteristics

More access to the barrier properties is provided by the temperature dependent IV-characteristics, depicted for the temperature range between 120 K and 300 K in fig. 4.16. Aside from barrier properties, also bulk properties affect the IV temperature evolution and should be discussed first. The temperature dependence of the forward current is more pronounced for the annealed single crystalline ZnO samples compared to the as-received ones. This indicates a change of the dominating donor level to a defect of higher activation energy by the annealing process.

The thermal activation energies of the series resistance was extracted with the assumption of $R_S \sim \exp (E_A/k_B T)$. In case of the as-received O-face ZnO sample, two regimes dominated by different defect levels were observed: at higher temperatures a deep level $E_A = 320 \pm 13$ meV dominates the temperature dependence of the series resistance, at lower temperatures a shallow level ($E_A = 56 \pm 2$ meV) freezes out. For the annealed O-face sample only a single regime was observed ($E_A = 2.1 \pm 0.2$ eV), similarly to the [annealed] Zn-face sample (23 $\pm$ 3 meV [361 $\pm$ 2 meV]), respectively.

Due to the temperature dependence of the mobility, these activation energies do not permit to directly conclude on the underlying defect states. Nevertheless, the mobility of comparable samples typically increases not more than one order of magnitude in the investigated temperature range [Vin+10; Kas+07]. Assuming a linear decrease of the mobility by one order of magnitude in the temperature range between 120 K and 300 K, the maximum discrepancy between the activation energies of the series resistance and carrier concentration can be estimated. The resulting deviations, relative to the values extracted from fitting $R_S(T)$, are
Figure 4.16: Temperature dependence of the current-voltage characteristics.
−25%/−11% (−10%) for the as-received (annealed) O-face sample and −18% for the annealed Zn-face sample, respectively. Several defect levels of similar activation energy are reported in the literature [Laj+10; Vin+10; Wen+07a].

For the as-received ZnO Zn-face sample, the temperature dependence of the series resistance vanishes after applying the correction of the temperature dependence of the mobility, indicating that possibly no freeze-out occurs in the observed temperature range. For the hetero-epitaxial sample no significant thermal activation of the series resistance could be observed, indicating both that the temperature dependence of the mobility affects the conductivity and that the dominating donor exhibits a comparably small activation energy yielding no freeze-out until 120 K. For the GaInZnO-sample, the extracted activation energy of the series resistance is $170 \pm 20$ meV, a defect level having a similar activation energy has been reported previously [Ers10]. Nevertheless, recent results indicate that for TAOS a percolation conduction model has to be considered especially for low net doping densities [Tak+05]. The conductivity is expected to depend on temperature as $\sigma \propto \exp(-AT^4)$; the fit of the temperature dependence of $R_S(T)$ yields $A = (153\pm7) K^{-4}$. As the accuracy of the fit within the investigated temperature range is comparable for both models, the dominating effect cannot be extracted here.

In the following, similarly to the procedure applied at room temperature, the $IV$-characteristics are fitted using equation 2.3. In case of the hetero-epitaxial sample and both as-received single crystalline samples, the ideal diode equation is not sufficient to describe the $IV$-characteristics in the entire voltage range investigated.

**Figure 4.17:** Temperature dependence of the effective barrier height and the ideality factor.
Figure 4.18: Correlation between mean barrier height and barrier distribution width for Schottky contacts fabricated (a) on n-ZnO (data from this work and [Laj08; Laj+09; KKK10; Wen+06; Mue11]) and (b) on various semiconductors using various contact metals (data from this work and [Cim+09; SAR11; Güll+07; HVK01; Bib03; Dök11; SA09; Ash+09; Aha+03; McC+96; Aca+04; Kar+04; GTY02; Mam09; WG91; Kim+11; Zhu+00b]). The dotted lines are linear fits through (0/0).

On the one hand, the increase of the reverse current for decreasing temperature by up to three orders of magnitude for the as-received ZnO Zn-face sample and the hetero-epitaxial sample indicate the formation of a parallel current path, probably related to vacuum-induced surface conduction. The pressure in the cryostat decreases with decreasing temperatures and thus the parallel current along the surface increases. The effect of an increased conductivity towards the surface, based on electron accumulation layers, and the vacuum-induced occurrence of this effect, is well known for zinc oxide [Kas+07; HK69; LCS08; Sch+06; Wen+10b]. Nevertheless, it has to be mentioned that the voltage dependence of the current in the respective regimes is not exactly linear indicating the presence of other transport mechanisms, i.e. thermionic field emission.

On the other hand, the influence of multiple barriers in the contacts is observed in the forward current regime of the hetero-epitaxial sample and both as-received single crystalline ZnO samples (cmp. fig. 4.16) [Müll+11].

Nevertheless, the evaluation of the IV-characteristics using equation 2.3 is possible, if a sufficient part of the IV-characteristic is dominated by only one of the barriers and the parallel
current is purely ohmic or sufficiently small. This is the case for the hetero-epitaxial sample and the as-received ZnO O-face sample. In contrast, for the as-received Zn-face sample, the overlap of the thermionic emission current and the parallel current require to model the parallel current. Due to the exponential voltage dependence in the forward bias shunt regime, it was assumed that the parallel current behaves like a second diode. It was modeled according to equation 2.3 with different barrier height and ideality factor and identical series and parallel resistance compared to the primary diode. Due to the more involved method required for the evaluation of the as-received Zn-face sample, the uncertainty of the calculated values is increased.

The effective barrier heights and ideality factors, extracted from the IVT measurements using formula 2.3, are summarized in fig. 4.17. In general, the effective barrier height decreases with decreasing temperature and the ideality factor increases, as expected for Schottky contacts that exhibit inhomogeneous barriers. Therefore, using formula 2.15 and 2.19, the mean barrier height $\Phi_{B,m}$, the width $\sigma$ of the barrier height distribution and the respective voltage dependencies $\rho_\Phi$ and $\rho_\sigma$ were extracted and are summarized in table 4.3. For the single crystalline samples, the mean barrier heights, as previously observed for the effective barrier heights, are significantly increased by the annealing process. Taking into account the profound improvements of the morphological quality, as revealed by AFM, the impact on the barrier height appears plausible. Also the width of the barrier height distribution increases slightly due to the annealing, but the ratio $\sigma/\Phi_{B,m}$ remains constant. The mean barrier height on the Zn-face is higher compared to the O-face sample, which is in accordance to previous investigations on opaque Ag$_x$O Schottky contacts fabricated also on hydrothermally grown ZnO [ADM07].

Using the mean barrier heights, the barrier lowering due to the Schottky effect $\Delta \Phi_{if}(RT)$ was calculated for zero bias, to be several ten millivolt depending on the net doping density of the samples (Cmp. table 4.3).

Except for the annealed Zn-face ZnO sample, for which the increased uncertainty of the deter-
Figure 4.19: Temperature dependence of (a) the effective and mean barrier height of the contact on the hetero-epitaxial sample extracted by IV- and CV-measurements, respectively, and (b) the width $\sigma$ of the Gaussian barrier height distribution extracted from the difference of mean and effective barrier height. The red dash-dotted line indicates $\sigma$ extracted from the temperature dependence of the effective barrier-height only; the grey box indicates the standard error of $\sigma$.

mined contact parameters was already mentioned, the mean barrier heights are between about 1.1 V and 1.3 V for all samples and the barrier distribution width ranges between 110 mV and 130 mV. Unexpectedly, the barrier distribution does not critically depend on the crystallinity of the samples. Especially, the comparison between amorphous and hetero-epitaxial samples reveals no significant difference. This is another proof of the weak changes occurring in TAOS band structure upon amorphization compared to the crystalline phase (cmp. sec. 2.1.2). Nevertheless, the similarity of the barrier distribution parameters indicates a common origin of the inhomogeneity.

The barrier potential fluctuations originate potentially either from the bulk of the semiconductor, the interface or the contact layer. As the crystallinity, the constituents, the unintentionally included impurities, the defects (as far as accessible from the temperature dependence of the series resistance), the surface termination and the surface morphology of the samples are very different, the semiconductor bulk and the interface are unlikely to cause the inhomogeneity. Therefore, a possible explanation are local variations of the work function of the contact material either due to fluctuations related to the nano-crystallinity of the contact material (cmp.
fig. 4.3), due to the partial interface amorphization or due to varying stoichiometry of the contact material (cmp. section 4.2). Similar barrier inhomogeneities were also observed for Schottky-contacts on hetero-epitaxially grown ZnO [Wen+06] consisting of thermally evaporated metallic Pd (which is polycrystalline, as indicated in a previous work of the same author [Wen+04]).

Remarkably, the ratio of mean barrier height and barrier height distribution width is constant even for different contact materials, deposited with different growth methods on zinc oxide (cmp. fig. 4.18 (a)). And even more surprising is the fact, that this ratio is similar for a wide variety of semiconductors as depicted in fig. 4.18 (b). Such a correlation of both distribution parameters is not expected for a Gaussian distribution. For other distribution functions, e.g. the log-normal distribution, such correlation was reported [Hor95]. Thus, the correlation possibly indicates the barrier inhomogeneities to be distributed in a non-Gaussian way. In general terms of asymmetry, this is supported by several spacial histograms of the effective barrier height extracted using BEEM [Zhu+00a; PAS93; Hor95]. Despite the fact, that some authors characterize the histograms by a Gaussian distribution, often the data exhibit an asymmetry, which is not expected for Gaussian-distributed barrier heights. A practical consequence of this asymmetry is the nonlinear relation between $\Phi_{B,\text{eff}}$ and $T^{-1}$, which was already observed by several authors and treated for example by a double-Gaussian distribution [Jia+02; Laj08].

Using an asymmetrical distribution like the log-normal distribution, a nonlinear dependence of the effective barrier height on the reciprocal temperature can be observed, too. Nevertheless, the temperature dependence of the effective barrier height of the TRC in this work, which follows quite well the relation expected for a Gaussian distribution, cannot be described even approximatively considering a log-normal distribution. The resulting barrier distribution would be unreasonably wide and the maximum of the distribution is located at more than 3 eV, which is unphysical. Conclusively, the effective barrier heights possibly obey an asymmetrical distribution, which is not the log-normal distribution for the contacts investigated in this work.

Nevertheless, there are reports of contacts for different material systems, which do not obey the latter correlation and which exhibit a temperature-independent barrier height and ideality factor [OWE81; Hat+02; SJC99]. This indicates the possibility to control the origin of the fluctuations. Further investigations have to be carried out in order to identify the exact nature of the contact material inhomogeneity.

The voltage dependency coefficient of the barrier distribution width $\rho_\sigma$ has been found to be negative for all contacts, implying a narrowing of the barrier distribution for positive bias and a broadening for reverse bias. The narrowing effect has profound impact on the $IV$-characteristics, despite $\rho_\sigma$ ranging only between about $-10$ mV/V and $-30$ mV/V. The effective barrier height is, not considering the voltage dependency of the mean barrier height $\rho_B$, lowered by several tens of millivolt per volt of applied reverse bias according to equation 2.15.

$^6$BEEM=ballistic electron emission microscopy.
The voltage-dependent saturation current therefore increases about one up to several orders of magnitude per volt of applied reverse bias. The respective increase of the reverse current with increasing reverse bias was clearly observed, e.g. for the as-received or the annealed ZnO O-face samples (cmp. fig. 4.15). A reliable extraction of $\rho_\Phi$ was in most cases not possible, as the uncertainty of the fit indicates (see table 4.3). Especially the large absolute values of $\rho_\Phi$ for the ZnO Zn-face samples are not plausible, as they would yield a dramatic change of the effective barrier height already within the investigated voltage range yielding several orders of magnitude higher or lower current flow than observed. Conclusively, the correlation-induced uncertainty of the Zn-face sample’s ideality factors hinders the precise determination of the mean barrier voltage coefficients. A plausible range for $\rho_\Phi$, complying with the measured data, is deduced to be between 0.01 and 0.08.

For the hetero-epitaxial sample, the mean barrier height extracted from CV-measurements is compared to the effective barrier height for the investigated temperature range (cmp. fig. 4.19 (a)). Generally, the mean barrier height is larger than the effective barrier height as expected for inhomogeneous barriers. The mean barrier height is almost constant at about 1.35 V for low temperatures and decreases slightly to about 1.2 V towards room temperature. The temperature dependence of the barrier distribution width, extracted from the difference of $\Phi_{B,m}$ and $\Phi_{B,eff}$ using equation 2.15, is depicted in fig. 4.19 (b). The latter values deviate at most by about 10% from the distribution width, which was calculated using the temperature dependence of the effective barrier heights only. Thus, the data is almost consistent with the assumed Gaussian barrier height distribution. Nevertheless, the observed minor discrepancy possibly originates from deviations from the Gaussian distribution.
4.4 Application of TRC in UV-photo-detectors

In order to detect UV light, while being blind to visible light, wide band gap semiconductors like ZnO are required. To achieve a high rejection ratio between UV and visible light, additionally a low trap density is needed to avoid sub-band gap absorption. Further important figures of merit are the external quantum efficiency

$$\eta_{\text{ext}} = \frac{|I_{\text{ph}}| / q A_{\text{opt}}}{(P/h\nu)} \quad (4.3)$$

and the responsivity $R = \frac{\eta_{\text{ext}}}{h\nu}$. Depending on the type of the photo-detector, $\eta_{\text{ext}}$ and $R$ may be enhanced by gain mechanisms, which are in most cases related to an external bias. Previous reports of photo-detectors based on zinc oxide and related materials are summarized in Table 4.4. Notably, only very few reports on fully transparent photo-detectors exist. As TRC

| Table 4.4: Characteristic properties of ZnO-based photo-detectors. Abbreviations: SB= Schottky barrier; MSM= metal-semiconductor-metal; nip= n-semiconductor-insulator-p-semiconductor. |
|---|---|---|---|---|---|---|---|
| substrate | type | electrode | Material | $\eta_{\text{ext}}$ (A/W) | $R$ (V) | UV-VIS Ratio | Ref. |
| opaque devices | | | | | | | |
| ZnO | SB | Pt | 0.63 | 0.185 | - | - | [End+07] |
| ZnO | MSM | Al | - | 400 | 5 | > 100 | [Liu+00] |
| ZnO | MSM | Ag | - | 1.5 | 5 | > 1000 | [Lia+01] |
| ZnO | MSM | Ni | 0.24 | 0.09 | 1 | > 100 | [You+06] |
| ZnO | MSM | Au | - | 30 | 3 | 10000 | [Liu+07] |
| ZnO | MSM | Au | - | 160 | 10 | - | [Ang+07] |
| MgZnO | MSM | Au/Cr | - | 0.37 | 5 | - | [Tab+10] |
| MgZnO | SB | Au | - | 173 | -1.5 | > 100000 | [Tab+10] |
| MgZnO | MSM | Au/Cr | - | 1200 | 5 | > 10000 | [Yan+01] |
| MgZnO | MSM | Au | - | 0.0001 | 10 | 1000 | [Ju+08] |
| MgZnO | MSM | Au | - | 0.0054 | 0.0012 | 2 | > 1000 | [Jia+08] |
| MgZnO | SB | Pt | 0.17 | 0.034 | 0 | > 1000 | [End+08] |
| MgZnO | MSM | - | 1.8 | 4 | > 1000 | [Zha+11] |
| fully transparent devices | | | | | | | |
| ZnO | SB | PEDOT:PSS | 1 | 0.3 | 0 | 1000 | [Nak+08b] |
| MgZnO | SB | PEDOT:PSS | > 0.9 | 0.3 | 0 | > 100 | [Nak+08a] |
| ITO/ZnO/NiO | nip | - | $\approx 0.003$ | $\approx 0.001$ | -5 | > 10 | [WVN07] |
| ZnO | SB | PtOx(Ag$_x$O) | 0.32 (0.22) | 0.1 (0.07) | 0 | > 1000 | this work |

combine a space charge layer or in other words an internal electric field with high transparency even in the UV spectral range, they are ideally suited for UV-light detection [Laj+11].
Sample preparation  By PLD, first an about 200 nm thick Al-doped ZnO film, serving as back side contact [Wen+06] and subsequently a 1 µm thick ZnO film were deposited on an as-received circular 2 inch in diameter a-plane sapphire substrate (cmp. inset of fig. 4.21). The oxygen partial pressure and the growth temperature were 0.02 mbar and 670°C, respectively. On the as grown film, TRC were deposited as described in section 4.1, with the exception that the deposition time and thus the thickness of the PtO\textsubscript{y} layer was reduced by a factor of four, as it turned out to perform best in terms of $\eta_{\text{ext}}$. The circular shape of the TRC was defined by molybdenum steel shadow masks. The ohmic Al-doped ZnO back contact layer was itself contacted by dc-sputtered gold layers. The samples were mounted and contacted on TO-18 sockets, including an 80°C - 30 min annealing step in air to harden the epoxy resin used for bonding the connecting wires.

4.4.1 Optical properties

The transmission spectrum of the TRC is depicted in fig. 4.20 (a). In order to exclude the zinc oxide absorption, the TRC layers were deposited directly on as-received fused quartz glass substrates with identical growth conditions as used for the photo-detectors. On zinc oxide, the transmission of the TRC differs slightly due to the different interface reflectivity. While the transmission of the platinum based contact is only weakly dependent on the wave length of the incident light, the transmission of the silver-based contact decreases remarkably for wave lengths below 550 nm. The latter effect is caused by absorption in the silver oxide. The onset of the absorption was determined by spectroscopic ellipsometry on thick Ag\textsubscript{x}O-films to be at about 2.5 ± 0.2 eV (cmp. section 4.1). The PtO\textsubscript{y} and the Ag\textsubscript{x}O contacts achieve a mean transmission in the visible spectral range of 75% and 73%, respectively. At the ZnO free exciton energy at room temperature (3.31 eV [Oez+05]), indicated by dashed lines in figures 4.20 (a) and 4.21), the PtO\textsubscript{y}- and the Ag\textsubscript{x}O-contacts still transmit 69% and 51% of the incident light, respectively.

4.4.2 Diode characteristics

Figure 4.20 (b) depicts the current-voltage characteristics of the transparent PtO\textsubscript{y}- and Ag\textsubscript{x}O-contacts recorded in the dark. According to the net doping density of $\approx 3 \times 10^{16} \text{ cm}^{-3}$ and the mobility, which is typically $> 50 \text{ cm}^2/\text{Vs}$ for similar samples\textsuperscript{7}, thermionic emission only was applied to describe the current in these diodes. For both diodes depicted in figure 4.20, the effective barrier height is 0.73 V. The series resistance for the PtO\textsubscript{y} (Ag\textsubscript{x}O)-contact is 450 (260) $\Omega$, respectively. As the reverse current of the diodes exceeds the reverse current predicted by thermionic emission theory (cmp. figure 4.20), the potential barrier is assumed to be inhomogeneous (cmp. sec. 4.3). The ideality factors of the contacts of 1.6 (1.2) for the

\textsuperscript{7}The highly conductive back-side contact layer inhibits reliable Hall effect measurements of the nominally undoped zinc oxide layer.
4 Transparent rectifying contacts

PtO_y (Ag_xO)-contacts comply with this assumption. Nevertheless, a parallel conduction path may also contribute to the reverse current. The extracted parallel resistance of the PtO_y-contact is $1 \times 10^7 \Omega$ compared to $1 \times 10^8 \Omega$ for the Ag_xO-contact. The rectification ratio at $\pm 1$ V is $1 \times 10^4$ for PtO_y and $1.5 \times 10^5$ for Ag_xO, respectively. Due to the annealing included in the socketing process, the contacts degrade, yielding lower effective barrier heights compared to the as-grown diodes (cmp. section 4.1). Such annealing induced degradation of the contacts has been previously observed for thicker and therefore opaque MESFET gate TRC [Fre+09]. Without annealing the effective barrier heights reach 0.82 (0.87) V for the presented PtO_y (Ag_xO)-contacts.

4.4.3 Photoresponse

The external quantum efficiency of the photo-detectors in photo-voltaic mode ($V = 0$) is depicted in fig. 4.21. For light with energy below the band gap of ZnO, photo-current generation is strongly suppressed, whereas for light above the band gap, a large fraction of the incident light is converted to an electric current. For both PtO_y and Ag_xO, the UV-VIS rejection ratio is at least $10^3$ for the blue, but exceeds $10^4$ for the red and green spectral range, which is among
Figure 4.21: External quantum efficiency in dependence of the wave length of the incident light. The dotted line indicates the spectral position of the maxima, located at the ZnO free exciton energy of 3.31 eV. For the PtO$_y$ (Ag$_x$O)-contact the maximal external quantum efficiency is 33% (22%). The inset depicts the device diagram.

the highest reported values (cmp. table 4.4). The maximum external quantum efficiency and responsivity for the PtO$_y$ (Ag$_x$O)-contact are 32% (22%) and 0.1(0.07) A/W, reached at an energy of 3.31 eV, which is about 60 meV below the fundamental band gap of ZnO. Conclusively, the photo carriers are either generated by ionization of shallow donors [Ohe81] or by generation and subsequent thermal dissociation of excitons, which have a binding energy in zinc oxide of about 60 meV.

The normalized detectivity \( D^* = R \left( \frac{\exp(\Phi_B/k_BT)}{(4qA^*T^2)} \right)^{1/2} \) for a Schottky photodiode complying with the thermionic emission model was determined [Nak+08b]. The maximum values were \( D^*_{\text{max}} = 1.3 \times 10^{11} \text{ cmHz}^{1/2} \text{W}^{-1} \) for PtO$_y$ as well as \( D^*_{\text{max}} = 0.9 \times 10^{11} \text{ cmHz}^{1/2} \text{W}^{-1} \) for Ag$_x$O, respectively. The detectivities are 3 orders of magnitude lower than recently reported PEDOT : PSS-Schottky contacts on ZnO [Nak+08b]: 8. However, this is due to lower barrier height of \( \Phi_B \) of 0.73 eV compared to 1.1 eV of PEDOT : PSS and the lower transmittance of the TRCs.

Nevertheless, the TRC exhibit a high UV-VIS rejection ratio and a comparably high responsivity (cmp. table 4.4) even without bias and therefore without power consumption during operation.

8poly(3,4-ethylenedioxythiophene):(styrenesulfonate)
5 Room-temperature-grown transparent conductive oxides

The best known conductors at room temperature are metals. They exhibit electrical conductivities up to several $10^5$ S cm$^{-1}$, which coincides with a high free charge carrier concentration (in the order of $10^{23}$ cm$^{-3}$) due to the metallic bond. As the spectral range of plasma absorption depends on the free carrier density (plasma frequency $\omega_p = \sqrt{n e^2/\varepsilon_0\varepsilon_{\infty} m^*}$), free carrier absorption onset is in the UV for metals. Therefore, metals are opaque in the visible spectral range.

For a rising number of applications, including for example flat panel displays, touch screens, solar cells or wind shield heatings, transparent conductors are required. In practice, transparent conductive oxides (TCOs) are widely applied for this purpose. The maximal free carrier density for which no plasma absorption occurs in the visible can be estimated to be of the order of about $10^{21}$ cm$^{-3}$. However, the dopant solubility anyway limits carrier densities for doped oxides to a respective range of about $1 \times 10^{21}$ cm$^{-3}$ [Ell01]. For such carrier densities, ionized impurity scattering limits the carrier mobility to several tens of cm$^2$/Vs [Min05; MSM01; Ell01]. In conclusion, the conductivity of homogeneously doped transparent conducting oxides is limited to several $10^4$ S cm$^{-1}$.

Common TCOs are impurity doped binary or ternary oxides including the elements Al, Ga, Zn, In, Sn, Cd and others [Min05]. A commercially widely established TCO, e.g. in liquid crystal displays, is indium tin oxide (ITO). Conductivities of the order of $10^4$ S cm$^{-1}$ and visible transmission in excess of 80% were already reported more than two decades ago [TMS88]. Due to the typical large area application of TCOs, especially in solar cells or displays, and the comparably simple processing, the price of the constituents is crucial. In figure 5.1 the average prices of various TCO constituents are summarized. Notably, the price of indium and gallium reaches several hundred dollars per kilogram, whereas other metals are at least a factor of ten cheaper. As the indium content

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\[\text{Figure 5.1: Average prices of selected metals relevant for TCO fabrication [KM10].}\]

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$^1$This can potentially be overcome by inhomogeneous TCOs either using modulation doping or zone confining [Ell01; Rob03; Rau93].

$^2$Nano-porous transparent conductors potentially exhibit a lower visible absorption than conventional TCO and similar conductivity [MF05].
Table 5.1: Electrical properties and transmission of low-temperature-grown ZnO-films for different dopants and growth methods (ALD=atomic layer deposition, DMS=d.c. magnetron sputtering, RMS=r.f. magnetron sputtering, PLD=pulsed laser deposition). \( \theta_{\text{growth}} \) denotes the growth temperature, \( d_{\text{film}} \) the film thickness, \( \sigma \) the conductivity, \( n \) the electron concentration, \( \mu \) the electron mobility, \( R_{\text{sheet}} \) the sheet resistance and \( T_{\text{VIS}} \) the mean transmission in the visible spectral range.

<table>
<thead>
<tr>
<th>dopant</th>
<th>method</th>
<th>( \theta_{\text{growth}} ) (°C)</th>
<th>( d_{\text{film}} ) (nm)</th>
<th>( \sigma ) (Scm(^{-1}))</th>
<th>( n ) (cm(^{-3}))</th>
<th>( \mu ) (cm(^2)/Vs)</th>
<th>( R_{\text{sheet}} ) (Ω/□)</th>
<th>( T_{\text{VIS}} ) (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>ALD</td>
<td>80</td>
<td>180</td>
<td>( \approx 3.3 \times 10^3 )</td>
<td>-</td>
<td>( \approx 17000 )</td>
<td>-</td>
<td>-</td>
<td>[Mey+08]</td>
</tr>
<tr>
<td>Al</td>
<td>DMS/RMS</td>
<td>50</td>
<td>300</td>
<td>( 2.2 \times 10^3 )</td>
<td>( 8 \times 10^{19} )</td>
<td>0.2</td>
<td>( \approx 15000 )</td>
<td>-</td>
<td>[LHS+05]</td>
</tr>
<tr>
<td>Al</td>
<td>DMS/RMS</td>
<td>&lt; 200</td>
<td>1000</td>
<td>( 1.1 \times 10^3 )</td>
<td>-</td>
<td>( \approx 9 )</td>
<td>( \approx 80 )</td>
<td>-</td>
<td>[GH06]</td>
</tr>
<tr>
<td>Al</td>
<td>PLD</td>
<td>165</td>
<td>280</td>
<td>( 2 \times 10^3 )</td>
<td>( \approx 8 \times 10^{20} )</td>
<td>( \approx 15 )</td>
<td>( \approx 18 )</td>
<td>-</td>
<td>[Agu+03]</td>
</tr>
<tr>
<td>Al</td>
<td>PLD</td>
<td>200</td>
<td>500</td>
<td>( 4 \times 10^3 )</td>
<td>( 6 \times 10^{20} )</td>
<td>44</td>
<td>( \approx 5 )</td>
<td>( \approx 80 )</td>
<td>[Mat+03]</td>
</tr>
<tr>
<td>Al</td>
<td>PLD</td>
<td>RT</td>
<td>1300</td>
<td>-</td>
<td>-</td>
<td>( \approx 425 )</td>
<td>-</td>
<td>-</td>
<td>[HAC+04]</td>
</tr>
<tr>
<td>Al</td>
<td>PLD</td>
<td>RT</td>
<td>100</td>
<td>( 2.5 \times 10^3 )</td>
<td>-</td>
<td>-</td>
<td>30</td>
<td>86</td>
<td>[Kim+00]</td>
</tr>
<tr>
<td>Al</td>
<td>PLD</td>
<td>RT</td>
<td>300</td>
<td>( 1.1 \times 10^3 )</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>38</td>
<td>[Kim+02b]</td>
</tr>
<tr>
<td>Al</td>
<td>PLD</td>
<td>RT</td>
<td>200</td>
<td>( 1.3 \times 10^3 )</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>85</td>
<td>[Sin+01]</td>
</tr>
<tr>
<td>Al</td>
<td>RMS</td>
<td>240</td>
<td>-</td>
<td>( 2 \times 10^3 )</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>( \approx 75 )</td>
<td>[Che+01]</td>
</tr>
<tr>
<td>Al</td>
<td>RMS</td>
<td>&lt; 200</td>
<td>( \approx 750 )</td>
<td>( 3.3 \times 10^3 )</td>
<td>( &gt; 8 \times 10^{20} )</td>
<td>-</td>
<td>4</td>
<td>-</td>
<td>[Jaa+03]</td>
</tr>
<tr>
<td>Al</td>
<td>RMS</td>
<td>RT</td>
<td>1150</td>
<td>-</td>
<td>( 2.1 )</td>
<td>( \approx 85 )</td>
<td>-</td>
<td>-</td>
<td>[Yoo+05]</td>
</tr>
<tr>
<td>Ga</td>
<td>PLD</td>
<td>200</td>
<td>500</td>
<td>( 4 \times 10^3 )</td>
<td>( \approx 1 \times 10^{21} )</td>
<td>( \approx 30 )</td>
<td>( 2.8 )</td>
<td>( \approx 80 )</td>
<td>[Mat+03]</td>
</tr>
<tr>
<td>Ga</td>
<td>PLD</td>
<td>RT</td>
<td>100</td>
<td>( \approx 5 \times 10^3 )</td>
<td>-</td>
<td>( \approx 20000 )</td>
<td>-</td>
<td>-</td>
<td>[HAC04]</td>
</tr>
<tr>
<td>Ga</td>
<td>PLD</td>
<td>RT</td>
<td>-</td>
<td>( 1.5 \times 10^3 )</td>
<td>( 1.96 \times 10^{21} )</td>
<td>4.9</td>
<td>-</td>
<td>-</td>
<td>[Bho+07]</td>
</tr>
<tr>
<td>Ga</td>
<td>RMS</td>
<td>RT</td>
<td>600</td>
<td>( 4.2 \times 10^3 )</td>
<td>( 2 \times 10^{21} )</td>
<td>10</td>
<td>6</td>
<td>( \approx 90 )</td>
<td>[Ass+03]</td>
</tr>
<tr>
<td>Ga</td>
<td>RMS</td>
<td>RT</td>
<td>1100</td>
<td>( 3.8 \times 10^3 )</td>
<td>( 1.3 \times 10^{21} )</td>
<td>18</td>
<td>1.6</td>
<td>( \approx 80 )</td>
<td>[For+04]</td>
</tr>
<tr>
<td>In</td>
<td>DMS</td>
<td>RT</td>
<td>140</td>
<td>( 2 \times 10^3 )</td>
<td>( 5 \times 10^{20} )</td>
<td>25</td>
<td>36</td>
<td>( \approx 80 )</td>
<td>[Jun+03]</td>
</tr>
<tr>
<td>In</td>
<td>RMS</td>
<td>&lt; 100</td>
<td>220</td>
<td>( 2.3 \times 10^3 )</td>
<td>( 3 \times 10^{20} )</td>
<td>48</td>
<td>27</td>
<td>82</td>
<td>[Gon+11]</td>
</tr>
</tbody>
</table>

In ITO is typically more than 80% [TMS88; Suz+01], a cost-efficient replacement material is required. Promising candidates are doped zinc-oxide-based TCOs. Zinc is highly abundant, comparably cheap and typical doping levels in these TCOs are only a few percents [For+04; Aga+04; Yoo+05], permitting to use even expensive dopants cost-efficiently. Most reports on the optimized growth of zinc-oxide-based TCOs include high growth temperatures, which permits to reach higher conductivity but is also more expensive in production. In table 5.1, an overview of several reports on the optical and electrical parameters of low-temperature-grown zinc-oxide-based TCOs is given. Conductivities reach several \( 10^3 \) Scm\(^{-1}\), approaching the previously discussed theoretical limit. Visible transmittance is typically in the range of 80%.

\(^3\)If multiple growth temperatures were reported, only the values for the lowest growth temperature are included.
In the following, the optimization of zinc oxide doped with aluminium or gallium intended for the use as ohmic source-drain electrodes in transparent field-effect transistors is presented. The growth process, conducted by pulsed laser deposition (PLD) on 10 × 10 mm\(^2\) quartz substrates, is optimized for room temperature. This permits to define electrodes by photolithographic lift-off using a photo-resist, which is stable up to 90°C, aside from the potentially lower production costs. To further comply with the lift-off process, a nominal film thickness of 100 nm was chosen. The content of Al\(_2\)O\(_3\) and Ga\(_2\)O\(_3\) and the oxygen growth pressure were varied between 0.1 wt% and 10 wt% in the ZnO PLD target and between 3 × 10\(^{-4}\) mbar and 0.1 mbar, respectively. Surface morphology, crystallinity, transport and optical properties were investigated and are discussed with respect to the intended application in a FET.

In order to determine the dopant content in the film, four samples (5% Al, 10% Al, 5% Ga, 10% Ga) with a nominal thickness of 1 μm were grown (\(p_{O_2} = 0.002\) mbar) and the dopant content was determined by energy dispersive X-ray spectroscopy (EDX) at several sample positions. The resulting transfer coefficients are \(Ga_{sample}[at\%]/Ga_2O_3_{target}[wt\%] = 0.64 \pm 0.05\) and \(Al_{sample}[at\%]/Al_2O_3_{target}[wt\%] = 0.50 \pm 0.04\), respectively. For all other samples, the dopant content was calculated using these transfer coefficients. The thickness of the samples was determined by spectroscopic ellipsometry by T. Böntgen and H. Franke (both Universität Leipzig) or by focused ion beam milling in combination with scanning electron microscopy by J. Lenzner (Universität Leipzig).

### 5.1 Surface morphology and crystallinity

![Atomic force micrograph of (a) ZnO:Ga (\(p_{O_2} = 0.002\) mbar and 3.2 at% Ga) and (b) ZnO:Al (\(p_{O_2} = 0.002\) mbar and 1.6 at% Al).](image)

**Figure 5.2**: Atomic force micrograph of (a) ZnO:Ga (\(p_{O_2} = 0.002\) mbar and 3.2 at% Ga) and (b) ZnO:Al (\(p_{O_2} = 0.002\) mbar and 1.6 at% Al).

Typical representations of the surface morphology of ZnO:Al and ZnO:Ga films, as revealed by atomic force microscopy (AFM), are depicted in fig. 5.2. The films exhibit a grainy surface...
structure without voids. For all investigated samples, the grain size was typically around 50 nm or below. Therefore, the films are possibly nano-crystalline. Symmetrical structures like e.g. hexagons were not observed. The rms-roughness was below 2 nm for the investigated samples. The X-ray diffraction patterns of ZnO:Al and ZnO:Ga films containing different dopant amounts and grown at 0.002 mbar are depicted in fig. 5.3. For comparison, the quartz substrate pattern is also included. As part of the samples have had already gold contacts for

\[\text{Figure 5.3: X-ray diffraction patterns of nominally 100 nm thick ZnO films grown at 0.002 mbar with various Al and Ga contents compared to as-received quartz substrate pattern.}\]

\[\text{The broad peak observed for quartz substrates is due to local atomic ordering.}\]
the transport measurements, gold (111) and (222) reflexes are sometimes observed, depending on the alignment of the gold contacts to the X-ray beam. Generally, reflexes related to the oxide film are observed occasionally and with small intensity only. This indicates a low crystallinity. Nevertheless, from the absence of distinct reflexes, amorphous phase cannot be deduced at this point, as the comparably low sample thickness could also account for a similar observation. From the FWHM of the observed reflexes, typically ranging between one and three degrees, the grain size can be estimated to be between 30 and 90 nm. This is consistent with the previous observation by AFM and the conclusion of nano-crystalline growth.

For both dopants, a weak peak at about 31.5° is occasionally observed. It can be attributed to the ZnO (100) reflex. Another weak reflex is detected for some samples at about 55° and is tentatively attributed to ZnO (110) due to the occurrence for both dopants. Remarkably, the ZnO (002) reflex is not observed, indicating that the zinc oxide did not grow in its preferred c-axis orientation [For+04; LHS05; Yoo+05]. This is possibly due to a comparably low kinetic energy regime during PLD-growth. Growth under comparable conditions but with a factor of two lower target-substrate distance and hence particles of higher kinetic energy hitting the substrate surface yields c-axis oriented ZnO films [Zip].

For a crystalline film, the intensity of the reflexes is expected to increase for increasing film thickness. The X-ray diffraction patterns for film thicknesses between 100 nm and 1150 nm are depicted in fig. 5.4. For ZnO:Al, no additional reflexes occur, when film thickness is increased. The peak intensity is comparably low even for the thickest film (only about 250 counts above noise level) substantiating the assumption of low crystallinity. The major part of the grains is (110) oriented, as the respective reflex dominates the spectrum and its intensity increases for increasing thickness. Only a small fraction of the grains is (100)-oriented, as the respective reflex occurs only occasionally and weak. This conclusion still holds if the grain sizes, as estimated from the FWHM, are considered. The (110) oriented grains are with \( w_{XRD} \approx 30 - 60 \) nm smaller compared to about \( w_{XRD} \approx 60 - 120 \) nm for the (100) oriented grains. For ZnO:Ga with a thickness up to 300 nm, a similar conclusion can be drawn. Here, the peak intensities are even lower, a ZnO (100) reflex can not be observed and crystallinity is lower compared to ZnO:Al. For a thickness of 1150 nm, a change of the growth mode possibly occurs. The ZnO (100) reflex now dominates, the respective ZnO (200) reflex (at about 65.5°), is observed and the (110) reflex is only weak. Conclusively, all films are nano-crystalline and do not grow c-axis oriented.

\[^5\]Using the Scherrer formula, the grain size \( w_{XRD} \) can be estimated from the FWHM of a diffraction reflex: \( w_{XRD} = K\lambda/(FWHM \cos(\theta)) \). \( K \) is the crystal-structure dependent Scherrer form-factor (approximated by 1 in this work) and \( \lambda = 1.54 \) nm the X-ray wavelength.
Figure 5.4: X-ray diffraction patterns of ZnO:Al (ZnO:Ga) films with different thickness grown at 0.002 mbar with 1.5 (1.9) at% of Al (Ga).
5.2 Transport properties

Using conductivity measurements and van der Pauw Hall-effect measurements at room temperature, conductivity, free charge carrier density and mobility were determined (cmp. fig. 5.5). As expected, all samples exhibit electron conduction. For the electron concentration $n$, two trends can be observed for both dopant metals. On the one hand, $n$ increases for decreasing oxygen partial pressure, which is possibly due to a change of the growth kinetics and the oxygen incorporation. For the net doping density, a similar pressure dependency has been observed for nominally undoped homo-epitaxially grown zinc oxide [Laj+10]. On the other hand, $n$ first increases for increasing dopant concentration. But this holds only up to about 3 at% (1.5 at%) for Ga (Al), for higher dopant concentrations $n$ decreases. This indicates a change of the doping mechanism, possibly related to the limited solubility of the metal atoms in ZnO or to the introduction of compensating defects. A similar behavior has been observed previously [Mat+03; Lu+07]. In conclusion, $n$ is maximal for $p_{O_2} = 3 \times 10^{-4}$ mbar and about 3 at% (1.5 at%) Ga (Al). Remarkably, by doping with Ga the electron concentration can be almost a factor of two higher compared to Al, approaching with $1.1 \times 10^{21} \text{cm}^{-3}$ already the theoretical limit [Ell01].

As for free carrier concentrations in the observed range ionized impurity scattering is a major scattering mechanism, the parameter dependence of the mobility somewhat opposes the behavior observed for $n$. The maximum mobility is reached for the combination of lowest dopant content and almost the highest oxygen growth pressure. The mobilities of ZnO:Ga and ZnO:Al are with about 10 cm$^2$/Vs comparably low (cmp. table 5.1) and significantly below the previously mentioned theoretical limit due to ionized impurity scattering. Conclusively, another scattering mechanism, probably grain boundary scattering, limits current transport in these samples. This is in accordance to the previously revealed nano-crystalline structure of the films.

The conductivity, which is proportional to carrier concentration and mobility, exhibits a maximum of 1250 (750) Scm$^{-1}$ for $p_{O_2} = 2 \times 10^{-3}$ mbar and about 3 at% (1.5 at%) of incorporated Ga (Al). Similar optimal growth pressures have been observed by previous reports [Kim+00; Kim+02b; Sin+01]. In succession to the comparably low mobility values, the maximal conductivities reached in this work are about a factor of two to four smaller than the best results obtained in other works for room temperature growth (cmp. table 5.1). A possible explanation is given in the next section.

---

6Solubility of Ga and Al in ZnO has been reported to occur at lower atomic percentages, than the maximum of $n$ is observed in this work [Yoo+02; Shi+07].
Figure 5.5: Free electron density, mobility and conductivity for Ga- (a, c, e) and Al- (b, d, f) doped zinc oxide as measured by Hall-effect in dependence of dopant content and oxygen growth pressure. The white circles indicate the measured points.
5.2.1 Influence of film thickness

An increase of conductivity by about 50% for film thickness increasing from about 100 nm to about 1150 nm is observed both for ZnO:Al and ZnO:Ga (cmp. fig. 5.6). Similar observations were reported for PLD grown and for sputtered films [Min05; For+04; Aga+04].

![Figure 5.6](image)

**Figure 5.6:** (a) Thickness dependence of the relative conductivity. (b) Thickness dependence of mobility and electron concentration. The films were grown at $p_{O_2} = 0.002$ mbar with a dopant content of 1.5 at% Ga or 1.6 at% Al.

While the carrier concentration is only weakly changing (for ZnO:Al) or even decreasing (for ZnO:Ga) with increasing thickness, the mobility is steadily increasing for both dopants. Thus, due to observed increase of mobility despite increasing carrier concentration, ionized impurity scattering is not the limiting scattering process. As already indicate previously, most probably, grain boundary scattering dominates. The grain sizes, as estimated from AFM and XRD, are of the order of the lowest measured film thickness or slightly below. Thus, with increasing thickness the number of grains available in the vertical domain increases and, considering the statistically distributed grain size, current flow can occur more and more among the largest grains. This is further supported by the observation, that the Zn:dopant ratio is independent from the vertical position in the film, as revealed by SNMS. Nevertheless, film temperature might be also increased for thicker films due to the longer growth time, which potentially affects the fraction of the electrically active incorporated dopants or other defects.
5.2.2 Investigation of the contact resistance

Aside from the bulk resistivity of the contact material, the contact resistance is another contribution to the overall resistance induced by an ohmic contact e.g. a TCO electrode. This may crucially affect the device performance, for example in organic TFTs [Kla+03]. It is generally defined as:

\[ R_c = \left( \frac{dj}{dV} \right)_{V=0}^{-1}. \]

According to the ratio of the underlying semiconductor’s sheet resistance \( R_{\text{sheet}} \) and the contact resistance \( R_c \), current chooses the path of least resistance from the contact to the semiconductor or vice versa. Therefore, the potential distribution under the contact is inhomogeneous; the voltage drops nearly exponentially from the edge of the contact with distance. The “1/e” decay length is denominated “transfer length” and defined as \( L_T = \sqrt{\rho_c/R_{\text{sheet}}} \), where \( \rho_c \) is the specific contact resistance. The transfer length can be interpreted as the contact length within most of the current flows into the semiconductor [Sch06]. Thus, it is a measure for the limit of lossless contact area downscaling, as above this limit the effective contact area is
smaller than the geometric contact area.

The transfer length method (TLM) for the determination of the contact resistance uses structures consisting of multiple contacts with variable spacing between them (cmp. inset of fig. 5.7). The total resistance $R$ between a neighbored pair of contacts is given by

$$R = \frac{R_{\text{sheet}} \Delta}{W} + 2R_c. \quad (5.1)$$

Here, $\Delta$ is the contact spacing and $W$ denotes the contact length (here 200 $\mu$m). From the contact resistance, the specific contact resistance can be determined according to [Sch06]:

$$R_c = \frac{\rho_c}{L_T W} \coth \left( \frac{L}{L_T} \right). \quad (5.2)$$

Including the definition of the transfer length yields to:

$$R_c = \frac{\sqrt{\rho_c R_{\text{sheet}} W}}{L_T} \coth \left( \frac{L}{\sqrt{\rho_c R_{\text{sheet}}}} \right). \quad (5.3)$$

The TLM mask used in this work consists of nine TLM test structures types (similar to the inset of fig. 5.7) with contact widths $L$ between 5 and 50 $\mu$m; each structures exhibits spacings

Figure 5.8: (a) Specific contact resistance and (b) Transfer length in dependence of the contact width.
Table 5.2: Overview of specific contact resistances for as-deposited (non-annealed) contacts to zinc oxide and related oxide semiconductors. If data for multiple doping levels was available, values next to the doping level of about $3 \times 10^{18} \text{ cm}^{-3}$ are given.

<table>
<thead>
<tr>
<th>Contact material</th>
<th>Semiconductor</th>
<th>Doping level $10^{18} \text{ cm}^{-3}$</th>
<th>$\rho_c$ $\Omega \text{cm}^2$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>ZnO</td>
<td>2</td>
<td>$8 \times 10^{-4}$</td>
<td>[Kim03]</td>
</tr>
<tr>
<td>Al/Pt</td>
<td>ZnO</td>
<td>2</td>
<td>$1.2 \times 10^{-5}$</td>
<td>[Kim03]</td>
</tr>
<tr>
<td>In</td>
<td>ZnO</td>
<td>$-$</td>
<td>$7 \times 10^{-1}$</td>
<td>[Aka00]</td>
</tr>
<tr>
<td>InZnO</td>
<td>ZnO</td>
<td>40</td>
<td>$1.1 \times 10^{-4}$</td>
<td>[Hu06]</td>
</tr>
<tr>
<td>Pt-Ga</td>
<td>ZnO</td>
<td>$-$</td>
<td>$4.1 \times 10^{-3}$</td>
<td>[Ili+02]</td>
</tr>
<tr>
<td>Ru</td>
<td>ZnO</td>
<td>3</td>
<td>$2.1 \times 10^{-3}$</td>
<td>[Kim+02a]</td>
</tr>
<tr>
<td>Ru</td>
<td>ZnO</td>
<td>0.4</td>
<td>$1.8 \times 10^{-3}$</td>
<td>[Lin+06]</td>
</tr>
<tr>
<td>Ta/Au</td>
<td>ZnO</td>
<td>0.1</td>
<td>$3.2 \times 10^{-4}$</td>
<td>[She+03]</td>
</tr>
<tr>
<td>Ti/Au</td>
<td>ZnO</td>
<td>0.2</td>
<td>$2 \times 10^{-2}$</td>
<td>[Kim00]</td>
</tr>
<tr>
<td>Ti/Au</td>
<td>ZnO</td>
<td>0.7</td>
<td>$7.3 \times 10^{-3}$</td>
<td>[Lee01]</td>
</tr>
<tr>
<td>Ti/Au</td>
<td>a-InZnO</td>
<td>5</td>
<td>$3 \times 10^{-3}$</td>
<td>[Lim08]</td>
</tr>
<tr>
<td>Au</td>
<td>a-InGaZnO</td>
<td>5</td>
<td>$8 \times 10^{-4}$</td>
<td>[Shi+08]</td>
</tr>
<tr>
<td>InSnO</td>
<td>a-InGaZnO</td>
<td>5</td>
<td>$1 \times 10^{-4}$</td>
<td>[Shi+08]</td>
</tr>
<tr>
<td>InZnO</td>
<td>a-InGaZnO</td>
<td>5</td>
<td>$1 \times 10^{-4}$</td>
<td>[Shi+08]</td>
</tr>
<tr>
<td>Ti</td>
<td>a-InGaZnO</td>
<td>5</td>
<td>$1 \times 10^{-4}$</td>
<td>[Shi+08]</td>
</tr>
</tbody>
</table>

Δ between 10 and 100 μm and each type exists ten times for averaging. A nominally 25 nm thick MgZnO layer grown by PLD similar to the channel layers used the TFTs in sec. 6.1.1 was patterned as described in sec. 3.1.3. Subsequently, the TCO layer was grown by PLD at room temperature with $p_{O_2} = 0.002 \text{ mbar}$ and a dopant content of 1.5 at% Ga or 1.6 at% Al. The sheet resistance of the MgZnO mesa is independent of the contact width and in good accordance to Hall effect measurements (cmp. fig. 5.7 (b)). The contact resistance depends significantly on the contact width (cmp. fig. 5.7 (a)). Equation 5.3 does not permit to fit the measured data adequately for a contact-width-independent specific contact resistance. By assuming $\rho_c \propto L^{-1}$, the measured data can be well described, as the fits in fig. 5.7 (a) reveal. The resulting specific contact resistances are depicted in fig. 5.8 (a). The dependence of $\rho_c$ on the contact width indicates an inhomogeneous contact formation [Jan+06]. Compared to previously reported specific contact resistivities of metal or TCO contacts to zinc oxide and related oxides (cmp. table 5.2), the values determined in this work for low contact widths are about a factor of 10-100 higher. Nevertheless, typically large contact pads with widths of 50 μm or more are used. For such values, the data measured in this work reveals similar results.

The transfer length, calculated from the sheet resistance and the specific contact resistance is depicted in fig. 5.8 (b). It is important to notice, that the transfer length is significantly smaller than the typical ohmic contact width for any device investigated in this work. Therefore, in
order to estimate device related contact resistances, the active contact area, which is limited by the transfer length, has to be taken into account.

5.3 Optical properties

The transmission of the TCO films, deposited on quartz substrates, was measured between 200 nm and 1.1 μm, as exemplarily depicted in fig. 5.9. Above 400 nm, ≥80% of the incident light is transmitted. For shorter wavelengths, zinc oxide and below 300 nm the quartz substrate absorbs. The modulation of the transmission spectra in the visible and the infrared range is due to film thickness interferences. The band gap energies of the films were extracted by extrapolating the linearly decreasing part of \((\ln(T)h\nu)^2\) plotted versus energy towards zero [Hos+02; HG86] and are depicted in fig. 5.10. Obviously, the band gap increases with electron concentration. Due to the large free electron density, a significant amount of states in the conduction band minimum are occupied, permitting a band-to-band transition only for higher photon energies. This effect is denominated Burstein-Moss shift (BM) and is described by [Gru+10]:

\[
\Delta E^{BM} = n^2 \frac{\hbar^2}{8} \left( \frac{3}{\pi} \right)^{\frac{2}{3}} \left( \frac{1}{m_e} + \frac{1}{m_h} \right).
\]  

This method in tendency underestimates the band gap [HG86].
Here, $h$ is Planck’s constant and $m_e$ and $m_h$ are the effective electron and hole masses, respectively. The band gap energies, calculated for $m_e = 0.28 m_0$ and $m_h = 0.59 m_0$ [MT68; Hue73] are depicted as solid line in fig. 5.10. Obviously, the band gap shift as predicted by equation 5.4 is larger than the observed shift for $n \geq 10^{20}$ cm$^{-3}$. Due to the high carrier concentration, the assumption of a parabolic conduction band and conclusively of constant effective mass holds no more. Therefore, a carrier concentration dependent effective electron mass according to the Pisarkiewicz model is introduced [PZL89]:

$$m'_e = m_e \sqrt{1 + 2D \frac{h^2}{4\pi^2m_e} (3\pi n)^{\frac{2}{3}}}.$$  (5.5)

The scaling factor $D$ is used for the adjustment of the nonparabolicity. The dashed line in fig. 5.10 depicts the Burstein-Moss-shift according to equation 5.4 under consideration of nonconstant effective mass for a normalization constant of $D = 6.5 \times 10^{19}$ s$^2$/kgm$^2$. Notably, the discrepancy between measured and calculated data is reduced. Furthermore, for high carrier concentrations, interaction between carriers, e.g. exchange interaction and screening, has to be considered. This is denominated as band gap renormalization (BGR) and here a semi-empirical model according to Lu et al. is applied:

$$\Delta E_{\text{BGR}} = An^{\frac{1}{3}} + Bn^{\frac{1}{2}} + Cn^\frac{1}{2}. $$  (5.6)
The coefficients of $A = 6.86 \times 10^{-9}$ eVcm and $B = 1.60 \times 10^{-7}$ eVcm$^{3/4}$ were calculated theoretically and $C = 7.76 \times 10^{-12}$ eVcm$^{3/2}$ was determined by polynomial fitting [Lu+07]. The band gap calculated considering BM, nonparabolicity and BGR is depicted by the dotted line in fig. 5.10. The dependence of the band gap on the electron density can be well described for most of the samples. In tendency, the deviation is larger for ZnO:Al than for ZnO:Ga. The ZnO:Al sample with the lowest electron concentration lies far out of the predicted range for the BM+nonparabolicity+BGR model but close to the BM-model, possibly indicating the occurrence of a semiconductor-metal-transition as previously observed [Lu+07]. Finally, the mean transmission $T_{\text{VIS}}$ in the visible spectral range between 400 and 800 nm was determined for each sample, in order to compare the applicability for transparent electronics. Obviously, the majority of the investigated samples exhibits high transmittance in excess of 80% as depicted in fig. 5.11. For ZnO:Ga, the transmission is slightly higher than for ZnO:Al. Generally, $T_{\text{VIS}}$ increases for increasing oxygen partial pressure. For increasing dopant content, $T_{\text{VIS}}$ first increases and decreases for dopant contents in excess of about 3 at%, similarly to the electron concentration.

### 5.4 Figure of merit

The requirements for an ideal TCO to be both highly conductive and highly transparent are contradictory, as high conductivity for example requires also high carrier concentration yielding plasma absorption. On the other hand, low absorption can be obtained using wide band gap materials, which tend to exhibit insulating behavior. In order to cope with this, at least partially contradictory relation, several figures of merit (FoM) have been introduced for the evaluation and comparison of TCOs. They differ within their weighting between optical
and electrical performance. The rather intuitive FOM $\sigma/\alpha$, considering conductivity and a mean absorption coefficient, gives comparably large weight to the optical performance. Thus, as this work is dedicated to the use of TCO in transparent electronics with comparably low requirements in maximal transmittance ($\geq 70\%$ according to [Wag03]), another FoM was chosen. Haacke [Haa76] suggested a FoM considering the transmittance in relation to the sheet resistance:

$$F_{\text{el}} = \frac{T^{10}}{R_{\text{sheet}}}. \quad (5.7)$$

The exponent of the transmission maximizes $F_{\text{el}}$ for $T = 0.9$, which is for most practically rel-

![Figure 5.12: Figure of merit in dependence of oxygen pressure and dopant content for (a) Ga and (b) Al. The open circles indicate the measured points.](image)

evant cases a good choice. For the PLD-grown TCO layers, $F_{\text{el}}$ is depicted in fig. 5.12. ZnO:Ga exhibits significantly higher $F_{\text{el}}$ compared to ZnO:Al. The maximum of $F_{\text{el}} = 3.7(1.3) \text{k}\Omega^{-1}$ occurs at $p_{O_2} = 0.002 \text{ mbar}$ and a Ga (Al) content of about 2.5 (1.5) at\%, which is almost identical to the maxima of the conductivity. This is due the overall high magnitude of $T_{\text{VIS}}$, which is only weakly pressure and dopant content dependent. Other reported TCO films yield $F_{\text{el}}$ up to almost 100 k$\Omega^{-1}$ (cmp. tab. 5.1). This is mainly due to the lower conductivity of the films investigated in this work, which has already been correlated with the low thickness chosen for this study.
Chapter 6: Transparent TRC-gated field-effect transistors and their applications

This chapter combines the elements of the previous chapters and investigates fully transparent MESFETs (TMESFETs) with TRC-based gates and TCOs source and drain electrodes. First, the channel material comprises of high-temperature PLD-grown MgZnO on sapphire substrates. The electrical properties of the TMESFET are investigated with respect to their reproducibility, their longterm stability and the impact of visible light illumination and elevated temperatures. Furthermore, the bias stress resistance and the dynamic properties of the TMESFET are studied. In the second part, the crystalline channel material is replaced by amorphous InGaZnO grown at room-temperature on glass and on flexible substrates. The second section investigates the application of TMESFETs in a transparent integrated circuit, with special focus on the effect of visible light illumination and elevated temperatures. Furthermore, the applicability of MESFETs for nerve cell signal sensing is studied.

6.1 TRC-gated field-effect transistors

The general concept of ZnO-based TFTs gated by reactively sputtered rectifying contacts has been introduced for opaque gates [Fre+08], demonstrating field-effect mobilities in excess of 10 cm²/Vs, on-off current ratios of 10⁸ and remarkably low voltage operation (\(SS < 150 \text{ mV/dec}\) and \(\Delta V_G < 3 \text{ V}\) required for complete switching). These properties are comparable to or better than the best reported MISFET devices based on comparable channel materials, as reviewed in [Gru+10]. The following section is dedicated to the transfer of the latter properties to fully transparent devices [Fre+10b; Fre+10a].

6.1.1 TMESFETs with MgZnO channel

Device fabrication The growth conditions of the channel layer were chosen similar to those used for successful realization of opaque MESFET [Fre+08]: The sintered target consists of ZnO with 0.25% of MgO, as previous investigations revealed an advantageous effect of the Mg for the stability of the MESFETs [Fre+10b]. Double-side polished 50 × 50 mm² a-sapphire substrates with precut cleaving grooves were used in order to obtain identical 10 × 10 mm²-samples. The nominally 25 nm thick channel layer of the MESFETs was grown using PLD
at an oxygen pressure of $p_{O_2} = 0.02$ mbar and a temperature of 670°C. This yields a decent crystallinity of the film as obvious from HRTEM image in fig. 4.3.

The functional components of the MESFETs were structured using photolithography, as described in detail in section 3.1.3. The TRC were grown by dc-sputtering (cmp. sec. 3) with the optimal conditions as described in section 4.1. The TCO of the source and drain electrodes with a nominal thickness of 100 nm was grown by PLD at room-temperature ($p_{O_2} = 0.016$ mbar, 3% Al in the target) with almost optimal conditions as described in section 5. The resulting structure was measured using atomic force microscopy as depicted in fig. 6.1 (b), revealing a conformal, void-free gate with a thickness of about 10 nm. The surface roughness of the substrate (rms=1.9 nm), the channel layer (rms=1.2 nm) and the TRC (rms=1.5 nm) are almost similar.

A microscopical image of a TMESFET is depicted in fig. 6.1 (a). As the image is recorded in front of the logo of the graduate school BuildMoNa with illumination from the back, the high transmittance is demonstrated. The overall device transmittance in the visible spectral range is limited by the gate transmittance, which was measured to be about 70% (60%) for the Ag(Pt)-based TRC (cmp. sec. 4.1). The transmittance of the sapphire substrate reaches almost 90% (cmp. fig. 4.2 (b)) and $T_{VIS}$ of the TCO range around 80% for the used ZnO:Al (cmp. sec. 5).

As the gate covers typically not more than one third of the device area, the overall device transmittance is in excess of 70% for both gate materials presented in this work. Thus, the criterion ($T_{VIS} > 70\%$) given for the application in transparent electronics by Wager [Wag03]

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**Figure 6.1:** (a) Image of a Ag-based TMESFET on a backside illuminated image of the logo of the graduate school BuildMoNa. The dotted line indicates the position of the channel mesa. S, D and G denote the source, drain and gate electrode. (b) Atomic force microscopic image of a Ag-based TMESFET.
6.1.1.1 General electrical properties

The transfer characteristics of a Ag- and a Pt-based TMESFET are depicted in fig. 6.2. The on-off drain current ratio reaches $1.3 \times 10^5$ ($1.4 \times 10^6$ for the Pt (Ag)-based TMESFET, which is slightly lower than for opaque Ag- and Pt-based MESFETs [Fre+09]. The off-current, which is limited by the gate current as depicted in fig. 6.2, increases compared to the opaque devices due to the thinning-related barrier height decrease of the TRC. Nevertheless, at least for the Ag-based TMESFET, the criterion for the application in transparent electronics ($I_{on}/I_{off} > 10^6$) is fulfilled [Wag03].

Both TMESFETs are normally-on, the turn-on voltage of the Ag-TMESFET is with $-1.26$ V about half a volt higher than for the Pt-device ($-1.71$ V). As both TFT were fabricated on parts of the same sample, this indicates a difference in the net doping density. This is confirmed by QSCV-measurements revealing $N_D - N_A = 3.0 \times 10^{18}$ cm$^{-3}$ and $N_D - N_A = 1.4 \times 10^{18}$ cm$^{-3}$ for the Pt- and the Ag-based TMESFET. The change of the net doping density is ascribed to the diffusion of silver into the MgZnO channel yielding the formation of acceptor-like defects and a reduction of the net doping density [Wen+10a]. In succession, the extension of the space charge layer is increased and the voltage required to pinch-off the channel is reduced (cmp.
6 Transparent TRC-gated field-effect transistors and their applications

Figure 6.3: Output characteristic of a Pt-based TMESFET in (a) logarithmic and (b) linear scale. The gate voltage was varied in steps of 0.2 V.

equation 2.1 and 2.22).

Using the net doping density and the channel’s width to length ratio $W/L = 10.75$, the field-effect mobility is determined from the maximum transconductance extracted from the transfer characteristic according to equation 2.25 to be $\mu_{FE} = 11.4 \pm 2 (11.9 \pm 2) \text{ cm}^2/\text{Vs}$ for the Pt-(Ag-) based TMESFET, which is almost similar to the Hall mobility of $16 \pm 1 \text{ cm}^2/\text{Vs}$. Both TMESFETs decently fulfill the last criterion $\mu_{FE} \gg 1 \text{ cm}^2/\text{Vs}$ for the application in transparent electronics [Wag03].

Low-voltage operation is observed for both TMESFETs, as only small voltage sweeps $< 3 \text{ V}$ are required for switching. The subthreshold slopes of $SS = 160 \text{ mV/dec}$ and $SS = 120 \text{ mV/dec}$ for the Pt- and the Ag-based TMESFET are among the lowest reported values for transparent TFT [Fre+10a; Gru+10].

The output characteristic of a Pt-based TMESFET is depicted in fig. 6.3 demonstrating the strong dependence on the gate voltage on the one hand and revealing on the other hand the clear distinction between a linear regime for low $V_{SD}$ and a pinch-off induced saturation for higher $V_{SD}$. It is worth noting, that the voltage dependence of the saturation current is weak, as obvious from the linear plot in fig. 6.3 (b).

From the linear regime of the output characteristic in the on-regime, the path resistance of
the channel is extracted to be of the order of 5 kΩ for the investigated channel geometry and doping. The path resistance comprises of the resistance of the TCO electrodes, the contact resistance between the TCO and the channel layer and the channel resistance.

\[
R_{\text{path}} = 2R_{\text{TCO}} + 2R_{\text{C}} + R_{\text{channel}}
\]

\[
= 2 \frac{L_{\text{TCO}}}{\sigma_{\text{TCO}} d_{\text{TCO}} W_{\text{TCO}}} + 2 \frac{\rho_{\text{C}}}{L_{\text{eff,TCO}} W_{\text{TCO}}} + \frac{L_{\text{channel}}}{\sigma_{\text{channel}} d_{\text{channel}} W_{\text{channel}}}
\]

The channel resistance is calculated from the respective channel conductivity and dimensions. The contact resistance was calculated from the specific contact resistance determined in sec. 5.2.2 extrapolated for the respective contact width of 430 µm and the effective contact area (considering the transfer length also extrapolated for the contact width). According to the determined values of the transfer length and the conductivity ratio between TCO and channel, it can be assumed that the current transport in the TCO occurs mainly laterally. Thus, in order to estimate the resistance between the contact needle and the contact edge next to the gate, roughly half of the length of the electrode has to be passed. In consequence, a path resistance of

\[
R_{\text{path}} \approx (0.3 + 0.4 + 3.9) \text{ kΩ}
\]

is deduced, which is in good accordance to the measured value. Obviously, the channel resistance dominates the path resistance. Nevertheless, both the TCO resistance and the contact resistance account for about ten percent of the path resistance, which yields a decrease of the transconductance within the linear regime and an underestimation of the field-effect mobility [Kim+07]. In the saturation regime, the channel resistance is significantly increased and the voltage drop along the parasitic resistances becomes negligible. Thus, for the accurate determination of the field-effect mobility of TMESFETs, the saturation conductance is to be preferred.
Figure 6.4: Statistical representation of the reproducibility of the transistor parameters for an Ag- and a Pt-based TMESFET sample, respectively. N = 35 (39) for the Ag- (Pt-) based TMESFETs. The solid lines depict normal distributions fitted to the data.

6.1.1.2 Device reproducibility

The distribution of the transistor parameters over a 10 × 10 mm sample, which included for the present case 35 (39) Ag- (Pt-) based TMESFETs, is depicted in fig. 6.4. The field-effect mobility distribution of the Pt-based TMESFETs obeys quite well a comparably narrow normal distribution around \( \mu_{\text{FE,mean}} = 11.1 \text{ cm}^2/\text{Vs} \) with a width of \( \sigma = 2.1 \text{ cm}^2/\text{Vs} \). For the Ag-based devices a bimodal behavior is observed with a high mobility part being almost similar to the Pt distribution (\( \mu_{\text{FE,mean}} = 9.7 \text{ cm}^2/\text{Vs}, \sigma = 1.8 \text{ cm}^2/\text{Vs} \)) and a low mobility part (\( \mu_{\text{FE,mean}} = 1.8 \text{ cm}^2/\text{Vs}, \sigma = 1.6 \text{ cm}^2/\text{Vs} \)).

The distributions of the logarithm of the on-off current ratio reveal a slightly broader distribution for the Ag-devices and a higher mean value for the Pt-based TFT (Pt: \( \log(I_{\text{on}}/I_{\text{off}})_{\text{mean}} = 4.8, \sigma = 0.5 \); Ag: \( \log(I_{\text{on}}/I_{\text{off}})_{\text{mean}} = 4.3, \sigma = 0.6 \)).

The Ag-based TMESFETs exhibit subthreshold slopes around 130 mV/dec, which is about 20 mV/dec smaller compared to the majority of the Pt-based TMESFETs (Pt: \( SS_{\text{mean,1}} = 158 \text{ mV/dec}, \sigma_1 = 3 \text{ mV/dec}, SS_{\text{mean,2}} = 317 \text{ mV/dec}, \sigma_2 = 20 \text{ mV/dec} \); Ag: \( SS_{\text{mean}} = 133 \text{ mV/dec}, \sigma = 20 \text{ mV/dec} \)). This difference is possibly related to the increased turn-on voltage for the Ag-based MESFETs. For both types of TMESFETs, a minor number of
devices, namely the ones with low on-off ratio, exhibit larger $SS$ as expected. In the following, instead of the turn-on voltage, the voltage at which $SS$ is reached, is used. Its definition contains less ambiguity compared to the turn-on voltage. The $V_{SS}$-distribution width is with about 0.1 V similar for both samples. A possible origin of this spread is the film thickness gradient on the samples being both cleaved from a large $50 \times 50 \text{ mm}^2$ substrate [Lor+10b]. In conclusion, the Pt-based TMESFETs exhibit higher mean values and less spread of the field-effect mobility and the on-off current ratio compared to Ag-based devices.
6.1.1.3 Operation stability of TMESFET at elevated temperatures

In order to study the effect of typical operational conditions, in the following the electrical parameters of the TMESFETs are investigated between room temperature and \(60^\circ\text{C}\). Preliminary studies on opaque contacts revealed, that for higher temperatures the devices start to degrade \[\text{[Laj08; Fre+09; Laj+11]}\]. The transfer characteristic evolution is depicted exemplarily for a Pt-based TFT in fig. 6.5, the respective evolution of the transistor parameters with temperature for Ag and Pt-based TMESFETs is depicted in fig. 6.6.

Generally, the transfer characteristic of the depicted Pt-TMESFET is only weakly affected by elevated temperatures. The on-off current ratio even increases weakly by about a factor of two, which has been previously observed similarly for opaque devices \[\text{[Fre+09]}\]. The Ag-TMESFET in contrast, exhibits in the same temperature range already a reduction of \(I_{\text{on}}/I_{\text{off}}\) by at least a factor of five starting at about 320 K. This onset of gate degradation is at least 20 – 30 K lower compared to opaque devices \[\text{[Fre+09]}\], indicating the reduction of the gate thickness to have an impact. A potential mean to overcome this effect is the passivation or encapsulation of the device.

The extracted field-effect mobility of the Ag-based device decreases slightly with increasing temperature, while \(\mu_{\text{FE, Pt}}\) remains approximately stable. The channel mobility is expected to
decrease with increasing temperature due to increased polar optical scattering. Nevertheless, as both device are fabricated on identical channel material and the decrease of $\mu_{FE}$ is only observed for one device, another contribution must exist, e.g. inhomogeneous contact resistance or the effect of the different gate degradation (cmp. second part of this paragraph). The subthreshold slope of the Pt-based TFT decreases by about 10% within the investigated temperature range, while $SS$ is expected to increase with $T$ (cmp. equation 2.27). The decrease of the off-current probably yields a decrease of $SS$, which superimposes with the temperature-induced increase. For the Ag-based TFT, the expected increase of $SS$ is observed, but it might be even enhanced by the increase of the off-current due to the gate degradation. The $SS$-voltage exhibits a positive shift of $\approx 0.15$ V ($\approx 0.25$ V) for the Pt- (Ag-) device, which has been similarly observed for opaque MESFETs [Fre+09].

In order to further enlighten the effect of the gate TRC on the transistor performance, their diode-characteristics are investigated. According to previous investigations, the contacts potentially exhibit laterally inhomogeneous barriers (cmp. sec. 4.3). The temperature dependence of $\Phi_{B,\text{eff}}$ and $n$ as extracted using thermionic emission only (cmp. sec. 2.2.1.1) is depicted in fig. 6.7. The obvious increase of $\Phi_{B,\text{eff}}$ and the decrease of $n$ with increasing temperature confirm the assumed barrier inhomogeneity. For temperatures above 325 K the Ag-based diode obviously starts to degrade, explaining the previous observation among the transistors parameters. $\Phi_{B,\text{eff}}$ and $n$ were fitted according to equation 2.15 and 2.19.

Figure 6.6: Temperature dependence of the transistor parameters for Ag- and Pt-based TMESFETs.
Figure 6.7: Temperature dependence of the effective barrier height and the ideality factor of the gate-diode of Ag- and Pt-based TMESFETs. The dashed and dotted lines are fits according to equations 2.15 and 2.19, respectively.

Table 6.1: Barrier height distribution parameters.

<table>
<thead>
<tr>
<th>Material</th>
<th>$\Phi_{B,m}$ (V)</th>
<th>$\sigma$ (mV)</th>
<th>$\rho_\sigma$</th>
<th>$\rho_\Phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag-TMESFET</td>
<td>1.41 ± 0.1</td>
<td>177 ± 17</td>
<td>−0.02 ± 0.01</td>
<td>0.03 ± 0.2</td>
</tr>
<tr>
<td>Pt-TMESFET</td>
<td>1.54 ± 0.03</td>
<td>189 ± 5</td>
<td>−0.033 ± 0.004</td>
<td>−0.14 ± 0.07</td>
</tr>
</tbody>
</table>

For both gate materials, a comparably large mean barrier height of 1.5 V is extracted. In accordance with the previously described correlation between $\Phi_{B,m}$ and $\sigma$ (cmp. sec. 4.3), $\sigma$ reaches about 190 mV. Comparable values of the voltage coefficients $\rho_\sigma$ and $\rho_\Phi$ have been observed previously for socketed Ag-based TRC (cmp. sec. 4.3, table 4.3).

Generally, while Pt-based TMESFETs exhibit a performance increase for increasing temperature, Ag-based devices are subjected to device degradation already below 60°C.

\[1\] For the fit of the Ag-device parameters, the data for temperatures above 325 K was not considered.
6.1.1.4 Operation stability of TMESFETs towards illumination by visible light

In this section, the effect of visible light illumination on the TMESFET performance is investigated. During operation as part of an integrated fully transparent electronic circuit, TMESFETs are exposed to visible light either from external light sources or from the active part of the display the TMESFETs are part of (light above the band-gap has to be shielded in order to avoid excessive photo-current generation (cmp. sec 4.4)). The samples were illuminated with red ($\lambda = 628$ nm; FWHM = 20 nm), green ($\lambda = 525$ nm; FWHM = 30 nm) and blue ($\lambda = 435$ nm; FWHM = 25 nm) LEDs. The irradiance was adjusted to about 10 W/m$^2$ for all LEDs, which is equivalent to luminance values of approximately 1000 cd/m$^2$, 57000 cd/m$^2$ and 22000 cd/m$^2$ for blue, green and red light, respectively. These values exceed the typical luminance of displays ($\approx 300$ cd/m$^2$) by far. The applied setup is illustrated in the inset of fig. 6.8.

The dark and the illuminated transfer characteristics are exemplarily depicted in fig. 6.8 for a Pt-based device. Red light obviously does not significantly affect the device operation. In contrast, blue and green light significantly shift the transfer curve to lower gate voltages and increase the off-current. The respective transistor parameters for both gate materials are
Figure 6.9: Characteristic transistor parameters for Ag- and Pt-based TMESFETs exposed to visible light.

depicted in fig. 6.9. The field-effect mobility remains constant for red light illumination and decreases up to 20% for blue light. Here, the net doping density determined from QSCV in dark conditions is used.

The on-off current ratio decreases with decreasing wavelength up to about one order of magnitude for Pt- and almost two orders of magnitude for the Ag-based device. The larger increase for the Ag-based device is possibly due to the larger transmittance of the Ag-based TRC compared to the Pt-based TRC (cmp. fig. 4.2). An even stronger effect for similar illumination has been observed for ZTO-based TMISFETs [Goe+07b].

The maximal increase of $SS$ for blue light for both devices by roughly a factor of two and the shift of $V_{SS}$ of about $-0.2(-0.4)\ V$ for Pt-(Ag-) based gates are both significantly lower than previous reports of transparent MISFETs [Goe+07b; Bar+06; Oht+06].

As the light-induced change is rather similar for both gate materials, it originates most probably from the channel layer. This is further supported by the similar behavior of opaque MESFET on similar channel material [Fre+10b], as light primarily affects the channel for these devices. Deep acceptor-like traps are a possible source of the observed effect. If light of sufficient photon energy yields the emission of electrons into the conduction band from occupied states, a photocurrent is generated. This explains the increase of the off-current, which is dominated by the reverse current of the gate diode, and the increase of $SS$. At the same time, a photo-voltage is generated which opposes the gate bias required to pinch-off the channel. Thus, a more negative gate potential is required to reach the off state. Nevertheless, previous studies of illuminated
ZTO-based TMISFETs relate the observed effects to the light-induced generation of additional defect states in the channel [Goe+07b], which cannot be excluded to also occur in the samples investigated in this work.

Conclusively, the TMESFET exhibit a comparably stable behavior upon illumination with visible light. Especially, as the origin of the observed effects are probably within the channel material, trap reduction by optimized growth potentially permits to further reduce the impact of visible light on the transistor performance.
6.1.1.5 Longterm stability of TMESFETs

In order to study the longterm stability of the TMESFETs, a sample of each gate material was investigated in regular intervals. The samples were stored between the measurements in dry air without light shielding. No encapsulation or passivation of the devices has been carried out. The time evolution of the transfer characteristic is depicted exemplarily for a Pt-based device in fig. 6.10. Notably, the transfer characteristic changes slightly for the Pt-based device within 151 days. Nevertheless, during the most recent measurement procedure an irreversible breakdown occurred. The respective transfer characteristic before (1) and after (2) breakdown are depicted in fig. 6.10. For measurements with $V_{SD} > 1$ V, it has been observed that the reverse gate bias required for reversible breakdown to occur decreases with time. While there was no breakdown observed for the as-fabricated device for $V_{SD}$ up to 2.5 V and $V_G$ as low as $-2.5$ V, after 39 days the first indication of a breakdown is observed for the most extreme voltage conditions applied. In contrast to the Pt-device, the Ag-based TMESFET exhibited a significantly faster degradation. For this device, the effect of reversible breakdown was appearing already 14 days after fabrication for lower applied voltages of $V_{SD} = 2$ V and $V_G \approx -1.5$ V. The decrease of the breakdown voltage is possibly due to the formation of additional defect levels within the channel.

![Figure 6.10: Time evolution of the transfer characteristic of a Pt-based TMESFET ($V_{SD} = 1$ V).](image-url)
Figure 6.11: Time evolution of the transistor parameters of Ag- and Pt-based TMESFETs for $V_{SD} = 1$ V.

The field-effect mobility, as extracted from the transfer characteristic’s transconductance, decreases for both gate materials by about 30-40% if the net doping density determined from the as-fabricated device is used. Within the accuracy of the QSCV measurements, a change of the net doping density with time cannot be excluded. While a decrease of the channel mobility is less probable, the observed decrease of $\mu_{FE}$ possibly originates from a decrease of the net doping density due to the introduction of compensating defect states. Due to the direct exposure of the channel layer to the atmosphere between ohmic electrodes and gate, external sources like hydrogen could be responsible for the observed effect [Toh+06]. Additionally, an increase of the resistivity of the TCO electrodes or the contact resistance may also play a (minor) role. $I_{on}/I_{off}$ of the Pt-based device degrades within the first month by about a factor of three and remains then almost constant for the next four months. In contrast, $I_{on}/I_{off}$ of the Ag-based device drops by almost three orders of magnitude within the first two months due to a significant increase of the off-current. Accordingly, $SS$ of the Ag-device is increasing by almost a factor of four, whereas the Pt-based device exhibits an almost constant $SS$ over time. $V_{SS}$ remains for both gate materials almost constant.

In order to further clarify the origin of the degradation, the gate contact’s current-voltage
characteristics were investigated. The initial state and the state after 121 days\(^2\) is depicted in fig. 6.12, revealing a significant difference in the time evolution.

Considering the forward regime, for the Ag-TRC the current in the exponential regime is decreasing with time, which is indicating an increase of the effective barrier height. The opposite effect occurs for the Pt-TRC.

The voltage dependence of the reverse current of the Ag-TRC is significantly increasing with time, yielding a more than one order of magnitude increased reverse current at \(-2\) V. Possibly, a profound change of the barrier potential fluctuations takes place. Conclusively, the voltage dependence of the barrier increases and additionally tunneling may play an increasingly important role in current transport. In contrast, for the Pt-TRC a comparably weaker increase of the reverse current with no significant change of the voltage dependence occurs. Thus, silver diffused into the channel is possibly contributing to the observed effect.

\(\Phi_{\text{B,eff}}, n\) and \(R_S\) of the TRC, as extracted using thermionic emission theory, are summarized in fig.6.13. \(\Phi_{\text{B,eff}}\) of the Pt-device evolves with time similar as the on-off current ratio: a weak performance decrease within the first month is followed by a stable behavior in the next four months. In contrast, \(\Phi_{\text{B,eff}}\) of the Ag-device increases slowly but continuously over time, at the

\(^2\)This time was chosen, as no comparable curve is available for the Pt-device after 151 days due to irreversible breakdown occurring prior to the diode measurement.
end by about 50 mV. The latter observation is not contradicting the strong decrease of the off-current, as within the diode measurements lower electrical fields are in effect and conclusively no breakdown occurs. The increase of the effective barrier height of the gate diode indicates, that at least in an area fraction higher barrier heights occur, e.g. due to post-oxidation of the contact material. This may also be partly responsible for the observed decrease of the breakdown voltage, via the formation of “spikes” of higher electrical fields.

The ideality factor decreases with time slightly for both devices, which somewhat contradicts the observed increase of the slope of the reverse current for the Ag-devices, as the ideality factor is introduced to model the voltage dependence of the barrier height. Thus, the contribution of tunneling to the current transport is further substantiated.

The series resistance remains almost constant for the Pt-TRC and increases significantly for the Ag-TRC.

In conclusion, while the Ag-based TMESFETs degrade significantly within two months, the Pt-based TMESFETs remain operational for a significantly longer period of time. Namely, the different evolution of the gate characteristics indicate different degradation mechanisms to occur. Nevertheless, both devices suffer from increasing breakdown probability, which finally
yields device failure in both cases. As the degradation might be related to the exposure of the channel and the gate contacts to external sources, e.g. humidity, the influence of encapsulation remains to be investigated in the future in order to be able to finally judge the longterm stability of the devices.
6.1.1.6 Bias stress stability of TMESFETs

In this paragraph, the effect of continuous positive and negative gate bias stress is investigated. The respective stress time dependence of the transfer curve is depicted exemplarily for a Pt-based TFT in fig. 6.14, revealing only weak changes during the applied stress time. The evolution of the transistor parameters is depicted for both gate materials in fig. 6.15 for positive gate bias and in fig. 6.16 for negative gate bias.

For positive gate bias stress, no degradation is observed for both devices. The Pt-based TFT exhibits an off-current decrease by a factor of two and conclusively a slight decrease of $SS$ by about 10%. All other parameters remain constant, whereas compared to reports on TMISFETs especially the constant switching point as indicated by $V_{SS}$ is noteworthy [SM08].

If negative gate bias is applied, the behavior of the Pt- and the Ag-based devices differs. The Pt-device performance is constant for $\mu_{FE}$ and $V_{SS}$ or even weakly increasing, in terms of an on-off current ratio doubling and a reduction off $SS$ by about 15%. In contrast, the Ag-based device exhibits significant degradation in terms of increasing off-current (more than one order of magnitude), conclusively increasing $SS$ (by about a factor of two) and decreasing field-effect mobility (by about 30%). A shift of $V_{SS}$ of about +0.3 V occurs. Predominantly, the degradation takes place within the first 1000 seconds of the bias stress. As the maximum
electrical field among the channel is significantly higher for reverse gate bias, it indicates, the existence of a threshold of the electrical field for the degradation.

In conclusion, Pt-based TMESFETs are within the investigated stress time stable towards positive and negative gate bias. Especially, no significant shift of the turn-on voltage is observed compared to the typically observed shifts of several volts for oxide-based TMISFETs [SM08; Goe+07a], which is attributed to trap states located at the interface between semiconductor and gate insulator. MESFETs do not have such an interface. A comparable stability has been observed for Ag-based opaque MESFETs [Fre+10b]. Their transparent counterparts are stable to positive gate bias, but partially degrade for negative gate bias within a short period of time. Here, the reduction of the gate thickness obviously decreases the device stability. As the devices investigated in this work are not passivated, the bias stability especially of the Ag-based devices can possibly be increased by encapsulation. Furthermore, optimized growth conditions and stoichiometry of the channel material also potentially affect the stability of the devices, as indicated by the beneficial effect of Mg on the long term stability of opaque MESFETs [Fre+10b] or the reduction of bias-stress induced shifts for MISFETs [Goe+07a].
Figure 6.16: Transistor parameters of Ag- and Pt-based TMESFETs in dependence of the time negative gate bias stress ($V_{SD} = 2$ V, $V_{G,Ag} = -2$ V and $V_{G,Pt} = -2.5$ V) is applied.
Figure 6.17: (a) Transfer characteristics of the Ag- and Pt-based TMESFETs used for pulsed measurements. Schematic representation of drain-lag (b) and gate-lag (c).

6.1.1.7 Dynamic effects

Current transistor applications require to a great extend rapid switching properties. Accordingly, the maximum operating frequency is an important figure of merit. A common method to determine the latter value are ring oscillators, consisting of an odd number of inverter circuits arranged in series [Sun+08; Shi+09; Pre+06]. Nevertheless, the deduction of the physical origin of the bottleneck and in consequence the effective control of device optimization is difficult with this method, as the primary output is a property of a device ensemble.

Another means for the determination of the dynamic properties of transistors is the application of pulsed bias to the gate or the drain electrode along with time-dependent measurements of the drain-current. Similar measurements have been carried out for GaN- and GaAs-based devices [Sas+95; Har+87; Roc85; Vet+01; MM03; Men+04], revealing the so-called drain-lag (DL) and gate-lag (GL) effects. The effects are named according to the electrode, to which a pulsed voltage is applied. A schematic representation of the observed effects is depicted in fig. 6.17 (b) and (c). While gate-lag behavior typically denotes a delayed increase of the absolute current value to its saturation value, drain-lag is characterized by a current overshoot and a subsequent decrease of the absolute current to the equilibrium value. Physically, the observed transients originate from trapping and detrapping of defect levels. As the transient’s
time constants are typically in the µs- or s-range, deep defect levels are potentially responsible for the observed effects (due to the exponential dependence between activation energy and emission rate). The traps are potentially located either at the channel’s interfaces or within its bulk. Previous investigations revealed, that the current transients can be best described by a stretched exponential function of the form [Vet+01]:

\[ I(t) = I_0 \left( 1 + A \exp \left[ -\left( \frac{t}{\tau} \right)^{\beta} \right] \right), \]  

(6.1)

Here \( I_0 \) denotes the equilibrium value, \( A \) the relative amplitude of the lag-contribution, \( t \) the time, \( \tau \) the time constant and \( \beta \in (0,1] \) the stretching exponent. For \( \beta = 1 \), the time dependence is exponential. Values of \( \beta < 1 \) are attributed to the presence of multiple trap levels of comparable emission rates or to the time variation of the electric potential or the carrier concentrations [Men+04]. The average time constant \( \bar{\tau} \) can be defined by [BBV05]:

\[ \bar{\tau} = \tau \Gamma \left( 1 + \frac{1}{\beta} \right), \]  

(6.2)

with \( \Gamma \) denoting the gamma function.

The transfer characteristics of the Ag- and Pt-based TMESFETs used for this experiment are depicted in fig. 6.17 (a), the respective transistor parameters are summarized in table 6.2. Except for the slightly different \( \mu_{FE} \) and the different \( V_{SS} \), the transistor properties are quite similar. A comparison of the experimentally observed gate-lag and drain-lag behavior of

| Table 6.2: Static transistor parameters of the devices used for dynamic measurements. |
|-------------|----------------|-----------|-------|
| \( I_{on}/I_{off} \) | \( \mu_{FE} \) (cm²/Vs) | \( SS \) (mV/dec) | \( V_{SS} \) (V) |
| Ag-TMESFET | \( 1 \times 10^5 \) | 7.4 ± 1 | 156 | -1.15 |
| Pt-TMESFET | \( 7 \times 10^5 \) | 15 ± 3 | 144 | -1.89 |

the Ag- and Pt-based TMESFETs is depicted in fig. 6.18 for a single pulse. The parameters of the stretched exponential fitting using equation 6.1 are summarized in table 6.3. The applied pulses with a frequency of 1 Hz exhibit flank rise and fall times of 100 ns. Thus, the potential change can be assumed here to occur instantaneously. Low and high potential flank responses are depicted separately. The scale is normalized to the amplitude of the current pulse, to compensate for the different static values of \( I_D \).

GL and DL effects are significantly enhanced for the Ag-gated TFT, yielding even for the comparably slow pulse sequence applied here a significant deformation of the rectangular pulse shape, as also the relative amplitudes from the fit indicate. In contrast, the Pt-based device
Figure 6.18: Drain current transients for pulsed gate bias (GL) between $V_G = 0$ V and $V_G = +1$ V with $V_{SD} = 2$ V and pulsed source-drain voltage (DL) between $V_{SD} = 0.5$ V and $V_{SD} = 1$ V with $V_G = 0$V. The upper figures represent the high pulse part, the lower figures the low pulse part.

exhibits only a very weak deviation between first measured current value and the equilibrium value ($< 2\%$ for all signal parts). A similar observation has been carried out for opaque MgZnO-based MESFETs, revealing lag-induced wave-form deformation for operating frequencies above 1 Hz for Ag-based MESFETs, while Pt-based MESFETs are compatible to frequencies of at least about 1 MHz [Kl"{u}+11]. Along with the previous observation of silver from the contact material diffusing into the semiconductor [Wen+10a], it can be concluded, that the silver has an essential contribution to the effect. This is substantiated by experimental and theoretical reports indicating silver to form a deep defect level in ZnO [Kan91; YAW06].

The typical effective time constants of the order of ten milliseconds for the Ag-based device is similar to the values observed for opaque ZnO-based MESFETs [Kl"{u}+11]. The effective time constants of the Pt-based devices range between a few milliseconds and more than 100 ms, which is to some extend due to the small relative contribution of the lag-effect and the respective ambiguity of the fitting.

In order to further characterize the lag effects on TMESFETs, temperature dependent measurements were carried out. Unexpectedly, no significant thermal activation of the time constants was observed for both gate materials. While usually trap state emission is temperature acti-
Table 6.3: Effective time constant and relative fraction of the GL-/DL-effect to the drain current pulse amplitude extracted by fitting of equation 6.1 to the transients depicted in fig. 6.18.

<table>
<thead>
<tr>
<th></th>
<th>GL</th>
<th>Ag-TMESFET</th>
<th>Pt-TMESFET</th>
</tr>
</thead>
<tbody>
<tr>
<td>up</td>
<td>( \tau ) (ms)</td>
<td>14.8 ± 1</td>
<td>92 ± 2</td>
</tr>
<tr>
<td></td>
<td>(</td>
<td>I_{0,\text{up}}A_{\text{up}}/(I_{0,\text{up}} - I_{0,\text{down}})</td>
<td>) (%)</td>
</tr>
<tr>
<td>down</td>
<td>( \bar{\tau} ) (ms)</td>
<td>12.1 ± 1</td>
<td>160 ± 40</td>
</tr>
<tr>
<td></td>
<td>(</td>
<td>I_{0,\text{down}}A_{\text{down}}/(I_{0,\text{up}} - I_{0,\text{down}})</td>
<td>) (%)</td>
</tr>
<tr>
<td></td>
<td>DL</td>
<td></td>
<td></td>
</tr>
<tr>
<td>up</td>
<td>( \tau ) (ms)</td>
<td>13 ± 2</td>
<td>6 ± 6</td>
</tr>
<tr>
<td></td>
<td>(</td>
<td>I_{0,\text{up}}A_{\text{up}}/(I_{0,\text{up}} - I_{0,\text{down}})</td>
<td>) (%)</td>
</tr>
<tr>
<td>down</td>
<td>( \bar{\tau} ) (ms)</td>
<td>20 ± 5</td>
<td>210 ± 200</td>
</tr>
<tr>
<td></td>
<td>(</td>
<td>I_{0,\text{down}}A_{\text{down}}/(I_{0,\text{up}} - I_{0,\text{down}})</td>
<td>) (%)</td>
</tr>
</tbody>
</table>

vated, the observed behavior is possibly due to the interference of two different contributions of opposite sign as revealed in a previous work for opaque MESFETs [Klü09; Sch11].

In conclusion, gate- and drain-lag effects were observed for TMESFETs, which are especially significant for Ag-based devices. As measurements on opaque MESFETs revealed, this effect is especially limiting the high-frequency operation. Thus, for HF purposes Pt-based TMESFETs are more promising.
6.1.2 TMESFETs with amorphous InGaZnO-channel

The MgZnO channel layers of the devices investigated in the previous paragraphs were epitaxially grown on sapphire substrates, permitting crystalline growth but being also costly due to high growth temperatures and substrate prices. In this section, an intentionally amorphous InGaZnO channel layer is fabricated on amorphous substrates. In succession, growth temperatures are lower and the prospective uniformity of device properties, especially required for large scale applications, is increased [Hos+08]. Furthermore, the use of flexible substrates becomes feasible [Nom+04]. Details concerning InGaZnO and related materials are summarized in sec. 2.1.2. In the first subsection, the properties of TMESFET grown on glass substrates are investigated, while in the second subsection TMESFETs fabricated on flexible polymer films are studied, namely in dependence of the bending radius.

6.1.2.1 TMESFET on glass substrates

![Graph](image)

Figure 6.19: (a) Transfer characteristic of a Ag-based TMESFET with an amorphous InGaZnO-channel. The dashed line denotes the gate current. (b) Transmittance spectrum of the gate electrode. (c) TRC IV-characteristic.

Corning 1737, a borosilicate glass, which is applied for display applications, was chosen as substrate for this investigation. The InGaZnO channel layer was grown by P. Barquinha (CENIMAT, Portugal) using a rf magnetron sputtering system. The target composition is...
2:4:1 (Ga:In:Zn), the film growth was conducted at room temperature with a thickness of (190 ± 20) nm as determined from AFM. The film was annealed prior to the device processing in air at 150°C for one hour in order to increase film and device performance [Lor+10b]. From QSCV-measurements, a net doping density of \( N_D - N_A = (2.6 \pm 0.1) \times 10^{16} \text{ cm}^{-3} \) was extracted. The Ag-based TMESFETs were processed similar to the previous section as described in sec. 3.1.3. Due to the increased etch resistance of the InGaZnO compared to the previously used MgZnO and the increased thickness of the film, the concentration of the phosphoric acid was doubled to 1 : 40 and the etching time was increased to 30 min.

The transfer characteristic of a normally-on InGaZnO-channel TMESFET is depicted in fig. 6.19. The device reaches an on-off current ratio of \( 1.2 \times 10^6 \), a field-effect mobility of \( 8.6 \pm 1.2 \text{ cm}^2/\text{V}s \) and a subthreshold slope of 136 mV/dec. Thus, the device properties are similar to the best values found for TMESFETs based on MgZnO channels (cmp. sec. 6.1.1). The mean transmittance in the visible spectral range of the gate electrode reaches \( T_{VIS} = 70 \% \) as the transmittance spectrum in fig. 6.19 (b) reveals \( (T_{VIS} = 84 \% \text{ for substrate + channel, only}) \). Thus, all criteria for transparent electronics, as given by [Wag03], are fulfilled, namely \( I_{on}/I_{off} > 10^6 \), \( \mu_{FE} \gg 1 \text{ cm}^2/\text{V}s \) and \( T_{VIS} \geq 70 \% \).

The diode characteristic of the gate TRC is depicted in fig. 6.19 (c). Using TED-theory (cmp. sec. 2.2.1), effective barrier height and ideality factor were determined to be \( (0.82 \pm 0.02) \text{ V} \) and 1.24, respectively, which is comparable to the values obtained on MgZnO as expected from sec. 4.3. The remarkable increase of the diode reverse current, which also dominates the transistor’s off-current indicates a significant voltage dependence of the barrier, as expected for laterally inhomogeneous barriers. Due to the reduced net doping density, the effect of tunneling can be neglected for the present channel material and temperature.
6 Transparent TRC-gated field-effect transistors and their applications

6.1.2.2 TMESFET on flexible substrates

With the successful fabrication of high quality TMESFETs on amorphous substrates, the use of cheap and lightweight flexible substrates becomes feasible. Thus, a 175 nm thick InGaZnO film was grown on 125 μm-thick transparent PEN-foil with similar growth conditions as in the previous section (also conducted by P. Barquihna, CENIMAT, Portugal). Subsequently, a Pt-gated TMESFET was fabricated as described in the previous paragraph and in sec. 3.1.3. While TVIS of PEN substrate+channel reaches 80 %, the gate electrode transmits on the channel layer still 73 % of the visible spectrum (cmp. fig. 6.21 (b)). A photograph of the bendable sample is depicted in fig. 6.20 (a) and the transfer and output characteristics of the as-fabricated device are depicted in fig. 6.21 (a) and (c). Obviously, the device is normally-off with a turn-on voltage of about 0 V. In consequence, the gate current increases almost instantly after the channel pinch-off vanishes for increasing gate voltage. As the gate current dominates in the on-regime, several device parameters are affected. The on-off-current ratio (of the drain current) is only $5 \times 10^3$. The subthreshold slope seems with 82 mV/dec very close to the theoretical minimum of about 60 mV/dec, but is probably underestimated. And finally, the field-effect mobility can be neither from the transfer nor the output characteristic reasonably extracted, as the transconductance is reduced by gate leakage currents in both cases. In order to overcome this issue, a thicker channel or a higher net doping density is required.

Nevertheless, the device shows a significant field-effect, as both the transfer curve and the output characteristic reveal and permits to study the effect of substrate bending. Exemplarily, the effect of tensile stress on the electrical performance of this device is investigated. The bending measurements were conducted about three days after fabrication of the device. During that time, on the one hand the on-off-current ratio increased significantly due to a decrease of the off-current. On the other hand, within the switching regime a significant

---

3Polyethylenaphthalat
Figure 6.21: Transfer (a) and output (c) characteristic of a as-fabricated Pt-based TMESFET with InGaZnO-channel grown on PEN foil. The dashed line indicates the gate current. For the output characteristic, the gate potential was varied between −0.5 V and 1 V in steps of 0.1 V. (b) depicts the spectral transmittance of the gate electrode.

deviation from the initial state can be observed. The increase of the drain current with increasing gate voltage shows a two-step behavior (cmp. black curve in fig. 6.22). A similar behavior has been observed for a TFT fabricated on comparable PEN substrate with InZnO channel using tungsten oxide gated MISFETs. Thus, it is assumed, that the origin of this effect is related to the combination of polymer substrate and amorphous oxide channel layer rather than to the gate contact. For example, a defect-induced increase of the doping density, spatially constrained to the vicinity of the substrate-channel interface, would decrease the extension of the space charge layer there and would require lower gate voltages for pinch-off as observed.

The tensile stress on the sample was induced via bending over metallic cylinders, as sketched in fig. 6.20 (b). The radii of the cylinders were between $r = 20.5$ mm and $r = 5$ mm, which is among the lowest values reported so far for bent oxide FETs [Nom+04; CMT10]. The strain occurred along the transistor channel as indicated in fig. 6.20 (c). For calculating the maximal strain occurring at the surface of the channel layer, it is assumed that the InGaZnO film covers the substrate entirely. Furthermore, source and drain contacts are neglected and no initial
The thickness of the substrate and the film are \( d_s = 125 \, \mu m \) and \( d_f = 175 \, nm \), respectively. The Young’s moduli are \( Y_f = 137 \, GPa \) [Par+10] (value of ZnO) and \( Y_s = 6 \, GPa \) [Bur10]. The transfer characteristics after bending with varying radii are depicted in fig. 6.22, the respective transistor parameters of the device are summarized in fig. 6.23. Notably, only weak changes of the off-current and the on-current occur for bending radii as low as 12.5 mm, as the on-off current ratio remains stable at about \( 3 \times 10^5 \). As the gate current is dominating in the on-regime, the extracted \( \mu_{FE} \) is with \( \approx 0.1 \, \text{cm}^2/\text{Vs} \) underestimating the true value, nevertheless it also remains stable for large radii. Also \( V_{SS} \) and \( S_S \) do not change significantly due to the bending. Remarkably, the previously mentioned two-step behavior vanishes, possibly indicating a relation to the strain in the film. For radii below 12.5 mm, the transistor performance degrades significantly. Namely, the on-current drops and conclusively the on-off current ratio and \( \mu_{FE} \) decrease. After bending to 5 mm, the field-effect is almost absent and the device is almost statically off.

Remarkably, the on-current of the gate-drain and the gate-source diode does not decrease sim-
Figure 6.23: Transistor parameters in dependence of the minimum bending radius and the maximal strain in the channel calculated using equation 6.3 for a Pt-based TMESFET. The dashed line indicates the onset of severe device degradation.

Similarly (not shown here). Thus, the occurrence of cracks in the channel material is improbable, as then the current path for the diode measurements would be also interrupted. The observed behavior is attributed to cracks occurring within the gate contact itself. They yield the formation of potential free stripes of the gate. In succession, the channel remains pinched-off underneath the insulated stripes, independently of the gate voltage. If now the remaining noninsulated regions of the gate are located at the edge of the gate, the recording of an almost unchanged diode characteristic (unless a reduction of the current due to the contact area loss, which has been observed) can be explained.

In conclusion, the comparably stable device performance for bending radii of 12.5 mm and above, is among the best values reported so far [Nom+04; CMT10; MCT11]. For lower radii, potentially cracks in the gate are formed yielding significant device degradation. Using optimized device geometries with strain reducing overlayers, the minimum bending radii can potentially be further reduced.
6.2 Applications

6.2.1 Towards integration: Inverter circuits

The simplest form of integrating transistors to gain new functionality is the combination of two transistors according to the circuit diagram given in fig. 6.24. The gate of the load transistor \(Q_L\) is short-circuited with its source and therefore a single output curve \((V_G = 0\, \text{V})\) is selected out of the set of output characteristics (cmp. red curve in fig 6.25 (a)). By tuning the input voltage applied to the gate of the switching transistor \(Q_S\), its channel conductivity is modified. As \(Q_L\) and \(Q_S\) form a voltage divider, the resulting output voltage, extracted between \(Q_S\) and \(Q_L\), is almost similar to the supply voltage \(V_{DD}\) as long as the \(Q_S\) channel resistivity is significantly higher compared to \(Q_L\) (cmp. the first points of the plot \(V_{OUT}\) vs. \(V_{IN}\), which is denoted as voltage transfer characteristic (VTC), in fig. 6.25 (b)). As soon as the channel resistivities become comparable, the voltage drops over both channels and \(V_{OUT}\) decreases rapidly. According to the inverse relation between the input voltage and the output voltage, this device can be understood as the simplest realization of an inverter circuit for binary logic.

The slope \(\frac{dV_{OUT}}{dV_{IN}}\) is denoted gain, its maximum pgm (peak gain magnitude), as this circuit is further applicable for voltage amplification. The gain is sensitive to the magnitude of the voltage dependence of the saturation current (e.g. due to channel length modulation). While the pgm is infinite for constant \(I_{SD,sat}\), it decreases for finite values. As \(\frac{dI_{SD,sat}}{dV_{SD}}\) decreases with increasing \(V_{SD}\), a higher supply voltage is expected to yield higher pgm, as the intersection between the output curves of both TFT occurs at higher \(V_{SD}\) (cmp. point 5 in fig. 6.25).

In terms of binary logic, the inverter circuit is within the switching regime in an undefined state. To characterize this for practical devices, the uncertainty level \(V_{UC} = \Delta V\big|_{dV_{OUT}/dV_{IN} = 1}\) is introduced, as sketched in fig. 6.25 (b) by the dotted lines and the grey area. For the ideal case of two identical FETs, it is centered on \(V_{IN} = 0\, \text{V}\).

Finally, if the switching transistor’s channel conductivity is further lowered, the supply voltage drops primarily among \(Q_L\). Thus, \(V_{OUT}\) is approaching zero. The transistor’s turn-on voltage sensibly affects the minimum achievable \(V_{OUT}\) as it is correlated with the available change.

**Figure 6.24:** Circuit diagram of a simple inverter circuit overlayed to an image of a fully transparent inverter circuit based on AgxO-gated TMESFET. The load transistor is depicted in red, the switching transistor in blue.
The VTC depicted in fig. 6.25 (b), as deduced from the \( Q_S \) and \( Q_L \) output curve in fig. 6.25 (a), shows the ideal case. Three deviations from the ideal case may occur:

- **Low input level:** \( V_{\text{OUT}} \) may drop significantly below \( V_{\text{DD}} \), especially for large values of \( V_{\text{DD}} \). This can be explained by the breakdown of \( Q_S \), as among this FET most of the potential drop occurs.

- **Switching regime:** Inequalities between the transistors yield a shift of \( V_{\text{IN,pgm}} \).

- **High input level:** \( V_{\text{OUT}} \) will increase as soon as gate leakage currents dominate, as the output-curve of \( Q_S \) is shifted to higher \( V_{\text{SD}} \). This is a MESFET-immanent effect and its onset depends on the barrier height and ideality factor of the gate diode.

In the following section, the application of TMESFET in simple inverter circuits are demonstrated. The devices were fabricated as described in section 3.1.3, the gates consist of Ag-based TRC (cmp. sec. 4.1), the ohmic electrodes consist of thin sputtered gold films \( (P = 5 \text{ W}, t = 10 \text{ s}, 100 \text{ sccm Ar}) \). The VTC of a Ag-gated TMESFET-based inverter circuit is depicted.
for various supply voltages in fig. 6.26; a microscopic image of the device is depicted in fig.6.24 in front of the logo of the graduate school BuildMoNa. While the high $V_{\text{OUT}}$-regime reproduces almost ideally the supply voltage, due to the steep increase of channel resistivity for reverse bias (cmp. transfer characteristic e.g. in fig. 6.2), in the low $V_{\text{OUT}}$-regime 0V is not reached due to smaller channel resistance change occurring for forward bias. For $V_{\text{IN}} > 0.7$ V, the gate-leakage related increase of $V_{\text{OUT}}$ is observed. It is worth noting, that the output interval, $[\approx 0.2$ V, $\approx V_{\text{DD}}]$, of these simple inverters is not compatible with the input interval of e.g. $[-1$ V,1 V]. Thus, in order to combine such a simple inverter circuit in series e.g. to build a ring oscillator, either FETs of variable gate dimensions or circuits with additional level shifter have to be used to match the intervals [Fre+10b; SS07].

The supply voltage dependencies of pgm, $V_{\text{UC}}$ and $V_{\text{IN,pgm}}$ are depicted in fig. 6.26. The pgm was determined by interpolating the measured data first, using piecewise cubic Hermite interpolation, which conserves the shape of the curve, avoids oscillatory solutions and conclusively overestimation of the pgm [FC80]. The pgm increases as expected drastically with $V_{\text{DD}}$, reaching with $pgm = 227$ for $V_{\text{DD}} = 4$ V the highest so far reported value for oxide-based fully transparent inverter circuits (cmp. table 6.4). Considering opaque oxide-based devices, only MESFET-based inverter circuits reveal comparable performance. This is further sub-
statiated, if the pgm normalized to the supply voltage is considered. The TMESFET-based inverters reach with up to 56 V \(^{-1}\) almost similar performance as their opaque counterparts but exceed the best reported non-MESFET values by a factor of four. The switching point is with less than 0.2 V deviation almost ideally located for all investigated supply voltages and the uncertainty level remains almost constant at about 0.35 V, which is already comparable with established GaAs-based MESFET devices (\(V_{UC} \approx 0.1\) V).

<table>
<thead>
<tr>
<th>Table 6.4: Comparison of inverter properties.</th>
</tr>
</thead>
<tbody>
<tr>
<td>channel material</td>
</tr>
<tr>
<td>---------------------</td>
</tr>
<tr>
<td>opaque devices</td>
</tr>
<tr>
<td>n-ZnO</td>
</tr>
<tr>
<td>n-ZnO</td>
</tr>
<tr>
<td>n-ZnO</td>
</tr>
<tr>
<td>n-ZnO</td>
</tr>
<tr>
<td>ZnSnO</td>
</tr>
<tr>
<td>n-InGaZnO</td>
</tr>
<tr>
<td>n-ZnO, pentacene</td>
</tr>
<tr>
<td>n-ZnO, p-ZnTe</td>
</tr>
<tr>
<td>n-InGaZnO, pentacene</td>
</tr>
<tr>
<td>n-In(_2)O(_3), p-SnO(_2)</td>
</tr>
<tr>
<td>a-InGaZnO</td>
</tr>
<tr>
<td>n-InGaZnO, p-CuO(_2)</td>
</tr>
<tr>
<td>Zn(<em>{0.997})Mg(</em>{0.003})O</td>
</tr>
<tr>
<td>fully transparent devices</td>
</tr>
<tr>
<td>n-InGaO</td>
</tr>
<tr>
<td>carbon nanotubes</td>
</tr>
<tr>
<td>n-ZnO, Pentacene</td>
</tr>
<tr>
<td>n-InGaZnO</td>
</tr>
<tr>
<td>Zn(<em>{0.997})Mg(</em>{0.003})O</td>
</tr>
</tbody>
</table>

6.2.1.1 Operational stability towards illumination with visible light

In this section the stability of the inverter VTC is studied under illumination with visible light [Laj+11]. For this purpose, the samples were illuminated with red (\(\lambda = 628\) nm; FWHM = 20 nm), green (\(\lambda = 525\) nm; FWHM = 30 nm) and blue (\(\lambda = 435\) nm; FWHM = 25 nm) LEDs. The irradiance was adjusted to about 10 W/m\(^2\) for all LEDs, similar to the previous study for the TMESFETs (cmp. sec. 6.1.1.4). The respective setup is illustrated in the inset of fig. 6.8. The VTC of a transparent inverter circuit measured under dark conditions and under illumination are depicted in fig. 6.27 (a). Obviously, red and green light does virtually not affect the VTC, whereas blue light slightly modulates the VTC. This is consistent with the previous
Figure 6.27: Influence of visible light on the VTC (a) of a transparent Ag-based inverter, the line color corresponds to the light color. (b) relative change of $V_{\text{OUT}}$ for $V_{\text{in}} = -1 \, \text{V}$ and $V_{\text{in}} = +1 \, \text{V}$ (according to sign in symbol). (c) absolute input voltage shift of pgm-point. (d) relative change of $V_{\text{uc}}$. (e) relative change of pgm.

study on single TMESFET, where the strongest change was similarly observed for blue light, while red and green light yielded weaker changes (cmp. sec. 6.1.1.4).

As the blue photon energy is lower than the fundamental band gap of MgZnO, it can be concluded that deep acceptor states in the channel provide the photo-generated carriers. As both gates act as photo-diodes (cmp. sec. 4.4), a photo-current is generated among both TFTs and contributes to the output-characteristic. This current increases with increasing source-drain voltage. For the almost ideal case of $V_{\text{IN}, \, \text{pgm}} = 0 \, \text{V}$, which is present here, both TFTs exhibit an almost identical source-drain voltage drop at pgm. Thus, a similar photocurrent is generated by both TFTs and the pgm-point does hardly shift. As soon as regions away from the pgm-point are considered, the asymmetrical potential drop distribution between both TFTs yields a difference in photocurrent-generation between both TFTs. Accordingly, for $V_{\text{IN}} < V_{\text{IN}, \, \text{pgm}}$, a larger photocurrent is generated by the switching transistor and the VTC
is shifted to lower $V_{OUT}$. For $V_{IN} > V_{IN, pgm}$, the VTC is shifted to higher $V_{OUT}$. This effect is especially obvious by the crossing of the blue light curve and the other curves.

Of course, the switching regime exhibits the most pronounced deviations, as it is most sensitive towards changes of the transistor characteristics. Here, blue light yields an input voltage shift of about $-50 \text{ mV}$, a 15%-increase of the uncertainty level and 40% decrease of the pgm (cmp. fig. 6.27 (c), (d) and (e)). The latter effect can be traced back to an increased voltage dependence of the saturation current due to the generated photo current. Nevertheless, with pgm/$V_{DD} = 36$ under blue-light illumination, the gain of the device still outperforms the reported (dark) values of other transparent inverter circuits (cmp. table 6.4).

For high $V_{OUT}$, no dependency on the incident light is observed, as the output voltage only weakly depends on the input voltage and accordingly on small photo-induced shifts. Thus, the deviation from the dark state is less than half a percent (cmp. of fig. 6.27 (b)). For input voltages $> 0.3 \text{ V}$, the switching transistors’ gate leakage currents yield an increase of the output voltage up to 0.7 V. Only for blue light, a weak 5% increase of $V_{OUT}$ for $V_{IN} = +1 \text{ V}$ is observed (see fig. 6.27 (b)). The minimal value of the output voltage (0.1 V) is close to the ideal value of 0 V. Here, blue light induces an increase to about 0.15 V, whereas for red and green light the output voltage remains nearly unchanged.

Conclusively, under red and green light the voltage transfer characteristic remains almost unchanged compared to the dark case. For blue light pgm, pgm-voltage and uncertainty level degrade slightly. The occurring changes are attributed to photo-carrier-generation. The increase of the off-current by more than one order of magnitude for blue-light illumination as observed previously for a single Ag-based TMESFET (cmp. sec. 6.1.1.4), plays a minor role for the operation of the inverter circuit.
6.2.1.2 Operational stability towards elevated temperatures

The evolution of the VTC with increasing temperature is depicted exemplarily for three temperatures in fig. 6.28 [Laj+11]. Obviously, the inverting functionality is conserved even for operating temperatures as high as 150°C. The most obvious change occurs for positive input voltages, which is depicted in terms of $V_{\text{out}}$ for $V_{\text{IN}} = +1$ V in fig. 6.28 (b). While a temperature increase up to about 90°C hardly affects the VTC here, the output voltage increases considerably for higher temperatures. This is due to an increased gate current of $Q_{S}$, as the clear correlation between $V_{\text{out}+1}$ and $I_{\text{in}+1}$ indicates. The current increase is caused by the thermally induced, irreversible degradation of the gate electrode for $T > 90^\circ$C. This has been previously investigated for opaque Ag$_x$O-based MESFETs where the degradation started at similar temperatures [Fre+09]. The previous study on TMESFET transfer characteristics and the gate diode characteristics revealed an even earlier onset of degradation (cmp. sec. 6.1.1.3).

In the switching regime, for increasing temperatures below 90°C, the pgm increases and shifts closer to the ideal switching point of $V_{\text{IN}} = 0$ V (see fig. 6.29 a and b). With the onset of gate degradation ($T > 90^\circ$C), the pgm decreases and the switching point shifts towards higher input voltages. The uncertainty level generally decreases with increasing
temperature. Nevertheless, during the onset of gate degradation the decrease is interrupted for about about 30 K (see fig. 6.29 c).

In summary, the inverter circuits remain operational in the entire investigated temperature interval between room temperature and 150°C. For temperatures below 90°C the increase of temperature positively affects the inverter parameters. Beginning at about 90°C the gate electrodes degrade and reduce device performance in the switching regime and in the high input level regime, namely the pgm and $V_{out,+1\,\text{V}}$. The uncertainty level and $V_{out,-1\,\text{V}}$ monotonically become more ideal with increasing temperature.
6.2.2 Measurements of neuronal action potentials

The human brain consists of several tens of billions of neurons, each of them interconnected with several thousands of synapses [Dra05]. This highly complex system enables us to see, to feel, to remember and finally to have consciousness of ourselves. For comparison: current high-end processors contain a few billions of transistors [Wik12] and only a few interconnects on average. Great efforts were and are undertaken to understand the brain’s functionality. One branch of these efforts aims the understanding of the inter-neuronal communication. Galvani’s experiments on frog legs\(^4\) are probably the first documented hints towards the electrical nature of the signal propagation in nerve cells. Later on, potential differences between the in- and outside of nerve cells were proven using an electrode stuck through the cell membrane [Col79], which lead to the development of the Hodgkin-Huxley model [HH52] of the action potential. The membrane-invasive method was further refined by patch-clamp technique, which reduced the stress exerted to the cell [SN76]. While the latter technique permitted numerous new insights in electro-physiology, it is nevertheless comparably space-consuming and therefore does not permit to investigate larger cell networks. As a consequence, non-invasive methods permitting increased probing point numbers were developed.

Two general concepts can be identified: multi-electrode arrays (MEAs) and multi-transistor arrays (MTAs). MEAs consist of several point-like electrodes which are connected via passivated ohmic conductive paths with external amplifiers. Such devices are comparably cheap and can even be fabricated fully transparent using TCOs and therefore permit the use of standard transmission microscopy. Nevertheless, they exhibit limited spatial resolution as each electrode needs a separate conductive path, which is also subjected to signal-to-noise ratio related size constraints.

In contrast, MTAs consist of an array of FETs, which are located in direct vicinity of the cells [JSW01; Fro+91]. Such short signaling paths are advantageous for the signal-to-noise ratio and on the other side a high spatial resolution of less than 10 \(\mu\)m was already demonstrated [Lam+12]. As silicon-based devices are widely explored and can be easily fabricated, they are applied in the majority of previous works. Unfortunately, the observation of the cells during the potential measurements by standard transmission microscopy is due to the absorbance of the Si inhibited. While this is less critical for single neuron studies, it becomes more important for the investigation of complex neuronal networks. A MTA with a high density of fully transparent FETs fits the requirements for this

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\(^4\)Luigi Galvani, Italian physician and physicist (1737-1798)
The TMESFETs investigated in this work combine two elementary properties, which are advantageous for cell signal detection: high optical transmittance and low voltage operation. Especially the high gain of the TMESFET-based inverter circuits makes the application as amplifiers for small signals promising. In this section, a general proof-of-concept for the detection of small signals within aqueous solution by MESFETs is presented. The work was carried out together with F. J. Klüpfel within the framework of his diploma thesis [Klü09] and it is currently being continued within his PhD.

### 6.2.2.1 Chip design and fabrication

For the measurements of the action potentials using MESFETs, a chip layout was developed, as depicted in fig. 6.31 (b). It consists of four identical and independent quadrants of four MESFETs each in order to provide redundancy. Each transistor terminal is contacted by a conductive path of 80 µm widths. The width was chosen in order to compromise low opaque area fraction of the chip and sufficiently high conductivity of the conductive paths. The cell electrode’s signal can be directly gripped via the gate contact enabling MEA measurements for comparison. The MESFET structure was taken from previous studies [Fre+08]. The four electrodes in each quadrant are quadratic with a length of either 40 or 100 µm. The insulation layer masks permit to chose between single voids for each electrode or a combined void for each set of four electrodes. The contact areas at the edge of the chip are prepared for the flip-chip mounting to the holder [Mag+96]. The high precision mask-aligner commonly used for photolithography is applied for the positioning and contacting of the chip with the holder depicted in fig. 6.31 (a) and (c). The reservoir for the cell medium is formed by a glass.

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5The path resistance is with about 75Ω for 15 nm thick gold small compared to the electrolyte and the channel resistance.
ring, which is glued with biocompatible silicone adhesive (RTV162Q, Momentive Performance Materials Inc.) on the chip.

On double-side polished a-sapphire substrates, an about 25 nm-thin layer of Mg$_{0.0025}$Zn$_{0.9975}$O (target composition) is grown by PLD ($T = 670^\circ$C, $p_{O_2} = 0.02$ mbar). Using standard photolithography (cmp. sec. 3.1.3) and etching, all structures are defined. The ohmic contacts consist of sputtered gold with a nominal thickness of 20 nm, chosen in order to maximize the yield during the development of the structures. The opaque Ag-based gate contact consists of a silver-oxide layer ($P = 30$ W, $t = 25$ s, 50 sccm Ar, 50 sccm $O_2$) and a gold capping layer ($P = 30$ W, $t = 15$ s, 100 sccm Ar). The electrodes were deposited after the gates and consist of an about 5 nm thin and transparent gold layer ($P = 5$ W, $t = 10$ s, 100 sccm Ar). Finally, the insulation layer consisting of 200 nm thick Al$_2$O$_3$ is deposited by PLD at room temperature in order to avoid thermal degradation of the MESFETs and to avoid decomposition of the photoresist used for the definition of the contact voids. The biocompatibility of the gold and the Al$_2$O$_3$ was confirmed using cells from the NG108 cell line [Sch10]. The used cell medium in this work comprises of DMEM$^6$, HS$^7$ and several antibacterials [Sch10].

### 6.2.2.2 Proof-of-principle

The transfer characteristic of a MESFET of the developed chip measured in air is depicted in fig.6.32 (a). The passivation using 200 nm thick room-temperature grown Al$_2$O$_3$ affects the device performance, as the on-off ratio reaches only $3 \times 10^3$, with the off-current being obviously limited by the gate leakage current.

Subsequently, the device was exposed to cell medium as depicted in fig. 6.31 (c) and the gate potential was introduced via a Ag/AgCl-electrode. First of all, also in this case the transfer characteristic reveals a significant field-effect, which is the fundamental requirement for cell potential measurements. Nevertheless, compared to the transfer characteristic measured in air, a significant current increase is observed. This is even pronounced for $V_G > 0.5$ V, as the measurement sweep was started at $V_G = 1$ V. This indicates a charging of the electrolyte/chip interface. The comparably large source-drain electrodes, with an area of 0.2 mm$^2$ each, enhance this effect. A further origin of the increased current, namely in the reverse current regime of the gate electrode, are leakage currents due to imperfections of the insulation layer. Finally, one has to consider, that the true gate voltage is smaller than indicated in fig. 6.32 (a) due to the voltage drop along the medium. The current peak occurring at $V_G = -0.5$ V is possibly related to an electro-chemical reaction in the aqueous environment.

Using the same MESFET, the detection of cell potentials was simulated by applying square pulses to the Ag/AgCl-electrode. The base gate voltage of 0.6 V was chosen to maximize the transconductance of the present MESFET to $g_m = 0.017$ mS. The pulse amplitude of

$^6$Dulbecco’s modified eagle medium

$^7$horse serum
ΔV = 4 mV is significantly lower than the action potential for nerve cells (typ. between 50 and 100 mV) and among typical experimentally observed values [Lam+12]. The respective current answer is depicted in fig. 6.32 (b), showing clearly the effect of the applied bias pulses. Thus, it is proven that MESFET are generally able to detect small voltage pulses in wet environments. For the device presented here the signal-to-noise ratio is only 3:2. Nevertheless, as the maximal transconductance of the devices depicted in fig. 6.2 is about one order of magnitude larger compared to the device used here, a significant potential for improvement remains.

In conclusion, the general applicability of MESFET for cell potential measurements was demonstrated and thus fully transparent TMESFET-based MTAs are a promising approach for a correlated real-time investigation of the location of a neuronal network and its electro-physiological activity.
7 Summary

Transparent rectifying contacts The patented concept of transparent rectifying contacts was successfully realized. With an optimized overall thickness of about 10 nm, the layer stacks of platinum oxide or silver oxide and the capping layer of platinum or gold, respectively, yield an overall visible light transmittance of about 60% and 70%, respectively. The effective barrier height of these contacts is with about 0.85 V for both contact materials only slightly lower compared to their opaque counterparts [Fre+09].

For the Pt-based TRC, an accumulation of metallic species in the vicinity of the interfacial region was observed via depth-resolved photo-electron spectroscopy, indicating a reduction of the oxidic contact material and confirming the applicability of the Schottky theory for the TRC.

Theoretical simulations pursued in this work reveal the necessity to carefully check for the applicability of thermionic emission model for the description of current flow in rectifying contacts depending on doping and mobility of the used semiconductor. According to the latter results, for some samples in this work, a combined thermionic emission/diffusion model was applied to correctly describe the current-voltage characteristics. This model has been extended in the framework of this work to consider the effect of barrier inhomogeneities.

The height of the potential barrier, which is crucial for the TRC functionality, was identified to exhibit significant lateral fluctuations. These can be satisfactorily described by a Normal distribution. Nevertheless, an unexpected empirical correlation \( \sigma/\Phi_B, m \approx 0.11 \) between mean barrier height \( \Phi_B, m \) and distribution width \( \sigma \) is potentially an indication for deviations from a Normal distribution. The latter correlation was even found for numerous metal/semiconductor Schottky-diodes.

The TRC concept is applicable to semiconductors of different crystallinity with similar electrical performance, as a comparison between Ag-based TRC on single crystalline ZnO, hetero-epitaxially grown ZnO and amorphous InGaZnO revealed.

For the detection of UV-radiation, TRC can be applied in UV-photodetectors yielding external quantum efficiencies of \( \eta_{ext} = 0.33 \) \( (0.22) \) for Pt- (Ag-) based contacts in photo-voltaic mode. Moreover, the UV-VIS rejection ratio is in excess of \( 10^3 \).

Transparent conductive oxides Optimized TCO-layers, grown by pulsed-laser deposition (PLD) and consisting of nano-crystalline ZnO doped with aluminium or gallium exhibit a conductivity of 750 Scm\(^{-1}\) and 1250 Scm\(^{-1}\), respectively. The mean transmittance in the vis-
ible spectral range is $> 80\%$ for both dopants. The optimization was constricted to room-
temperature growth and film thickness of nominally 100 nm for compatibility to device fabrica-
tion. By increasing the thickness by one order of magnitude, conductivity can be increased
even further by about a factor of 1.5 for both dopants. The specific contact resistivity was
determined using a TLM approach to be of the order of $10^{-3} \Omega \text{cm}^2$ for typical device contact
dimensions in this work. The figure of merit considering optical and electrical performance
via transmittance and sheet resistance reaches $1.3 \text{k} \Omega^{-1}$ and $3.7 \text{k} \Omega^{-1}$ for the optimal growth
conditions of ZnO:Al and ZnO:Ga, respectively.

**Transparent MESFETs with MgZnO channel layers**  Finally, by combining TRC, TCO and
a nominally 25 nm thick MgZnO channel layer, grown at high-temperature by PLD on sapphire
substrates, TMESFETs were fabricated and characterized. A mean device transmittance in
the visible in excess of 70\%, a field effect mobility of about $11 \text{cm}^2/\text{Vs}$ and an on-off current
ratio $I_{\text{on}}/I_{\text{off}}|_{\text{Ag}} = 1.4 \times 10^6$ ($I_{\text{on}}/I_{\text{off}}|_{\text{Pt}} = 1.3 \times 10^5$) is reached. The subthreshold slopes of
$SS = 120$ (160) mV/dec were observed for the Ag-based (Pt-based) TMESFET, being only
about a factor of two above the thermodynamic limit of about 60 mV/dec at room tempera-
ture. Moreover, only small gate voltage sweeps of less than 3 V are necessary to fully switch the
channel conductivity. Thus, the performance of the opaque MESFETs was successfully trans-
ferred to the TMESFETs and their general suitability for application in transparent electronics
was demonstrated. The reproducibility and the long-term stability of the device characteristics
is higher for Pt-based TMESFETs compared to the Ag-TMESFETs. While the latter degrade
severely already within less than two months when exposed to dry air, Pt-TMESFETs showed
comparably stable behavior for more than 150 days. For elevated temperatures up to 60°C,
Pt-TMESFETs are stable while Ag-TMESFETs already show an onset of device degradation.
When exposed to visible light, the threshold voltage of the TMESFETs shifts not more than
0.4 V; the off-current increases up to two orders of magnitude. With decreasing photon energy,
the light-induced effect is reduced. While Pt-TMESFETs showed no degradation within 5.5 h
of positive or negative bias-stress, Ag-TMESFETs are stable towards positive gate bias stress
but exhibit a reduction of the on-off ratio by about one order of magnitude when exposed to
negative gate bias stress. The application of pulsed gate or drain bias reveals the presence of
trap-induced gate and drain lag behavior in TMESFETs. The time constants, extracted from
fitting by a stretched exponential model, are of the order of ten to hundred milliseconds. The
amplitude of the current transients with respect to the pulse amplitude is in all investigated
cases significantly larger for the Ag-based TMESFETs.

**Transparent MESFETs with InGaZnO channel layers**  Using amorphous, room-temperature
grown InGaZnO channel layer on glass substrates (post-growth annealed at 150°C), Ag-
TMESFETs of similar performance compared to their crystalline counterparts with high-
temperature-grown channels ($T_{\text{VIS}} > 70\%$, $\mu_{\text{FE}} \approx 9 \text{cm}^2/\text{Vs}$, $I_{\text{on}}/I_{\text{off}} = 1.2 \times 10^6$, $SS = $
136 mV/dec) were fabricated. Aside from potential cost reductions, the benefit of low process temperatures is the compatibility to flexible plastic substrates. This is demonstrated by a Pt-based TMESFET, fabricated on PEN-foil with an InGaZnO channel layer, showing an almost stable behavior when being bent to radii $\geq 12.5$ mm, which is similar to strains of $\leq 0.5\%$.

**Transparent inverter circuits**  By integrating two Ag-TMESFETs, transparent inverter circuits were realized, which exhibit low-voltage high-gain operation. A maximum gain of $pgm = 227$ at a supply voltage of $V_{DD} = 4$ V and an uncertainty level of $V_{UC} = 0.36$ V are demonstrated, being so far the best reported parameters for transparent inverter circuits. The devices are stable towards illumination by visible light, only blue light causes a weak performance reduction. Furthermore, elevated temperatures $\leq 90^\circ$C yield increased device performance, namely in terms of increased gain. Gate degradation yields performance loss for higher temperatures; nevertheless, the inverter circuits remain operational even up to $150^\circ$C.

**MESFETs for nerve cell action potential measurements**  A chip layout for nerve cell action potential measurements based on MESFETs was developed. With that, the general possibility to use MESFETs for small signal sensing in wet environments was demonstrated.

**Outlook**  As the TRC in this work were fabricated using a comparably simple DC-magnetron sputtering system, a further performance increase is expected from the transition to a rf-sputtering system in the near future. Both, better control of the growth kinetics and in-situ deposition of a TCO-capping layer for increased device transmission then become feasible. The exact type of the barrier height distribution within the TRC and thus an explanation for the observed $\Phi_{B, m} - \sigma$-correlation may be revealed by applying ballistic electron emission microscopy with the requirement of high spatial resolution to provide good statistics. According to the observed limited longterm stability of the bare TMESFET, encapsulation and passivation of the devices are important issues to be investigated thoroughly in the future. Moreover, further studies of the defects responsible for the observed lag effects and illumination induced characteristic changes will permit to increase device performance. The fabrication of TMESFET-based ring oscillators will give a further insight into the integration of TMESFETs in general and also into their maximum operating frequency. The transfer of the fabrication to larger substrate sizes and scalable growth processes is important to reveal the practical relevance of this new concept for transparent electronics. A promising example for this technology is the combination of TMESFETs with OLEDs, enabling the fabrication of low-voltage transparent displays. Further development of TMESFET-based nerve-cell sensing chips will pave the way to detection of electro-physiological activity and real-time cell location via optical transmission microscopy.
8 Appendix

Details of the numerical simulation of the diffusion barrier heights

Exact solution for the position of the maximum of the barrier potential

\[ \Phi(x) = \Phi_B - \frac{eN_d}{\epsilon} \left( wx - \frac{x^2}{2} \right) - \frac{e}{16\pi\epsilon x} \quad (8.1) \]

**Figure 8.1:** Sketch of the image-charge induced barrier lowering (amplified effect for clarity). The dotted line indicates the barrier shape without Schottky-effect, the image force potential is indicated by the dash-dotted line and the resulting barrier potential considering Schottky-effect is indicated by the solid line.

The barrier potential in abrupt approximation under consideration of the Schottky-effect (cmp. fig. 8.1) is given by
Setting the first derivative in $x$ to zero, yields a cubic equation in $x$. The physically relevant solution of this equation, giving the position of the maximum potential barrier for the Schottky effect is

$$x_m = \frac{2}{3} w \cos \left[ \frac{\pi}{3} + \arccos \left( \frac{\frac{27}{32\pi N_D w^3} - 1}{w^3} \right) \right] + \frac{w}{3}.$$ (8.2)

This solution exist only for

$$(V_{bi} - V - \frac{kT}{e}) > \frac{9e^2 \sqrt{N_D}}{32e^2 \pi^2}.$$ (8.3)

as the maximum of the potential vanishes with the approach of flat band condition.


[End+08] H. Endo, M. Sugibuchi, K. Takahashi, S. Goto, K. Hane, and Y. Kashiwaba. “Fabrication and characteristics of a Pt/Mg\textsubscript{x}Zn\textsubscript{1-x}O Schottky photodiode on a ZnO single crystal”. phys. stat. sol. c 5 (2008), pp. 3119–3121.


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H. Frenzel, A. Lajn, H. von Wenckstern, M. Grundmann, Transparent rectifying metal-metal oxide-semiconductor contact structure and method of fabrication and application, german patent No. 10 2009 030 045

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