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Fabrication and characterization of Schottky barrier diodes on rutile TiO₂

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Abstract

Schottky barrier diodes (SBDs) were fabricated by depositing Pd, Pt or Ni on single crystal, conductive n-type rutile TiO₂ using e-beam evaporation. As-grown and nominally undoped rutile TiO₂ single crystals are semi-insulating, and were heat-treated in forming gas flow, N₂ flow or H₂ gas to obtain conductive n-type crystals displaying electrical conductivities in the range of (0.5 – 8) × 10⁻² Ω⁻¹ cm⁻¹. Additionally, SBDs were deposited on Nb-doped conductive n-type rutile TiO₂ with a conductivity of around 0.25 Ω⁻¹ cm⁻¹. Generally, SBDs displaying a rectification of up to eight orders of magnitude were obtained, when comparing the current under reverse and forward bias. The extracted ideality factors were in the range of 1.1 – 4.0. From Capacitance-Voltage measurements, the built-in voltage was derived to be around 1.2 V–1.9 V, depending on the doping concentration of the specific TiO₂ single crystal. Series resistances as low as 19 Ω were achieved. A considerable variation in the electrical characteristics of different SBDs deposited on the same crystal was found, regardless of the metal or doping strategy used. Moreover, the SBD characteristics change over time, particularly seen as a degradation in rectification, mainly related to an increase in the current under reverse bias. Additional surface treatments such as boiling in H₂O₂ and etching in HF do not have a significant effect on the quality of the SBDs. Clear indications for poor adhesion between TiO₂ and Pd are shown. In conclusion, we demonstrate the fabrication of SBDs which are suitable for studying the fundamental properties of metal/TiO₂ junctions and the characteristics of electrically-active defects in TiO₂ using space-charge spectroscopy.

1. Introduction

Rutile titanium dioxide (TiO₂) is a wide-bandgap semiconductor (E₇ = 3.2 eV [1–4]) well-known for its photo-catalytic properties [5, 6], rendering TiO₂ a promising material for photo-catalytic water-splitting as well as photo-catalytic water purification [6–10]. Conductive n-type TiO₂ is of particular interest for such applications due to its lower resistivity and more pronounced optical absorption in the visible and infrared part of the electromagnetic spectrum compared to pristine TiO₂ [11–14]. It is possible to achieve n-type doping in TiO₂ by incorporating Nb [13, 15–17] or by heat-treating TiO₂ in hydrogenating or reducing atmospheres [11, 14, 15, 18–20]. Hydrogenated as well as reduced TiO₂ have been used in photo-catalytic applications [11, 12, 14, 21]. However, there is still no agreement on the nature of the main donors in hydrogenated and/or reduced TiO₂ [22–24]. Defects are also believed to play a role in the optical absorption in the visible and infrared part of the electromagnetic spectrum displayed by conductive n-type TiO₂ [14, 25–28]. Thus, understanding the properties of defects in TiO₂ is important to improve photo-catalytic applications involving TiO₂.

In applications for photo-catalysis, systems consisting of TiO₂ and noble metals, such as Pd, Pt, Au or Ag, display a better performance compared to just TiO₂ [29–33]. This is believed to be due to an improved charge
transfer at the interface between the metal and TiO$_2$ due to the formation of a rectifying junction [34]. Besides photo-catalytic applications, rectifying metal/TiO$_2$ junctions are also of interest for UV photo-detectors [35], hydrogen sensors [36] and switching devices [37–39].

In order to improve metal/TiO$_2$ junctions for all applications mentioned above, the charge transfer across the interface needs to be understood better. This requires knowledge regarding the electrical characteristics of rectifying metal/TiO$_2$ junctions, where simplified model systems are often a superior starting point for such investigations. Besides studying the properties of the metal/TiO$_2$ junctions themselves, the junctions can also be used to probe the properties of defects in TiO$_2$ using space-charge spectroscopy [16, 40, 41]. Thus, the fabrication of Schottky barrier diodes (SBDs) involving conductive TiO$_2$ single crystals obtained by employing different doping strategies paves the way for systematic defect studies in such material as well as enables investigations of the fundamental properties of the corresponding metal/TiO$_2$ junctions.

SBDs have been achieved on TiO$_2$ using Pt [42–44], Pd [45–47], Ni [48] and Au [19, 49–51]. The characteristics of these SBDs show a varying degree of non-ideal behaviour. Although there is a considerable amount of literature on SBDs involving TiO$_2$, only a few reports exist comparing SBDs on differently doped TiO$_2$ crystals fabricated in the same laboratory. Additionally, there is a general concern about the long-term stability of metal/TiO$_2$ junctions [42, 46, 52], but the change in electrical characteristics over time has not been addressed in depth. In hydrogenated TiO$_2$, the incorporated H might affect the SBDs. It has been shown that the current in junctions formed between different metals and n-type single crystalline TiO$_2$ is sensitive to hydrogen in the ambient [49], and a reaction between H and Pd may cause SBDs to degrade [46, 47, 49].

In the present work, we have systematically studied the electrical behaviour of junctions formed between Pd, Pt, Ni as well as Al and n-type TiO$_2$ single crystals doped with Nb or doped by heat-treatments in hydrogenating or reducing atmospheres. The concentration of interstitial hydrogen (H$_i$) in the different types of TiO$_2$ crystals was measured. The variation in SBD characteristics for diodes deposited on the same TiO$_2$ crystal was investigated. First, SBD characteristics using different metals are compared. SBDs were obtained for Pd/TiO$_2$, Pt/TiO$_2$ and Ni/TiO$_2$ with up to eight orders of magnitude in rectification. Following this, a comparison of Pd/TiO$_2$ SBDs using TiO$_2$ with different dopants and different H$_i$ concentration is presented. The diode characteristics showed a pronounced change over time, related to a decrease in overall rectification. Detailed measurements concerning the degradation are presented. The fabricated Pd/TiO$_2$ junctions are found to exhibit suitable electrical characteristics for studying fundamental junction properties and the characteristics of electrically-active defects in TiO$_2$ using space-charge spectroscopy.

2. Experimental

Rutile TiO$_2$ single crystals with a thickness of $0.5$ mm exhibiting different surface orientations grown by the float-zone (FZ) method or the Verneuil (V) method were purchased from MTI Corporation [53] and Shinkosha [54], respectively. In the following, a TiO$_2$ crystal with surface orientation ($X$) is denoted as TiO$_2$(X). Nominally undoped FZ- and V-grown single crystals were obtained, while V-grown single crystals doped with 0.05wt% of Nb were also acquired. Nominally undoped TiO$_2$ single crystals were transparent and semi-insulating with a conductivity of $\sigma < 10^{-7}\Omega^{-1}$ cm$^{-1}$. The as-received wafers were cut into pieces measuring approximately $5 \times 5$ mm$^2$ using a laser cutter. After cutting, all crystals were cleaned in an ultrasonic bath with acetone, isopropanol and de-ionized water for 5 min each (standard cleaning procedure).

Afterwards, the undoped samples were exposed to one of the following heat treatments (annealings):

1. Annealing in forming gas (FG) flow (N$_2$ + H$_2$ with [H$_2$]/[N$_2$] $\approx$ 1/9) at temperatures between 500 °C and 600 °C. The annealing duration was 35–90 min. After annealing, the samples were cooled-down rapidly in the gas flux.

2. Annealing in closed ampoules filled with approximately 0.5 bar of H$_2$ gas. The ampoules were evacuated before filling with H$_2$. These crystals were annealed at temperatures between 400 °C and 600 °C for 10–90 min. After annealing, the crystals stayed in the ampoules during cool-down.

3. Annealing in N$_2$ flow at temperatures between 980 °C and 1200 °C. The typical annealing duration was in the order of hours (1.25–25 h). After annealing, the samples were taken out of the furnace and the cool-down occurred in N$_2$ flow.

A tube furnace was used for annealing. All TiO$_2$ crystals were put into the furnace after the desired annealing temperature was reached. In the following, TiO$_2$ crystals which have been annealed in FG flow, H$_2$ gas or N$_2$ gas are denoted as FG-TiO$_2$, H$_2$-TiO$_2$ and N$_2$-TiO$_2$, respectively. Nb-doped crystals are denoted as Nb-TiO$_2$. 

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Ni, Pd, Pt and Al were deposited onto TiO₂ single crystals subjected to the heat-treatments described above, and Pd was deposited onto Nb-TiO₂ crystals (thickness ~150 nm). Circular metal contacts displaying areas of 

\[(0.67 - 6.36) \times 10^{-3} \text{cm}^2\]

were obtained using a shadow mask. Either eutectic InGa was applied to or a stack of Ti/Al was deposited onto the back side of these crystals as Ohmic contacts. All metal depositions were performed using e-beam evaporation. In between depositing or applying metals, the crystals were cleaned using the standard cleaning procedure described above. Typically, between 15 to 20 SBDs are obtained on a piece of TiO₂ crystal (see figure 1 for an overview of the resulting sample layout). Some crystals were subjected to surface treatments prior to the deposition of the circular Ni, Pd or Al contacts. These crystals were exposed to boiling H₂O₂ for 1–3 min, and some of them were additionally exposed to HF for 5 min. Crystals that were exposed to HF in addition to H₂O₂ will be denoted as TiO₂(X)-HF in the following.

Fourier-Transform infrared spectroscopy (FT-IR) was used to determine the concentration of H, denoted as [H] in TiO₂ single crystals. The investigated TiO₂ single crystals had a surface orientation of (001). Infrared (IR) transmittance spectra were measured using an evacuated Bruker IFS 125HR spectrometer equipped with a globar light source, a KBr beamsplitter, and a liquid-nitrogen-cooled InSb detector. The IR beam was kept at normal incidence (±3°) with respect to the (001) surface of the TiO₂ single crystals. Measurements were performed at room temperature using a spectral resolution of 1 cm⁻¹. [H] was determined from the integrated area of the optical absorption associated with a local vibrational mode of H, [55] using a calibration factor determined by Johnson et al [56].

The electrical conductivity, \(\sigma\), and resistivity, \(\rho\), of TiO₂ single crystals was determined using a four-point probe measurement according to the van-der-Pauw method [57, 58]. The measurement utilized a Keithley 7001 switching system, a Keithley 2182A nano-volt-meter and a Keithley 6221 current source. Eutectic InGa pads were used as Ohmic contacts in the corners of the TiO₂ single crystals.

A sample for Scanning Transmission Electron Microscopy (STEM) was prepared by focused ion beam (FIB) using a Ga-ion JEOL JIB-4500. Before milling, a 700 nm W film was deposited in order to protect the underlying sample against Ga damage.

Current-Voltage (IV) measurements were carried out on the metal/TiO₂ junctions under dark conditions at variable temperatures in the range between 25 K and 330 K using a Keithley 6487 unit. Measurements below room temperature were performed in vacuum and within a closed-cycle He cryostat. Capacitance-Voltage (CV) measurements were carried out under dark conditions using an Agilent 4284A LCR meter at six different probing frequencies \(f_{\text{meas}}\) between 1 kHz and 1 MHz. According to the Mott-Schottky theory of metal-semiconductor junctions, the barrier height, \(\Phi_B\), depends on the metal work function, \(\Phi_m\), and the semiconductor electron affinity, \(\chi_s\): \(\Phi_B = \Phi_m - \chi_s\) [59]. Rectifying junctions are formed for \(\Phi_B > 0\), while Ohmic contacts are obtained for \(\Phi_B < 0\). The expected barrier height \(\Phi_B\) for SBDs between TiO₂ and Pd, Pt, Ni as well as Al are summarized in table 1. Here, an electron affinity of \(\chi_s = 4.33\) eV for TiO₂ was assumed [60].

From IV measurements, the series resistance, \(R_s\), shunt resistance, \(R_{sh}\), ideality factor, \(\eta\), and average rectification was deduced. \(\eta\) incorporates all the effects that make the device non-ideal [61]. Here, \(R_s\) represents the transport of charge carriers through the bulk (on-state resistance) and through the Ohmic contact. \(\rho_{IV}\) was calculated from \(R_s\), extracted from IV measurements on SBDs, and sample dimensions; \(\rho_{IV} = R_s A/l\).

\(l = 500 \mu\text{m}\) is the crystal thickness, and \(A\) is the area of the different SBDs. \(R_{sh}\) determines the amount of reverse leakage current. The average rectification of the diodes was calculated by computing the ratio between the average current under reverse and forwards bias. For averaging, the voltage ranges between ±2 V and ±4 V for \(V\) was chosen. Diodes that showed a rectification lower than one order of magnitude after contact deposition.
were disregarded. From CV measurements, the donor concentration, \( N_d \), and the built-in voltage, \( V_0 \), were deduced, using the depletion approximation \([59]\). In order to calculate \( N_d \), knowledge of the static relative dielectric constant for TiO\(_2\), \( \varepsilon_{\text{TiO}_2} \), is required. Here, a value of \( \varepsilon_{\text{TiO}_2} = 160 \) at room temperature was assumed \([62, 63]\).

### 3. Results and discussion

#### 3.1. TiO\(_2\) single crystals

\( N \)-type TiO\(_2\) single crystals with a bluish color and conductivities in the range from \( (0.5 - 8) \times 10^{-2} \ \Omega^{-1} \ \text{cm}^{-1} \) were obtained by heat-treating as-received nominally-undoped TiO\(_2\) single crystals in forming gas flow, N\(_2\) flow or H\(_2\) gas. Similarly, the Nb-doped TiO\(_2\) single crystals exhibited also \( n \)-type conductivity (\( \sigma = 0.25 \ \Omega^{-1} \ \text{cm}^{-1} \)) and a dark bluish color. It is generally observed that conductive \( n \)-type TiO\(_2\) single crystals display a bluish color \([18, 25, 26, 65-68]\). The relation between the electrical conductivity and optical absorption of the heat-treated TiO\(_2\) single crystals is investigated further in \([69]\).

Figure 2 displays infrared absorption spectra recorded on as-received TiO\(_2\) single crystals (nominally undoped as well as Nb-doped) and heat-treated TiO\(_2\) single crystals. Data are shown for the wavenumber region where optical absorption associated with a local vibrational mode of H\(_2\) can be seen \([55]\). From the integrated area of this line, \( [\text{H}_2] \) in the samples can be estimated \([56]\). Typically, nominally-undoped TiO\(_2\) single crystals display [H\(_2\)] in the range of \( 10^{17} \ \text{cm}^{-3} \), while Nb-doped crystals show [H\(_2\)] below the detection limit of the measurement which is estimated to be below \( 1 \times 10^{15} \ \text{cm}^{-3} \). [H\(_2\)] of TiO\(_2\) single crystals heat-treated in FG flux or H\(_2\) gas increases, while TiO\(_2\) single crystals annealed in N\(_2\) display a decreased [H\(_2\)] concentration compared to nominally-undoped TiO\(_2\) crystals. H\(_2\) is reported to be a shallow donor in TiO\(_2\) \([55, 70, 71]\), and is likely to be responsible for the conductivity observed in samples heat-treated in FG flux or H\(_2\) gas \([69]\). Notably, no change in the [H\(_2\)] of the samples was observed over the course of a few months when storing the crystals at around \(-20 \ ^{\circ} \text{C} \) \([69]\). \( \sigma \), however, decreased slightly with time. \( \sigma \) was measured on FG-TiO\(_2\) crystals after annealing, and

| Metal | Metal work function \([64]\) \( \Phi_m \) (eV) | Expected barrier height \( \Phi_B \) (eV) |
|-------|---------------------------------|----------------|
| Pd    | 5.12                            | 0.8            |
| Pt    | 5.65                            | 1.3            |
| Ni    | 5.15                            | 0.8            |
| Al    | 4.28                            | —              |

| Moisture work functions and expected barrier heights \( \Phi_B \) for metal/TiO\(_2\) junctions, assuming \( \chi_{\text{TiO}_2} = 4.33 \ \text{eV} \) \([60]\). Rectifying junctions are expected for Pd, Pt and Ni, while for Al, Ohmic contacts are expected. |

**Figure 2.** Infrared absorption spectra of the 3278 cm\(^{-1}\) H\(_2\) vibrational line for as-received samples (semi insulating and Nb-doped), and after annealing in different environments (H\(_2\), N\(_2\) or FG). The spectra were baseline corrected and are vertically offset for visual clarity.
remeasured 40 days later. These measurements showed a reduction of ~5% in \( \sigma \) after 40 days of storage, which was larger than the relative standard deviation of the measurements (~1%).

### 3.2. Metal/TiO\(_2\) junctions

#### 3.2.1. Influence of the choice of metal

Figure 3 shows IV curves recorded on junctions between FZ-grown FG-TiO\(_2\)(001) and various metals. Rectifying junctions are formed for Pd/TiO\(_2\), Pt/TiO\(_2\) and Ni/TiO\(_2\), while Ohmic contacts are obtained for Al/TiO\(_2\), as anticipated from the expected barrier heights stated in table 1. The highest rectification observed was eight orders of magnitude and was observed for Pd/TiO\(_2\) junctions. Usually, independent of the exact annealing condition, rectifications between 2 – 5 order of magnitude are achieved for Pd, Pt as well as Ni contacts on TiO\(_2\). Series resistances in the order of \( \Omega \) to 1 M\( \Omega \) were obtained. Typically, ideality factors between 1.1 and 4.0 are found. \( \eta \) larger than 2 can, for example, be related to the presence of a highly-compensated interfacial layer or to recombination in the depletion region [19, 59, 72].

#### 3.2.2. Influence of surface orientation and treatment

In figure 3, one can observe a significant spread in electrical characteristics of the SBDs deposited on the same TiO\(_2\) single crystal (see figure 1). There is a wide spread in the values for the current under reverse as well as forward bias. The differences in electrical characteristics seen for SBDs deposited on the same TiO\(_2\) crystal originate from a spread in values of \( R_s \), \( R_{sh} \) and \( \eta \), suggesting lateral inhomogeneities over distances of around 1 mm (see figure 1). Particularly, the differences seen for \( \eta \) suggest significant surface inhomogeneities, e.g., due to lateral inhomogeneities in the density of interface states or the thickness of a highly-compensated interfacial layer [57, 72, 73]. The spread observed for \( R_s \) and \( R_{sh} \) could also be related to surface inhomogeneities. \( R_s \) will here mainly comprise of contributions from the bulk resistivity and the contact resistance of the Ohmic contact, and especially the resistance of the Ohmic contact could be influenced by surface inhomogeneities [37]. \( R_{sh} \) is related to leakage currents whose magnitude might, for example, be sensitive to the density of defects within the space-charge region [74]. In figure 4, the average rectification determined for metal/TiO\(_2\) junctions is shown, fabricated using FZ-grown FG-TiO\(_2\)(001), FG-TiO\(_2\)(110) or FG-TiO\(_2\)(100) crystals, all treated in boiling H\(_2\)O\(_2\).
that the contact resistance is dependent on the doping concentration of the crystal. The relative deviation in resistance, but for more resistive crystals, contact resistance becomes important. Moreover, this result suggests Doping levels suitable for electrical measurements were achieved by annealing in forming gas at 3.2.4. In same crystal crystals doped using different strategies, both between the differently treated crystals, and between SBDs on the to W between different diodes is similar for all crystals, as shown in the inset of 3.2.3. Comparison between resistivity and SBD series resistance Values for of FZ-grown H$_2$-TiO$_2$ crystals annealed at different temperatures between 400 °C and 600 °C for durations of 10–90 min were measured prior to metal contact deposition. In figure 5, the resistivity estimated from IV measurements, $\rho_{IV}$, for several SBDs on each H$_2$-TiO$_2$ crystal, is plotted as a function of resistivity, $\rho$. As shown in the figure, the least resistive crystals have values for $\rho_{IV}$ very close to $\rho$. For more resistive crystals, $\rho_{IV}$ are larger than $\rho$. This result indicates that for conductive crystals, the bulk resistivity is limiting the series resistance, but for more resistive crystals, contact resistance becomes important. Moreover, this result suggests that the contact resistance is dependent on the doping concentration of the crystal. The relative deviation in $\rho_{IV}$ between different diodes is similar for all crystals, as shown in the inset of figure 5.

3.2.4. Influence of doping
Doping levels suitable for electrical measurements were achieved by annealing in forming gas at 600 °C for ~1 h, in H$_2$ at 450 °C for 30–60 min, or in N$_2$ at 1100 °C for ~90 min. Figure 6 shows IV curves recorded on Pd/TiO$_2$ junctions comprising FZ-grown H$_2$-TiO$_2$(001), V-grown FG-TiO$_2$(001), V-grown N$_2$-TiO$_2$(001) and V-grown Nb-TiO$_2$(001). Rectifying junctions are obtained regardless of the doping procedure used. The resulting junctions exhibit ideality factors from 1.1 to 4, and values for the series resistance in the order of 10 Ω to 100 MΩ. A large spread in electrical characteristics is also seen for Pd/TiO$_2$ junctions comprising TiO$_2$ crystals doped using different strategies, both between the differently treated crystals, and between SBDs on the same crystal (see figure 1). In figure 6, one can observe a significant spread in the values of $R_{ov}$, $R_{sh}$ and $\eta$ of the SBDs deposited on the same TiO$_2$ single crystal, resulting in a wide range of values for the current under reverse as well as forward bias, similar to what is seen in figure 3. Notably, Nb-doped TiO$_2$ displays the same spread in electrical characteristics. Thus, one can conclude that the inhomogeneity causing the large spread in electrical characteristics is not caused by heat-treating the samples in reducing or hydrogenating atmospheres. Moreover, H is not likely to play a role in the observed inhomogeneity taking into account that the Nb-doped TiO$_2$ crystals were shown to contain significantly less H$_2$ than the hydrogenated or reduced TiO$_2$ crystals (see figure 2).
3.2.5. Schottky barrier height and Built-in voltage

The determination of barrier heights from IV characteristics is only reliable if the current is determined by thermionic emission [75]. For the SBDs studied here, this is not the case, since $\eta$ is larger than 1.1 at room temperature [75]. The SBDs that exhibited the lowest values of $\eta$ were measured also at lower temperatures $T$. IV-T curves from a Pd/H$_2$-TiO$_2$ junction are plotted in figure 7(a). $\eta(T)$ displays an abnormal decrease with
Increasing $T$, as shown in the inset. Such a temperature-dependence leads to a non-linear shape of the Richardson plot $\ln \left( \frac{I_r}{T^2} \right)$ versus $1/T$, where $I_r$ is the reverse saturation current [75], and the value for the effective Richardson constant $A^*$ and $\Phi_B$ could not be extracted. A similar temperature dependence of $\eta$ was found regardless of the crystal growth method, choice of metal or the doping procedure used. These measurements are in line with previously reported temperature-dependent IV data measured on Schottky junctions involving TiO$_2$ [44, 48, 76]. Recently, $\Phi_B$ has been deduced from $T^2$ data measured on junctions involving TiO$_2$ that display similar non-ideal behaviour [48, 76]. In [76] and [48], $\Phi_B$ was extracted assuming barrier height inhomogeneities (BHI) and using a model proposed by Werner and Gütterl [77]. For the junctions studied here, however, which were measured at lower temperatures, this model can only explain the non-ideal behaviour of IV measurements recorded at $T$ larger than $\sim 100$ K–$150$ K. For $T < 100$ K, the requirement of a linear relationship between $\eta$ and $\Phi_B$, which confirms the existence of BHI [78], is not fulfilled. In addition, the modified Richardson plot provides reasonable values for $A^*$ and $\Phi_B$, but only in the temperature range above 100 K. Therefore, it is possible that BHI affect the current transport, but at low temperatures, other mechanisms are also important.

The built-in voltage for Pd/TiO$_2$ junctions was determined from CV measurements. Figure 7(b) shows results of CV measurements recorded on Pd/TiO$_2$ junctions comprising FZ-grown FG-TiO$_2$(001), V-grown N$_2$-TiO$_2$(001) and V-grown Nb-TiO$_2$(001) crystals. The representation of CV measurements as $1/C^2$ versus $V$ are straight lines, suggesting a homogeneous donor concentration in the depletion region. Notably, CV measurements at different $f_{\text{meas}}$ display a slight dispersion. $V_0$ was determined to be 1.2 V–1.3 V for Pd/FG-TiO$_2$(001), 1.4 V–1.6 V for Pd/N$_2$-TiO$_2$(001) and 1.8 V–1.9 V for Pd/Nb-TiO$_2$(001) junctions, depending on $f_{\text{meas}}$. Notably, a $N_d$ of $1.4 \times 10^{19}$ cm$^{-3}$ was determined for the Nb-TiO$_2$(001) crystal, being close to the Nb concentration of $1.38 \times 10^{19}$ cm$^{-3}$ expected in these crystals according to the wt% of Nb specified by the supplier [54]. Thus, the determination of $N_d$ from CV measurements is corroborated. The $V_0$ deduced is larger than expected, considering the theoretically calculated SBD heights given in table 1.

The results shown in figure 7(b) show that the fabricated Pd/TiO$_2$ junctions are suitable for space-charge spectroscopy techniques, such as deep-level transient spectroscopy [79] or thermal admittance spectroscopy [80], and hence the junctions can be used to study electrically-active defects in TiO$_2$ [41]. It is, however, important to verify the suitability of a specific junction for space-charge spectroscopy, i.e., junctions suitable for space-charge spectroscopy should display low series resistance as well as ideality factors close to 1 [57].

3.2.6. Time-evolution of electrical characteristics

Pd/TiO$_2$ junctions were stored at $-20$ °C for several months, and IV curves were recorded every few days. Most Pd/TiO$_2$ junctions exhibit a decrease in rectification over the course of a few weeks regardless of the doping used for the TiO$_2$ crystal. It has been reported previously that the electrical characteristics of rectifying metal/TiO$_2$ junctions change over time, and a reaction between H and Pd has been suggested to be the cause of the degradation [46, 47, 49]. Figure 8(a) displays IV curves from a Pd/TiO$_2$ junction recorded at different times after initial contact deposition. The junction comprises a FZ-grown FG-TiO$_2$(001) crystal. The series resistance and ideality factor of the Pd/TiO$_2$ junction do not change significantly over the course of several weeks, while the current under reverse bias notably increases, and thus the overall rectification decreases. Such a degradation was
typically observed for the SBDs comprising FG-TiO2(001) crystals. Pd/TiO2 junctions comprising TiO2 crystals doped using heat-treatments in H2 or N2 also display a similar degradation behaviour. Thus, the observed degradation is related to a decrease in shunt resistance of the Pd/TiO2 junctions. Figure 8(b) shows the current under reverse bias as a function of time. Initially, there is very little change in the magnitude of the reverse current. After a few weeks, a pronounced increase in the current under reverse bias can be seen. We fitted this increase with a first-order kinetics expression: $I(t) = I_0 - \alpha \cdot \exp(-t/\tau)$, where $t$ is time, $I_0$ and $\alpha$ are constants that vary with applied voltage and $\tau$ is the characteristic time constant. At room temperature, the best fit was obtained for $I_0 = 2.3 \mu A$, $\alpha = 4.8 \mu A$ for $-2$ V and $I_0 = 7.2 \mu A$, $\alpha = 14.7 \mu A$ for $-4$ V; and $\tau = 21$ days for both $-2$ V and $-4$ V.

In FG-TiO2, H is expected to be the main donor, and thus the observation regarding the series resistance is in accordance with the observation that $[H_i]$ does not change in similarly treated samples. Interestingly, this is contrary to expectations taking the large diffusion constant for $H_i$ in TiO2 ($D \sim 0.2 \text{m}^2/\text{hour}$ at room temperature) into account [81].

In order to study the observed degradation further, IV curves of the Pd/TiO2 junctions comprising a FZ-grown H2-TiO2(001) crystal were recorded every few days until the Pd contacts were removed after 42 days. During contact removal, some of the surface was polished off, leaving a rougher surface compared to as-received crystals. Fresh Pd contacts were deposited on the same crystal piece. The average rectification after first contact deposition was initially 5.2. Just before the contacts were removed, the average rectification had dropped to 1.8. Finally, after re-deposition of contacts, the average value increased to 3.0. This experiment demonstrates that a new annealing procedure is not required to improve the quality of the SBDs, and that the degradation is related to the interface. Interestingly, only $R_{sh}$ changes over time, suggesting that the change at the Pd/TiO2 interface related to the observed degradation does not affect the barrier itself. This observation may indicate that the degradation is caused by enhanced tunnelling of charge carriers through the space-charge region. The origin of such an enhanced tunnelling is, however, unclear. Studying the defects present at the Pd/TiO2 interface using space-charge spectroscopy could help shedding light on the role of defects in TiO2 regarding the observed leakage current [41].

3.3. Adhesion of Pd on TiO2

In an attempt to study the interface between Pd and TiO2, STEM was performed on a FIB sample fabricated from the edge of a Pd/TiO2 junction, covering both the junction and plain TiO2. Figure 9 displays a STEM micrograph recorded on a Pd/TiO2 junction after preparing a lamella using FIB. A gap between the Pd contact and TiO2 crystal is clearly visible. A 100 nm thick Pd layer was confirmed present by energy-dispersive x-ray spectroscopy and high-angle annular dark-field imaging. However, it was found that the adhesion of Pd on TiO2 crystals is poor. During FIB milling, local stress relaxation or heating induced by the beam at the Pd-TiO2 interface may have caused the Pd-film to detach. Poor Pd-adhesion was also found during fabrication of the samples: Some Pd contacts detached from the TiO2 during cleaning in acetone and isopropanol in an ultrasonic bath.
4. Conclusion

We have studied the formation of metal/TiO₂ junctions comprising Pd, Pt, Ni and Al. For this purpose, different strategies for obtaining conductive n-type TiO₂ single crystals were employed. Conductive n-type TiO₂ with conductivities ranging from \( (0.5 \to 8) \times 10^{-2} \ \Omega^{-1} \ \text{cm}^{-1} \) was obtained by heat-treatments in hydrogenating or reducing atmospheres. For comparison, Nb-doped TiO₂ \((\sigma = 0.25 \ \Omega^{-1} \ \text{cm}^{-1})\) was also utilized to form metal/TiO₂ junctions. Rectifying junctions are obtained for Pd/TiO₂, Pt/TiO₂ and Ni/TiO₂ regardless of the doping procedure or the surface orientation of the TiO₂ crystals, while Al forms an Ohmic contact with TiO₂.

From CV measurements, the built-in voltage was deduced to be around 1.2 V to 1.9 V, depending on the doping concentration of the specific TiO₂ single crystal. A large spread in electrical characteristics is found for SBDs fabricated on the same TiO₂ crystal regardless of the doping strategy or the surface orientation. Ideality factors extracted from IV measurements were in the range of 1.1 to 4.0 at room temperature, whereas values for the series resistance range from \( \sim 10 \ \Omega \to 100 \ \text{M}\Omega \). Most Pd/TiO₂ junctions exhibit a degradation over time. The degradation is related to an increase in the current under reverse bias voltage, whereas the series resistance and ideality factor stay approximately constant. The degradation can be described by first-order kinetics with a time constant of 21 days at room temperature. Adhesion between Pd and TiO₂ appears to be poor, which could be one of the reasons for the large spread in electrical characteristics of SBDs. Importantly, we demonstrated the fabrication of Pd/TiO₂ junctions which can be used to study fundamental properties of metal/TiO₂ junctions and electrically-active defects in TiO₂ using space-charge spectroscopy.

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References

[1] Nowotny M, Bak T and Nowotny J 2006 The Journal of Physical Chemistry B 110 16270
[2] Vos K 1977 J. Phys. C: Solid State Phys. 10 3917
[3] Vos K and Krusemeyer H 1974 Solid State Commun. 15 949
[4] Pascual J, Camassel J and Mathieu H 1978 Phys. Rev. B 18 5606
[5] Ni M, Leung M, Leung D and Sumathy K 2007 Renew. Sustain. Energy Rev. 11 401
[6] Fujishima A, Zhang X and Tryk D 2008 Surf. Sci. Rep. 63 515
[7] Carp O, Huisman C and Heller A 2004 Prog. Solid State Chem. 32 33
[8] Cong Y, Zhang J, Chen F and Anpo M 2007 J. Phys. Chem. C 111 6976
[9] Nitta A, Takushima M, Takase M and Ohtani B 2019 Catal. Today 321–322 2
[10] Hoffmann M, Martin S, Choi W and Bahnemann D 1995 Chem. Rev. 95 69

Figure 9. STEM high-angle annular dark field cross-sectional image of a Pd/TiO₂ junction.
[11] Wang Z et al 2013 Adv. Funct. Mater. 23 5444
[12] Zheng Z, Huang B, Lu J, Wang Z, Qin X, Zhang X, Dai Y and Whangbo M 2012 Chem. Commun. 48 5733
[13] Atambo M O, Variano D, Ferretti A, Ateii S S, Caldas M J, Molinari E and Selloni A 2019 Physical Review Materials 3 045401
[14] Pan X, Yang M, Fu X, Zhang N and Xu Y 2013 Nanoscale 5 3601
[15] DeFord J and Johnson O 1983 J. Appl. Phys. 54 889
[16] Kobayashi K, Takata M, Fujimura Y and Okamoto S 1986 J. Appl. Phys. 60 4191
[17] Sahasrabudhe G, Krizan J, Bergman S, Cava R and Schwartz J 2016 Chem. Mater. 28 3630
[18] Breckenridge R and Hasler W 1953 Phys. Rev. 91 793
[19] Farah M, Lapicque F and Matlosz M 1998 J. Electrochem. Soc. 145 3550
[20] Chester P and Bradhurst D 1963 Nature 199 1056
[21] Naldoni A, Allieta M, Santangelo S, Marello F, Fabbri F, Cappelli S, Bianchi C, Paiero R and Dal Santo V 2012 JACS 134 7600
[22] Ohlsen W and Johnson O 1973 J. Appl. Phys. 44 1927
[23] Shannon R 1964 J. Appl. Phys. 35 3414
[24] Harris I and Schwarnacher R 1980 J. Electrochem. Soc. 127 1186
[25] Bogomolov V and Mirlin D 1968 Physica Status Solidi (b) 27 443
[26] Cronemeyer D 1959 Phys. Rev. 113 1222
[27] Lu T, Lin L, Wu S, Xu X and Cheng G 2002 Surf. Coat. Technol. 158–159 431
[28] Chen J, Lin L and Jing F 2001 J. Phys. Chem. Solids 62 1257
[29] Wu J, Lu S, Ge D, Zhang L, Chen W and Gu H 2016 RSC Adv. 6 67502
[30] Maeda K 2014 Catalysis Science & Technology 4 1949
[31] Sathaiya D M and Karmalkar S 2006 Parker G H and Mead C A 1969
[32] Shimomura K, Kadono R, Koda A, Nishiyama K and Mihara M 2015 Card H and Rhoderick E 1971
[33] Weber J, Lavrov E and Herklotz F 2012 Shima H, Zhong N and Akinaga H 2009
[34] Johnson O, DeFord J and Shaner J 1973
[35] Werner J and Güttler H 1991
[36] Rawat G, Kumar H, Kumar Y, Kumar C, Somvanshi D and Jit S 2017 IEEE Electron Device Lett. 38 633
[37] Tung R 1992 Phys. Rev. B 45 13509
[38] van der Pauw L 1958 Physica Status Solidi (a) 75 K99
[39] Naldoni A, Allieta M, Santangelo S, Marello F, Fabbri F, Cappelli S, Bianchi C, Paiero R and Dal Santo V 2012 JACS 134 7600
[40] Michaelson H 1977
[41] Porta P and Keijzers C 1988
[42] Szydlo N and Poirier R 1980
[43] Saxsahrabudhe G, Krizan J, Bergman S, Cava R and Schwartz J 2016 Chem. Mater. 28 3630
[44] Schierbaum K, Kirner U, Geiger J and Göpel W 1991
[45] Porte V, White W and Roy R 1972
[46] Butler M and Ginley D 1978 J. Electrochem. Soc. 125 228
[47] Schroer D 2006 Semiconductor Material and Device Characterization (New York: Wiley)
[48] Bonkerud J, Zimmermann C, Weiser P, Vines L and Monakhov E 2020 Determining the dielectric constant of rutile TiO2 from implanted H-profiles, In preparation
[49] Parker R 1961 Phys. Rev. 124 1719
[50] Michaelson H 1977 J. Appl. Phys. 48 4729
[51] Johnson O, Ohlsen W and Kingsbury P Jr 1968 Phys. Rev. 175 1102
[52] Khomenko V, Langer K, Rager H and Fett A 1998 J. Solid State Chem. 141 257
[53] Valigi M, Cordischi D, Minelli G, Natale P, Porta P and Keijzers C 1988
[54] Huber F 1968 J. Electrochem. Soc. 115 203
[55] Kobayashi H, Kishimoto K, Nakato Y and Tsuhombura H 1993 Sensors and Actuators: B. Chemical 13 125
[56] Kobayashi H, Kishimoto K and Nakato Y 1994 Surf. Sci. 306 393
[57] Kumar A, Sharma K, Chand S and Kumar A 2018 Superlattices Microstruct. 122 304
[58] Yamamoto N, Tonomura S, Matsumura T and Tsuhombura H 1980 Surf. Sci. 92 400
[59] Altmann H, Bengt A, Asar T, Ayderen U, Sarakavak B, Ozen Y, Altundal S and Oncelik S 2010 Surf. Interface Anal. 42 1257
[60] Szydlo N and Poirier R 1980 J. Appl. Phys. 51 3310
[61] Fu Q, Wagner T, Olliges S and Carstanjen H 2005 J. Phys. Chem. B 109 944
[62] float-zone-grown r-TiO2 from MTI Corporation, https://www.mtixtl.com/tio2substrates.aspx, accessed: 2019-12-05
[63] dePauw L 1938 Philips Tech. Rev. 20 220
[64] Blood P and Orton J 1992 The Electrical Characterization of Semiconductors: Majority Carriers and Electron States Academic Techniques of Physics vol 13 (New York: Academic)
[65] Weber J, Lavrov E and Herklotz F 2012 Physica B 407 1456
[66] Shimomura K, Kadono R, Koda A, Nishiyama K and Mihara M 2015 Physical Review B—Condensed Matter and Materials Physics 92 075203
[67] Card H and Rhoderick E 1971 J. Phys. D: Appl. Phys. 4 1589
[68] Parker G H and Mead C A 1969 Appl. Phys. Lett. 14 21
[69] Sathaiya D M and Karmalkar S 2006 J. Appl. Phys. 99 093701
[70] Rhoderick E 1982 IEEE Proc. I. Solid State and Electron Devices 129 1
[71] Rawat G, Kumar H, Kumar Y, Kumar C, Somvanshi D and Jit S 2017 IEEE Electron Device Lett. 38 633
[72] Werner J and Güttler H 1991 J. Appl. Phys. 69 1522
[73] Tung R 1992 Phys. Rev. B 45 13509
[79] Lang D V 1974 J. Appl. Phys. 45 3023
[80] Pautrat J, Katircioglu B, Magnea N, Bensahel D, Pfister J and Revoil L 1980 Solid-State Electron. 23 1159
[81] Hupfer A, Monakhov E, Svensson B, Chlygin I and Lavrov E 2017 Sci. Rep. 7 1