On the permittivity of titanium dioxide

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Conductive rutile TiO₂ has received considerable attention recently due to multiple applications. However, the permittivity in conductive, reduced or doped TiO₂ appears to cause controversy with reported values in the range 100–10,000. In this work, we propose a method for measurements of the permittivity in conductive, n-type TiO₂ that involves: (i) hydrogen ion-implantation to form a donor concentration peak at a known depth, and (ii) capacitance–voltage measurements for donor profiling. We cannot confirm the claims stating an extremely high permittivity of single crystalline TiO₂. On the contrary, the permittivity of conductive, reduced single crystalline TiO₂ is similar to that of insulating TiO₂ established previously, with a Curie–Weiss type temperature dependence and the values in the range 160–240 along with the c-axis.

The static and low-frequency dielectric constant, ε, of rutile TiO₂ has been surrounded with controversy since as early as 1952, when Nicolini reported an extremely high value of around 10,000 for the permittivity of ceramic rutile TiO₂. Similar values of (1 – 3) × 10⁴ were later observed by Parker and Wasilik for single crystalline rutile TiO₂. It was immediately realized, however, that such high values may be a result of an incorrectly designed experiment or an incorrect interpretation. Indeed, the method used in Ref. is based on capacitance measurements over the full thickness of the crystal, where metallic contacts are deposited on opposite sides. Parker and Wasilik suggested that, in the case of non-negligible free carrier concentration, i.e., non-negligible effective net doping, Schottky contacts can be unintentionally formed (see Supplementary Material for a description of the Schottky contact). This is particularly relevant in the case of reduced TiO₂, where oxygen vacancies give rise to n-type doping. In such samples, the total capacitance of the crystal is determined predominantly by the depletion region associated with the Schottky contact, or "by an electron-deficient barrier layer at the electrode-crystal interface such as has been proposed to explain the action of contact rectifiers" as formulated by Parker and Wasilik with a reference to the original work by Schottky. Nowadays, Schottky rectifiers or Schottky diodes, as the modern accepted term, are widely used in semiconductor science and technology.

Based on these findings, Parker performed new theoretical and experimental studies of ε in rutile TiO₂ crystals. Special care was taken to prepare highly resistive TiO₂ by “heavy oxidation” as phrased in Ref. Highly resistive, oxygen-rich rutile TiO₂ crystals were then investigated by measuring the capacitance between a parallel plate capacitor with the crystal inside. Permittivity of 170 and 86 were measured at 300 K along with the c- and a-axes, respectively. At 1.6 K, the permittivity along with the c- and a-axis were deduced to be 257 and 111, respectively. No frequency dependence was observed in the frequency range 10²–3 × 10⁶ Hz.

Later, Samara and Peercy measured pressure and temperature dependencies of ε. Similar to the previous investigations, ε was determined from capacitance measurements. No frequency dependence was assumed, based on the findings by Parker, and the measurements were performed at 100 kHz. It has been shown that data can be fitted over the whole temperature range by the modified Curie–Weiss law derived first by Barrett for perovskite-type crystals:

\[ \varepsilon = A_0 + \frac{C_0}{\frac{1}{2}T_1 \coth \left( \frac{T_1}{T_2} \right) - T_0} \]

where \( T \) is temperature, and \( A_0, C_0, T_1, \) and \( T_0 \) are fitting parameters. At 296 K, the permittivity along with the c- and a-axes was determined to be 166.7 and 89.8, respectively. As the temperature was decreased to 4 K, the permittivity increased to 251 along with the c-axis and to 114.9 along the a-axis. These values are close to those determined by Parker.

Reports on extremely high ε of reduced single-crystalline rutile TiO₂ continue to appear in the literature. For example, Chu has reported values in a range of 100 – 10,000. The permittivity was deduced from impedance...
measurements over the full crystal thickness, with gold contacts deposited on opposite sides of the sample. This concept is similar to that used in the earlier studies. Recently, Li et al. reported a colossal dielectric permittivity in hydrogen-reduced rutile TiO₂ crystals. Similar to earlier studies, ε was deduced from impedance measurements of the crystal with silver contacts. One can notice, however, that neither Chu nor Li et al. has considered formation of Schottky barriers at the metal-TiO₂ interface and the corresponding depletion regions, which was considered by Parker and Wasilik.

In this study, we intentionally form Schottky diodes on reduced single-crystalline rutile TiO₂ and utilize their properties to deduce ε. The method involves: (i) hydrogen ion-implantation to form a donor concentration peak at a known depth, and (ii) capacitance–voltage measurements for donor profiling.

Results and discussion

Annealing of bulk TiO₂ in reducing and hydrogen-rich atmosphere has long been known to result in conductive, n-type bulk material (see, for instance, Ref.10). Two main mechanisms are believed to be responsible: (i) formation of donors assigned to oxygen vacancies (VO) and titanium interstitials (Tii) in the reducing atmosphere and (ii) introduction of interstitial hydrogen (Hi) donors during hydrogenation. Besides, Hi can interact with acceptors and passivate them, increasing the net n-type conductivity. We have demonstrated previously that annealing of single-crystalline TiO₂ wafers in N₂ at 1100–1200 °C or in forming gas (FG), 10%at. H₂ and 90%at. N₂, at 600 °C leads to increase in conductivity of the wafers. In the case of heat treatment in FG, the increase can be correlated with concentration of Hi. For annealing in N₂, the increase in conductivity occurs without a corresponding increase in hydrogen concentration. These observations support the feasibility of the two mechanisms that involve VO/Tii and Hi. The effect of hydrogen-induced donors was also used to form a pronounced donor profile at a well-defined depth by ion implantation.

In the present study, single-crystalline rutile TiO₂ wafers with a size of 5 × 5 mm² and a conductivity of < 10⁻⁷ Ω⁻¹ cm⁻¹ were heat treated in forming gas (FG) at 600 °C for 90 min or in N₂ at 1100 °C for 60 min. As a result of the heat treatments, the conductivity of the TiO₂ samples has increased to 0.01–0.07 Ω⁻¹ cm⁻¹. Subsequently, Pd contacts with a diameter of around 400 μm were deposited. A stack of Ti/Al layers was deposited over the whole back side surface of the samples as the back side contact. Current–voltage (I–V) measurements reveal a rectification of up to eight orders of magnitude, indicating that Pd Schottky diodes are formed. The I–V measurements show that at the reverse bias conditions the dc impedance of the Pd Schottky contact dominates over the bulk dc impedance of the samples. It should also be emphasized that the size of the Pd contacts is significantly less than the sample size. Further measurements are performed at the reverse bias, when the impedance associated with the Schottky barrier and the depletion region is dominant.

Capacitance–voltage (CV) measurements are a well-established technique for probing the depth distribution of donors and acceptors. Figure 1 depicts CV measurements at different temperatures (Tmeas) for a sample annealed in N₂ at 1100 °C for 60 min (TiO₂–N₂). The CV measurement performed prior to H⁺ implantation is shown with red, dotted curve (Fig. 1a). The measurement is carried out at 300 K and shows decreasing capacitance with increasing reverse bias, as expected for a Schottky diode (see Supplementary Material). Blue, solid curves represent measurements recorded at different Tmeas. Figure 1a shows that capacitance of the Schottky diode decreases with increasing reverse voltage, V, as expected for a diode.

Figure 1. Capacitance (a) of a TiO₂–N₂ sample (probing frequency 60 kHz) and the N(V)ε₀ε product (b) as functions of applied voltage. The red, dotted curve shows the as-prepared sample, i.e., after the N₂ heat treatment but prior to H⁺ implantation. The blue, solid curves are for the H-implanted sample measured at different temperatures (Tmeas). The peaks in N(V)ε₀ε are indicated by the drop-down lines. The corresponding capacitance values, obtained at the same applied voltages, are also marked in (a).

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Within the depletion approximation (see Ref.16 or Supplementary Material), one can derive the following expression:

\[ N(V)\varepsilon_0 \varepsilon = \frac{C^3}{qA^2} \left( \frac{dC}{dV} \right)^{-1}, \]

where \( N(V) \) is the doping concentration at the depth of the depletion region for a given \( V \), \( \varepsilon_0 \) is the vacuum permittivity, \( \varepsilon \) is the relative permittivity, \( C \) is the capacitance at the given \( V \), \( q \) is the electron charge and \( A \) is the area of the diode. Since \( \varepsilon_0 \) and \( \varepsilon \) do not depend on \( V \), the product \( N(V)\varepsilon_0\varepsilon \) will maintain the shape of \( N(V) \).

Figure 1b displays \( N(V)\varepsilon_0\varepsilon \) as a function of \( V \). For the as-prepared sample prior to \( H^+ \) implantation, the data reveal a somewhat non-uniform, but monotonous \( N(V)\varepsilon_0\varepsilon \) as a function of \( V \). Hydrogen implantation leads to formation of a pronounced peak in \( N(V)\varepsilon_0\varepsilon \). One can thus identify the voltages at which the edge of the depletion region reaches the peak of \( N(V)\varepsilon_0\varepsilon \), as indicated in Fig. 1b with filled circles. For example:

- For \( T_{\text{meas}} = 100 \text{ K} \), the depletion region edge reaches the donor concentration peak at \( V_{\text{peak}} = -3.8 \text{ V} \) (Fig. 1b). This voltage corresponds to the capacitance \( C_{\text{peak}} = 160 \text{ pF} \), indicated in Fig. 1a.

- For \( T_{\text{meas}} = 250 \text{ K} \), the depletion region edge reaches the donor concentration peak at \( V_{\text{peak}} = -6.2 \text{ V} \) (Fig. 1b). This voltage corresponds to the capacitance \( C_{\text{peak}} = 131 \text{ pF} \), indicated in Fig. 1a.

On the other hand, the depth of the implantation peak for hydrogen-induced donors is known from secondary ion mass spectrometry (SIMS) measurements: \( d_{\text{peak}} = 0.97 \mu \text{m} \) (see Supplementary Material).

Within the depletion approximation, the capacitance, \( C \), and the depletion depth, \( d \), are related as \( C = \varepsilon_0\varepsilon A/d \). One can thus find \( \varepsilon \) from:

\[ \varepsilon = \frac{C_{\text{peak}}d_{\text{peak}}}{\varepsilon_0 A}. \]

The results of the analysis from Fig. 1 and Eq. (3) are summarized in Table 1. No frequency dependence has been observed within the range between 1 kHz and 1 MHz (see Supplementary Material).

It should be noted, however, that in some cases we could not perform this analysis at the given experimental conditions. The method relies on the implanted hydrogen profile being well within the depletion region of the Schottky diode. This requires a careful choice of the implantation energy, in order to provide a suitable implantation depth. However, the depletion region depends on (i) the concentration of ionized donors, (ii) the Fermi level in the material, and (iii) the permittivity. Since all these factors can change with temperature, a given implantation depth may not be suitable for all temperatures. In addition, in order to reliably resolve the implanted peak, the concentration of implanted hydrogen donors should significantly exceed the background donor concentration.

At the same time, the concentration of the implanted hydrogen cannot be too high, in order to avoid a strong effect on the depletion region depth and/or to prevent phase transformations. One of the examples is illustrated in Fig. 1b, where the curve for \( T_{\text{meas}} = 300 \text{ K} \) does not reveal a well-defined donor concentration peak. In this particular case, two effects are believed to occur: (i) the concentration of the background ionized donors appears to be comparable to the concentration of the implanted donors, and (ii) the implanted donor peak is too close to the maximum depletion depth. However, at lower temperatures, \( T_{\text{meas}} \leq 250 \text{ K} \), the apparent concentration of ionized background donors decreases, and the implantation peak becomes more prominent.

The analysis described by Fig. 1 and Eqs. (2) and (3) has been applied for more detailed studies of \( \varepsilon \) in a number of samples annealed in FG (TiO\(_2\)-FG) and the TiO\(_2\)-N\(_2\) samples. Figure 2 demonstrates that \( \varepsilon \) determined in the present study is very close to that determined for insulating, oxygen-rich rutile TiO\(_2\) by Samara and Peercy\(^6\). For reduced TiO\(_2\), \( \varepsilon \) along with the c-axis is in the range 160 – 240 for temperatures 50 – 300 K. It decreases as temperature increases and can be described by the modified Curie–Weiss law. We do not observe a significant difference in \( \varepsilon \) between reduced TiO\(_2\) (annealed in N\(_2\) at 1100 °C) and reduced-hydrogenated TiO\(_2\) (annealed in FG at 600 °C).

**Conclusion**

In conclusion, measurements of the permittivity, \( \varepsilon \), in conductive single-crystalline TiO\(_2\) are challenging and causing controversy. We propose a method for deducing \( \varepsilon \) from capacitance measurements. The method involves formation of Schottky barrier diodes and hydrogen implantation. The implantation results in a well-pronounced donor concentration profile, corresponding to the implanted hydrogen profile. The donor profile is

| Temperature, K | \( V_{\text{peak}, \text{V}} \) | \( C_{\text{peak}, \text{pF}} \) | \( \varepsilon \) |
|---------------|----------------|----------------|------|
| 100           | −3.8           | 160            | 211  |
| 150           | −4.6           | 151            | 199  |
| 200           | −5.6           | 140            | 185  |
| 250           | −6.2           | 131            | 173  |

Table 1. Data used for analysis of temperature dependence of \( \varepsilon \) for the TiO\(_2\)-N\(_2\) sample with CV data plotted in Fig. 1. The implantation depth \( d_{\text{peak}} = 0.97 \mu \text{m} \). The diode area \( A = 8.3 \times 10^{-4} \text{ cm}^2 \).
then characterized using capacitance–voltage measurements, and ε can be deduced. We observe that ε of reduced, conductive rutile TiO$_2$ is similar to that of oxygen-rich, insulating rutile TiO$_2$ established previously. We cannot confirm claims of colossal dielectric permittivity in hydrogenated and reduced rutile single-crystalline TiO$_2$.

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Methods

A. Samples. The study was performed on Verneuil-grown rutile TiO$_2$ single crystals with a surface orientation of (001), purchased from Shinkosha Co., Ltd. As-received crystals were 0.5 mm thick with double-side polished surfaces, nominally undoped, transparent, and semi-insulating with a conductivity of $\sigma < 10^{-7}$ $\Omega^{-1}$ cm$^{-1}$. Conductive $n$-type TiO$_2$ samples of bluish colour were obtained by heat treatments in forming gas (FG) flow (N$_2$ + H$_2$ with [H$_2$]/[N$_2$] = 1/9) at 600 $^\circ$C for 90 min (hydrogenating and reducing heat treatment) or in N$_2$ flow at 1100 °C for 60 min (reducing heat treatment). The heat treatments resulted in increased conductivity of the samples in the range 0.01–0.07 $\Omega^{-1}$ cm$^{-1}$. Subsequently, circular 150-nm thick Pd contacts with a diameter of about 400 μm were deposited through a shadow mask. A back side contact was made by depositing a stack of Ti/Al layers over the whole back side surface of the wafer: (1) a 10-nm Ti-layer on TiO$_2$ and (2) a 150-nm Al-layer on Ti. This resulted in Schottky diodes with a rectification of up to eight orders of magnitude. After initial electrical measurements, the samples were implanted at room temperature with 200-keV H$^+$ ions to different doses in the range $6 \times 10^{12}$–$3 \times 10^{14}$ cm$^{-2}$.

B. Experimental set-up. Secondary ion mass spectrometry (SIMS) measurements were performed using a Cameca IMS 7f spectrometer with a primary beam of 15-keV Cs$^+$ ions. A constant erosion rate was assumed for depth-calibration, where the crater depths were measured using a DekTak Stylus Profilometer.

After the electrical measurements, each Schottky diode was measured by the profilometer for accurate determination of the diode area.

Capacitance–Voltage (CV) measurements were carried out under dark conditions at temperatures in the range between 20 and 300 K using an Agilent 4284A LCR Meter at six different probing frequencies between 1 kHz and 1 MHz and with a probing AC amplitude of 30 mV. The LCR-meter was used in two modes: (1) so-called parallel mode ($C_p$-$G_p$) and (2) so-called series mode ($C_s$-$R_s$).

Figure 2. Temperature dependence of the c-axis permittivity (ε) of conductive, n-type TiO$_2$ obtained after heat treatments in FG and N$_2$; and a modified Curie–Weiss dependence with the parameters determined by Samara and Peercy (solid curve).

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Author contributions
E.V.M, L.V., J.B and C.Z. have planned the experiment. J.B., C.Z. and P.W. performed experimental measurements. J.B. wrote the main body of the text. All the authors have contributed to writing the manuscript. All the authors reviewed the manuscript.

Competing interests
The authors declare no competing interests.

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