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On the dielectric constant of titanium dioxide

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Abstract

Conductive rutile TiO₂ has received considerable attention recently due to a number of applications. However, the static dielectric constant in conductive, reduced or doped TiO₂ appears to cause controversy with reported values in the range 100-10000. In this work, we propose a method for measurements of the dielectric constant in conductive, n-type TiO₂ that involves: (i) hydrogen implantation to form a donor profile at a known depth, and (ii) capacitance-voltage measurements for donor profiling. We can not confirm the claims stating an extremely high dielectric constant. On the contrary, the dielectric constant of conductive, reduced rutile TiO₂ is similar to that of insulating rutile TiO₂ established previously, with a Curie-Weiss type temperature dependence and the values in the range 160-240 along the c-axis.

Introduction

The static and low-frequency dielectric constant, ϵ , of rutile TiO_2 has been surrounded with controversy since as early as 1952, when Nicolini [1] reported an extremely high value of around 10,000 for the dielectric constant of ceramic rutile TiO_2 . Similar values of $(1 - 3) \times 10^4$ were later observed by Parker and Wasilik [2] for single crystalline rutile TiO_2 . 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. [2] is based on capacitance measurements over the full thickness of the crystal, where metallic contacts are deposited on opposite sides. Parker and Wasilik [2] suggested that, in case of non-negligible free carrier concentration, i.e., non-negligible effective net doping, Schottky contacts can be unintentionally formed. This is particularly relevant in the case of reduced TiO_2 , 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” as formulated by Parker and Wasilik [2].

Based on these findings, Parker [3, 4] performed new theoretical and experimental studies of ϵ in rutile TiO_2 crystals. Special care was taken to prepare highly resistive TiO_2 by “heavy oxidation” as phrased in Ref. [3]. Highly resistive, oxygen-rich rutile TiO_2 crystals were then investigated by measuring the capacitance between a parallel plate capacitor with the crystal inside. Dielectric constants of 170 and 86 were measured at 300 K along the c- and a-axes, respectively. At 1.6 K, the dielectric constants along the c- and a-axis were deduced to be 257 and 111, respectively. No frequency dependence was observed in the frequency range $10^2 - 3 \times 10^6$ Hz.

Later, Samara and Percy [5] 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 [3], and the measurements were performed at 100 kHz. It has been shown that data for the dielectric constant, ϵ , can be fitted over the whole temperature range by the modified Curie-Weiss law derived first by Barrett [6] for perovskite-type crystals:

$$\epsilon = A_0 + \frac{C_0}{\frac{1}{2}T_1 \coth\left(\frac{T_1}{2T}\right) - T_0}, \quad (1)$$

where T is temperature, and A_0 , C_0 , T_1 and T_0 are fitting parameters. At 296 K, the dielectric constant along the c- and a-axes was determined to be 166.7 and 89.8, respectively. As the temperature was decreased to 4 K, the dielectric constants increased to 251 along the c-axis and to 114.9 along the a-axis. These values are close to those determined by Parker [3].

Reports on extremely high ϵ of reduced rutile TiO₂ continue to appear in the literature. For example, Chu [7] has reported values in a range of 100 – 10000. The dielectric constants were 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 [2]. Recently, Li et al. [8] 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 [7] nor Li et al. [8] have considered formation of Schottky barriers at the metal-TiO₂ interface and the corresponding depletion regions, which was considered by Parker and Wasilik [2].

Results and discussion

Annealing of TiO₂ in reducing and hydrogen-rich atmosphere has long been known to result in conductive, n-type material (see, for instance, Ref. [9]). Two main mechanisms are believed to be responsible: (i) formation of donors assigned to oxygen vacancies (V_O) and titanium interstitials (Ti_i) in the reducing atmosphere [10] and (ii) introduction of interstitial hydrogen (H_i) donors during hydrogenation [11,12]. Besides, H_i can interact with acceptors and passivate them, increasing the net n-type conductivity. We have demonstrated previously [13,14] that annealing of TiO₂ 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. In the case of heat treatment in FG, the increase can be correlated with concentration of H_i . 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 V_O/Ti_i and H_i . The effect of hydrogen-induced donors was used to form a pronounced donor profile at a well-defined depth by ion implantation.

Capacitance-voltage (CV) measurements are a well-established technique for probing the depth distribution of donors and acceptors. Fig. 1 depicts CV measurements at different temperatures (T_{meas}) for a sample annealed in N₂ at 1100°C for 60 min (TiO₂-N₂). The red, dotted curve represents measurements performed at 300 K on the as-prepared, conductive sample, i.e., after the N₂ heat treatment but prior to H⁺ implantation. Blue, solid curves represent measurements recorded after the sample was implanted with 200-keV H⁺ to a dose of $3 \times 10^{13} \text{ cm}^{-2}$. The different blue curves represent measurements recorded at different T_{meas} . Fig. 1(a) shows that capacitance of the Schottky diode decreases with increasing reverse voltage, V , as expected for a diode.

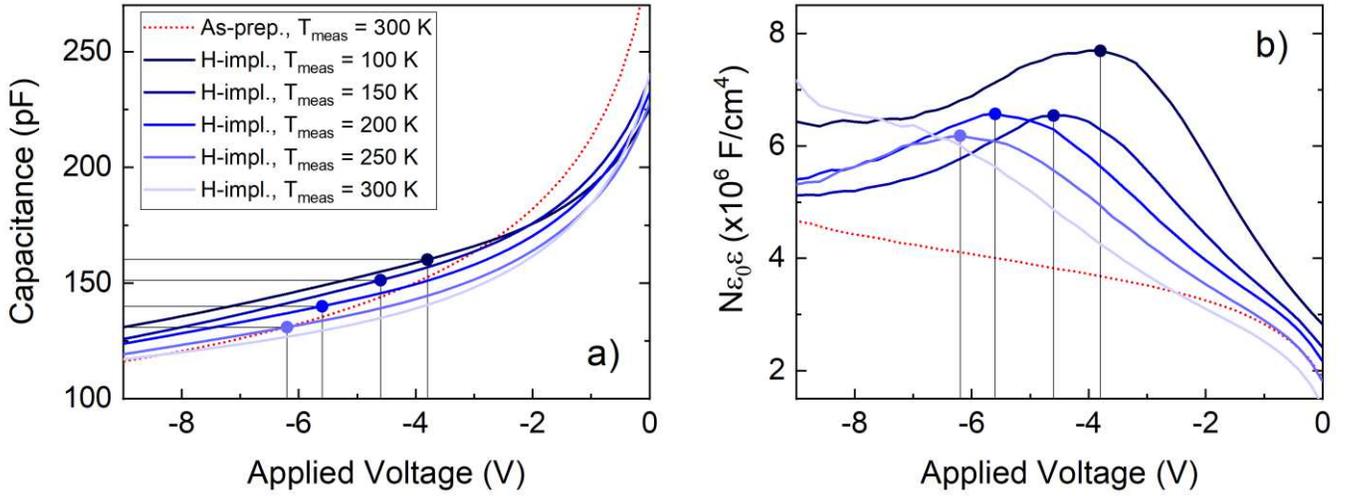


Fig. 1. Capacitance (a) of a TiO₂-N₂ sample (probing frequency 60 kHz) and the $N(V)\epsilon_0\epsilon$ product (b) as functions of applied voltage. The red, dotted curve shows the as-prepared sample, i.e., after the N₂ heat treatment but prior to H⁺ implantation. The blue, solid curves are for the H-implanted sample measured at different temperatures (T_{meas}). The peaks in $N(V)\epsilon_0\epsilon$ are indicated by the drop-down lines. The corresponding capacitance values, obtained at the same applied voltages, are also marked in (a).

Within the depletion approximation [15], one can derive the following expression:

$$N(V)\epsilon_0\epsilon = \frac{C^3}{qA^2} \left(\frac{dC}{dV} \right)^{-1}, \quad (2)$$

where $N(V)$ is the doping concentration at the depth of the depletion region for a given V , ϵ_0 is the vacuum permittivity, ϵ is the relative permittivity, or dielectric constant, C is the capacitance at the given V , q is the electron charge and A is the area of the diode. Since ϵ_0 and ϵ do not depend on V , the product $N(V)\epsilon_0\epsilon$ will maintain the shape of $N(V)$.

Fig. 1(b) displays $N(V)\epsilon_0\epsilon$ as a function of V . For the as-prepared sample, the data reveal a somewhat non-uniform, but monotonous $N(V)\epsilon_0\epsilon$ as a function of V . Hydrogen implantation leads to formation of a pronounced peak in $N(V)\epsilon_0\epsilon$. One can thus identify the voltages at which the edge of the depletion region reaches the peak of $N(V)\epsilon_0\epsilon$, as indicated in Fig. 1(b) with filled circles. For example, at 100 K, the depletion region edge reaches the donor concentration peak at $V_{\text{peak}} = -3.8$ V, and at 250 K it occurs at $V_{\text{peak}} = -6.2$ V. These voltages correspond to the capacitance values indicated in Fig. 1(a) with filled circles. For example, for measurements at 100 K, the reverse bias $V_{\text{peak}} = -3.8$ V (voltage when the depletion region reaches the

donor peak concentration) corresponds to $C_{\text{peak}} = 160$ pF. Similarly, for measurements at 250 K, the reverse bias $V_{\text{peak}} = -6.2$ V (donor peak concentration) results in $C_{\text{peak}} = 131$ pF. On the other hand, the depth of the concentration peak for hydrogen-induced donors is known from secondary ion mass spectrometry (SIMS) measurements: $d_{\text{peak}} = 0.97$ μm (see Supplementary Material).

Within the depletion approximation, the capacitance, C , and the depletion depth, d , are related as $C = \epsilon_0 \epsilon A / d$. One can thus find ϵ from:

$$\epsilon = \frac{C_{\text{peak}} d_{\text{peak}}}{\epsilon_0 A} . \quad (3)$$

The results of the analysis from Fig. 1 and Eq. (3) are summarized in Table I. 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. This is illustrated in Fig. 1(b), where the curve for $T_{\text{meas}} = 300$ K does not reveal a well-defined donor concentration peak.

Table I. Data used for analysis of temperature dependence of ϵ for the $\text{TiO}_2\text{-N}_2$ sample with CV data plotted in Fig. 1. The implantation depth $d_{\text{peak}} = 0.97$ μm . The diode area $A = 8.3 \times 10^{-4}$ cm^2 .

Temperature, K	V_{peak} , V	C_{peak} , pF	ϵ
100	-3.8	160	211
150	-4.6	151	199
200	-5.6	140	185
250	-6.2	131	173

The analysis described by Fig.1 and Eqs. (2) and (3) has been applied for more detailed studies of ϵ in a number of samples annealed in FG ($\text{TiO}_2\text{-FG}$) and the $\text{TiO}_2\text{-N}_2$ samples. Fig. 2 demonstrates that ϵ determined in the present study is very close to that determined for insulating, oxygen-rich rutile TiO_2 by Samara and Percy [5]. For reduced TiO_2 , ϵ along 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 ϵ between reduced TiO₂ (annealed in N₂ at 1100°C) and reduced-hydrogenated TiO₂ (annealed in FG at 600°C).

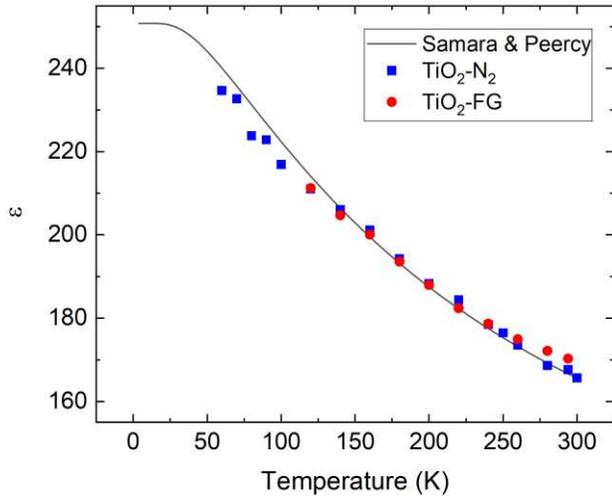


Fig. 2. Temperature dependence of the c-axis dielectric constant (ϵ) of conductive, n-type TiO₂ obtained after heat treatments in FG and N₂; and a modified Curie-Weiss dependence with the parameters determined by Samara and Peercy [5] (solid curve).

Conclusion

In conclusion, measurements of the static dielectric constant, ϵ , in conductive TiO₂ are challenging and causing controversy. We propose a method for deducing ϵ 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 then characterized using capacitance-voltage measurements, and ϵ can be deduced. We observe that ϵ of reduced, conductive rutile TiO₂ is similar to that of oxygen-rich, insulating rutile TiO₂ established previously. We can not confirm claims of colossal dielectric permittivity in hydrogenated and reduced rutile TiO₂.

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Methods

A. Samples

The study was performed on Verneuil-grown rutile TiO₂ single crystals with a surface orientation of (001), purchased from *Shinkosha Co., Ltd.* [16]. As-received crystals were 0.5mm thick with double-side polished surfaces, nominally undoped, transparent, and semi-insulating with a conductivity of $\sigma < 10^{-7} \Omega^{-1} \text{cm}^{-1}$. Conductive *n*-type TiO₂ samples of bluish colour were obtained by heat treatments in forming gas (FG) flow (N₂ + H₂ with [H₂]/[N₂] \approx 1/9) at 600°C for 90 min (hydrogenating and reducing heat treatment) or in N₂ flow at 1100°C for 60 min (reducing heat treatment). After the heat treatments, circular 150-nm thick Pd contacts with a diameter of around 400 μm were deposited through a shadow mask, resulting in Schottky barrier diodes with a rectification of up to eight orders of magnitude [17]. After initial electrical measurements, the samples were implanted at room temperature with 200-keV H⁺ ions to different doses in the range $6 \times 10^{12} - 3 \times 10^{14} \text{cm}^{-2}$.

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 K 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).

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Figures

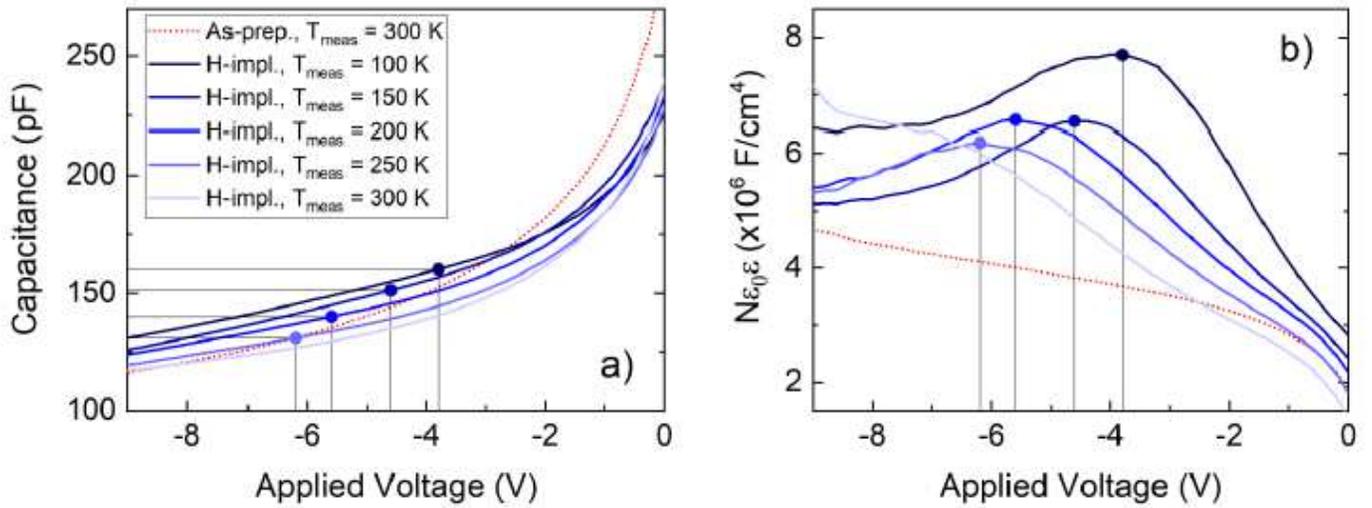


Figure 1

Capacitance (a) of a TiO₂-N₂ sample (probing frequency 60 kHz) and the $N(V)\varepsilon_0\varepsilon$ 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 (T_{meas}). The peaks in $N(V)\varepsilon_0\varepsilon$ are indicated by the drop-down lines. The corresponding capacitance values, obtained at the same applied voltages, are also marked in (a).

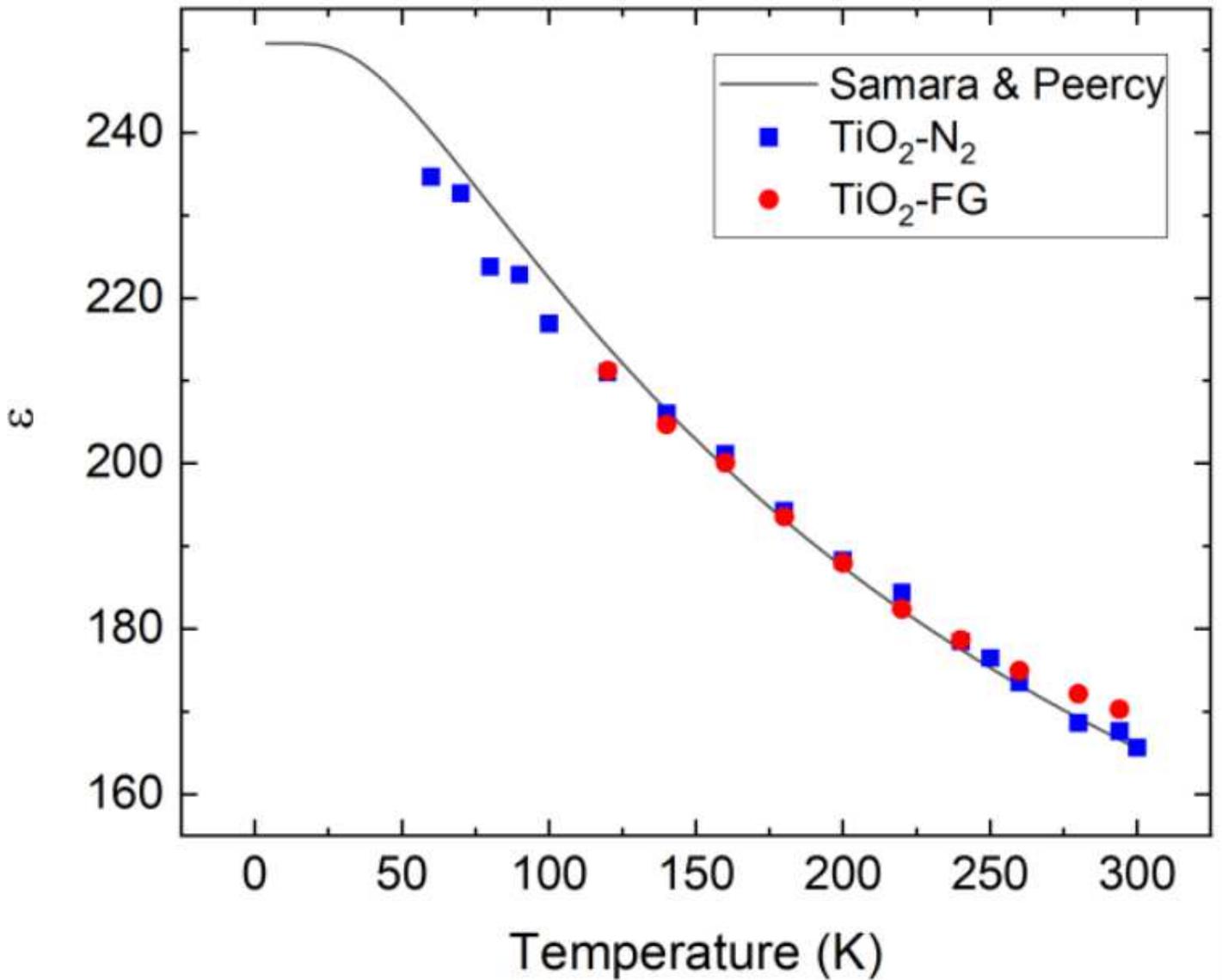


Figure 2

Temperature dependence of the c-axis dielectric constant (ϵ) of conductive, n-type TiO₂ obtained after heat treatments in FG and N₂; and a modified Curie-Weiss dependence with the parameters determined by Samara and Peercy [5] (solid curve).

Supplementary Files

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- [epsrTiO2SciRepSupplementary.pdf](#)