Hydrogen: A metastable donor in TiO$_2$ single crystals

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The properties of TiO$_2$ (110) single crystals are greatly changed after hydrogen is doped into them through electrochemical hydrogen charging, in which the crystals have been placed in 0.01M NaOH solution to deposit hydrogen on their electrodes through the electrolysis of water. The changes in properties, including great increases in leakage current, strong dielectric dispersions over 10^2–10^6 Hz, and a strong aging phenomenon suggest that hydrogen is a donor in TiO$_2$ while ionized hydrogen is not bound to an oxygen site by a strong O–H bond. This behavior of hydrogen, which can be characterized as a metastable donor, is different from the usual donor behavior of hydrogen in oxides and should be interesting for a better understanding of the behavior of hydrogen in oxides. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2900957]

The behavior of hydrogen in oxides has been a topic of extensive investigations. On one hand, hydrogen is a ubiquitous impurity in various oxides. It can be introduced into oxides from precursors, from annealing gases,[1] or even from aqueous vapor in ambient atmosphere.[2] On the other hand, hydrogen behaves quite differently from one oxide to another. In some oxides, hydrogen forms deep gap states in all of its three charge states, H$^+$, H^0, and H$^-$; while in other oxides, hydrogen gives rise to a shallow level at the conduction band edge and acts as a donor.[3–5] As an example, hydrogen has been predicted theoretically[6] and proven experimentally[7] as a shallow donor in ZnO. It must possess a high stability in ZnO to survive high-temperature sintering or crystal growth. As a matter of fact, it is generally believed that as a donor, hydrogen ionizes to H$^+$ with the electron being delocalized in the oxide conduction band and then H$^+$ forms a single strong O–H bond to an O site; in contrast, when hydrogen is a deep impurity, it will only form some longer, weaker bonds to more than one neighboring oxygen and exist as a metastable interstitial.[5] Metastable interstitial hydrogen has been observed in proton-exchanged LiNbO$_3$. A sharp peak at around 3500 cm^{-1} can always be observed in the infrared absorption spectra of proton exchange process–treated LiNbO$_3$, which is the characteristic absorption peak for the stretch mode of the O–H bond, as hydrogen has replaced some lithium ions in LiNbO$_3$. When the acidity of the melt in the proton exchange process is high enough, another broad peak at 3280 cm^{-1} can also be observed, which is only metastable and will disappear through an annealing process.[8] Obviously, these two peaks should correspond to two different states of hydrogen with quite different stabilities. The broad peak should indicate the existence in LiNbO$_3$ of hydrogen with a much lower stability, which is possibly a deep impurity forming only long and weak bonds to neighboring oxygen sites. In a previous investigation, hydrogen has been doped into TiO$_2$ single crystals through an electrochemical method.[9] Presently, a study on the behavior of hydrogen in TiO$_2$ single crystals has been conducted in terms of dielectric and conduction analyses, which strongly suggest that hydrogen acts a donor in TiO$_2$ while ionized hydrogen is not bound to an oxygen site by a strong O–H bond. Such behavior of hydrogen in oxides, which can be characterized as metastable donor, is different from the usual donor behavior of hydrogen in oxides and should help in understanding more fully the behavior of hydrogen in oxides.

Rutile (110) single crystals, $10 \times 10 \times 0.5$ mm^3 and two sides polished, were used in the investigation. Circular silver electrodes (DuPont 1183) with a diameter of 2 mm were fired onto the centers of the two major surfaces of the crystals. The crystals were immersed in a 0.01M NaOH solution, and a 4.5 V dc voltage was imposed between the silver electrodes of the crystals and a counter Pt electrode in the solution, with the former acting as the cathode and the latter acting as the anode. The imposed dc voltage induced electrolysis of water, and hydrogen was deposited on the silver electrodes of the crystals. Hydrogen generated in this electrochemical process can diffuse and react with oxides; hereafter, this process is referred to as electrochemical hydrogen charging. The solution was kept stirred by a magnetic agitator, and the temperature was kept constant at 20 °C. The hydrogen charging was interrupted from time to time and the crystals were taken out, washed with de-ionized water and acetone, and dried for measurement. Using the two silver electrodes of the crystals, the frequency spectra of capacitance and dielectric loss of the crystals were measured on an impedance analyzer (Agilent 4294 A), and the *I-V* characteristics of the crystals were recorded through an electrometer/high resistance meter (Keithley 6517). All measurements were conducted at ambient temperature (20 °C).

It should be pointed out that the single crystals were chemically stable in water. There were no discernible changes in the properties of the crystals after they had been immersed in the 0.01M NaOH solution for dozens of hours without application of any voltages. The changes induced by electrochemical hydrogen charging can be reliably ascribed to the reaction of hydrogen. Some representative results obtained for a single crystal are reported in the following. Figures 1 and 2 show the frequency spectra of capacitance and
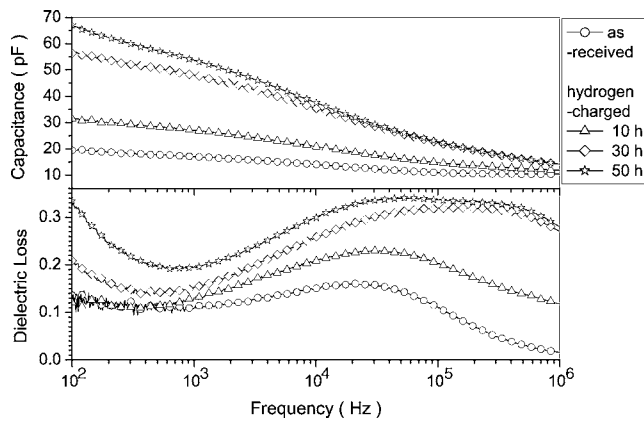
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FIG. 1. Frequency spectra of capacitance and dielectric loss of a TiO$_2$ single crystal measured at different times: as received and after a series of periods of electrochemical hydrogen charging.

FIG. 3. (Color online) Frequency spectra of capacitance and dielectric loss of a hydrogen-charged TiO$_2$ single crystal in the course of the aging process.

dielectric loss and *I-V* characteristics of the crystal measured as received and after different periods of electrochemical hydrogen charging, respectively. To be consistent, every time that electrochemical hydrogen charging was interrupted, the frequency spectra were measured after the crystal was stabilized for 0.1 h and the *I-V* curve was measured after the crystal was stabilized for 0.2 h. Obviously, electrochemical hydrogen charging had induced great changes in both the dielectric properties and the conductivity of the single crystal. The leakage current was increased by more than four orders of magnitude after 50 h of electrochemical hydrogen charging. It is reasonable to conclude that some free charge carriers were formed in the single crystal through electrochemical hydrogen charging. In a previous investigation, a peak at 3280 cm^{-1} had been observed in the infrared absorption spectra of hydrogen-charged TiO$_2$ single crystals,[8] which gives a direct evidence for the incorporation of hydrogen in the TiO$_2$ lattice. As predicted by some theoretical investigations,[3–5] hydrogen is a shallow donor in TiO$_2$, and it has been proposed that free electrons are formed in the following way:

$$H_{ads} \rightarrow H_i^{\bullet} + e', \qquad (1)$$

where H$_{ads}$ represents an adsorbed hydrogen atom generated from electrochemical hydrogen charging and H$_i^{\bullet}$ is an ionized

hydrogen in an interstitial site of TiO$_2$ lattice. The great increase in leakage current can be explained well by the donor behavior of hydrogen in TiO$_2$.

For the as-received crystal, the capacitance showed a little dispersion over the testing frequency range and the dielectric loss peak was around 3×10^4 Hz. For the hydrogen-charged single crystal, the capacitance showed much stronger dispersions and the dielectric loss peak occurred at some higher frequencies. For example, after 50 h of electrochemical hydrogen charging, the capacitance was increased by more than two times at 10^2 Hz and by only 40% at 10^6 Hz, and the dielectric loss peak was around 2×10^5 Hz. Among the various polarization mechanisms in oxide crystals,[10] orientation polarization is responsible for dispersions over the testing frequency range (10^2–10^6 Hz), which occurs when two or more equivalent positions for an ion are present. There must be some defects, such as oxygen vacancy and titanium vacancy, in small concentrations in the as-received single crystal. The defects must be associated in some ways with a formed dipole moment, and orientation polarization of the dipole moment is accomplished through ion jump, leading to the observed little dispersion. Accordingly, the strong dispersions in the hydrogen-charged crystal must be due to orientation polarization of hydrogen-related dipoles through jumping of H$^+$ between some equivalent positions. There exists a strong aging behavior in the properties of hydrogen-charged single crystals. The results obtained for the above single crystal after 50 h of electrochemical hydrogen charging are shown in Figs. 3 and 4. The moment when electrochemical hydrogen charging was finally stopped was taken as the starting point of aging, and its dielectric properties and *I-V* characteristics were successively measured after a series of periods of aging time. As shown in Fig. 3, the dielectric properties of the single crystal were found to change systematically in the course of aging. With increasing time of aging, the slope of the capacitance-frequency curve, or dispersion, was gradually decreased; while the dielectric loss peak was moving to the low frequency side and its value was gradually decreased. After 500 h of aging, the frequency spectra of capacitance and dielectric loss were almost the same to those obtained for the as-received crystal. At the same time, the leakage current was gradually decreased in the course of aging. After 500 h of aging, the leakage current was only two times as big as that measured for the as-received crystal. So the effects of hydrogen on the properties of TiO$_2$ single crystals gradually weakened and finally disappeared through the
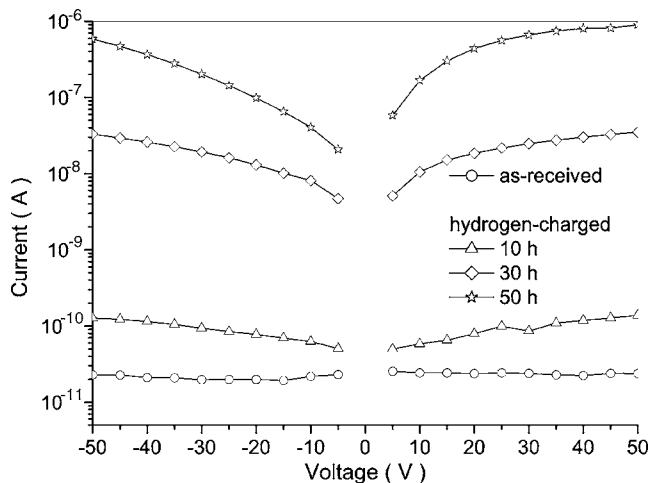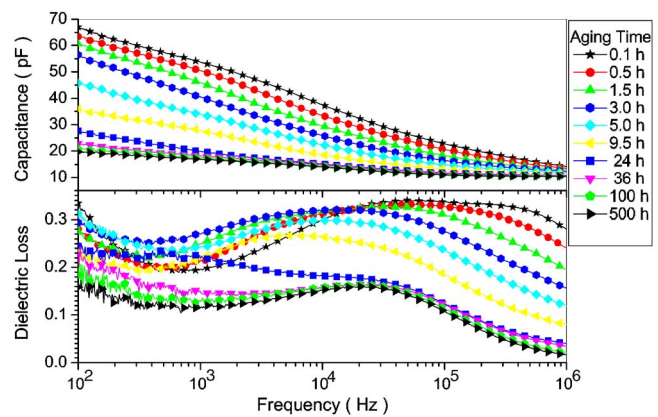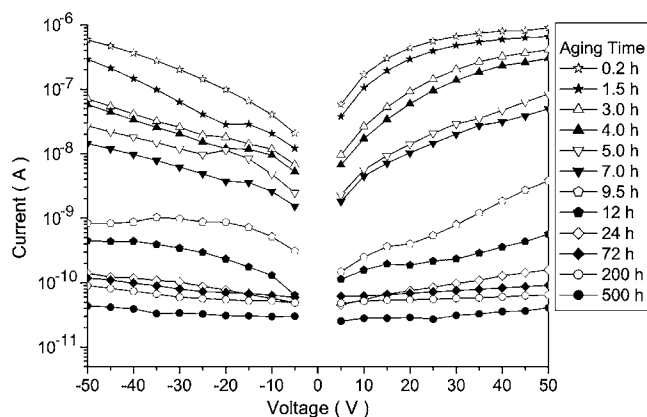

FIG. 2. *I-V* characteristics of a TiO$_2$ single crystal measured at different times: as received and after a series of periods of electrochemical hydrogen charging.

FIG. 4. *I-V* characteristics of a hydrogen-charged TiO$_2$ single crystal in the course of the aging process.

aging process, which indicates that hydrogen is only metastable in TiO$_2$ and will gradually diffuse out. A possible mechanism for the outdiffusion of hydrogen from TiO$_2$ can be expressed as

$$2H_i^{\bullet} + 2e' \rightarrow H_2. \tag{2}$$

With the outdiffusion of hydrogen, the free electrons generated by the ionization of hydrogen and hydrogen-related dipoles were eliminated, so the dielectric and conduction properties of TiO$_2$ were both restored.

The question now arises on the nature on the interaction between H$^+$ and neighboring oxygen sites. As a donor, hydrogen has been expected to form a single strong O–H bond perpendicular to the Ti–O bonding plane after ionization in TiO$_2$.[4] The aging behavior shown in Fig. 3, however, suggests something quite unexpected. It is well-known that the frequency at the dielectric loss peak represents a dielectric relaxation frequency (denoted f_c),[10] which is the frequency for ion jump between equivalent positions. Frequency f_c follows an Arrhenius law expressed as

$$f_c = f_0 \exp(-U/k_B T), \tag{3}$$

where U denotes the activation energy required for the ion jump. Obviously, f_c shifts to a higher frequency with increasing temperature.[11,12] It is strange that for the hydrogen-charged crystals in this study, the dielectric loss peak was moving to the low frequency side with increasing aging time at a constant temperature. It seems that the activation energy for the jumping of H$^+$ is not a constant in this system. As mentioned above, the concentration of hydrogen in the single crystals is gradually decreased in the course of aging. Although an exact mechanism is still lacking, it is reasonable to assume that the activation energy for the jumping of H$^+$ depends on the concentration of hydrogen in TiO$_2$. The lower the concentration is, the bigger the activation energy is and the smaller the jumping frequency f_c is. Such activation energy should not result from an O–H bond, which is independent of the concentration of hydrogen. The possibility that hydrogen could act as a donor while it is not bound to an oxygen site by an O–H bond has to be considered. As a matter of fact, the low stability of hydrogen in TiO$_2$ has already implied the absence of a strong O–H bond for hydrogen.

A similar aging behavior has been observed in electrochemically hydrogen-charged BaTiO$_3$ and SrTiO$_3$ single crystals,[13,14] whose dielectric loss peaks are also moving to

the low frequency side in the course of aging. Hydrogen doped through electrochemical hydrogen charging may also act as a metastable donor in BaTiO$_3$ and SrTiO$_3$. Several investigations have shown that hydrogen can be doped into perovskite titanates through annealing in atmospheres containing H$_2$.[1,12,15] It is believed that hydrogen doped through annealing acts as a donor in the titanates with a strong O–H bond formed and a heat treatment at some elevated temperatures is needed to remove hydrogen from them.[15] There have been no reports on any obvious aging behavior at ambient temperature induced by hydrogen in them. Some researchers have pointed out that hydrogen doped at different times or through different ways may behave quite differently in oxides.[4,15] So depending on the doping methods, there may be two different donor states, namely, stable donor (doped through annealing) and metastable donor (electrochemically doped), for the behavior of hydrogen in oxides. Further investigations are being conducted on the relationship between these two different donor states.

In summary, the properties of electrochemical hydrogen charging–treated TiO$_2$ (110) single crystals indicate that hydrogen acts as a metastable donor in TiO$_2$; that is, it ionizes to H$^+$ with a free electron formed, while H$^+$ is not bound to an oxygen site by a strong O–H bond. The great increases in leakage current must be due to free electrons ionized from hydrogen, the strong dielectric dispersions over the frequency range of 10^2–10^6 Hz should be explained by orientation polarization of hydrogen-related dipoles, and the strong aging behavior indicates variable activation energy for the jumping of H$^+$ and a low stability of hydrogen in TiO$_2$ lattice. Hydrogen as a metastable donor may be different from a donor bound to an oxygen site by a strong O–H bond in oxides, and further investigations should be carried out.

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