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## Spontaneous recovery of hydrogen-degraded TiO<sub>2</sub> ceramic capacitors

W. P. Chen,<sup>a)</sup> Y. Wang, J. Y. Dai, S. G. Lu, X. X. Wang, P. F. Lee, H. L. W. Chan, and C. L. Choy

Department of Applied Physics and Materials Research Center, The Hong Kong Polytechnic University, Hong Kong, People's Republic of China

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Degradation of  $TiO_2$ -based ceramic capacitors was observed after hydrogen incorporation on the termination electrodes of the capacitors via electrolysis of water. Fourier-transform infrared (FTIR) absorption spectra analysis of polished rutile single crystals clearly showed that hydrogen was incorporated into the  $TiO_2$  lattice through the treatment. Hydrogen reduces  $Ti^{4+}$  to  $Ti^{3+}$  and increases the concentration of charge carriers. The degradation was found to exhibit a strong dependence on time at room temperature. The degraded properties were spontaneously recovered through an aging process, showing a spontaneous recovery unique to  $TiO_2$ -based ceramic capacitors. It is proposed that hydrogen is metastable in  $TiO_2$  and that hydrogen-induced degradation has different stabilities among various oxide-based components and devices. © 2004 American Institute of Physics. [DOI: 10.1063/1.1637942]

The effects of hydrogen incorporation in materials have been extensively studied, particularly on metals (hydrogen embrittlement) and silicon-based devices (passivation of dangling bonds). In recent years, however, more and more attention has been paid to the reactions between hydrogen and metal oxide materials.<sup>1–3</sup> In our previous studies, we found that hydrogen reacts with many metal oxides at an ambient temperature in some electrochemical processes, including electroplating<sup>4</sup> and the electrolysis of water.<sup>5,6</sup> These ambient temperature reactions usually induce obvious degradations in the properties of these oxide-based components and devices. A systematic understanding of the reactions is of great importance for improving the reliability of metal oxide-based electronic components and devices.<sup>7</sup>

For many oxide-based components and devices, the degradation induced by the reaction of hydrogen is permanent and stable at room temperature. Sometimes, an annealing in an oxidizing atmosphere can recover the degraded properties.<sup>4,8</sup> Obviously, the hydrogen-induced defects in those oxides responsible for the degradation can only be eliminated by high-temperature oxidizing reactions. When we studied hydrogen-induced degradation in TiO2-based ceramic capacitors, however, we obtained a quite unexpected result. Although hydrogen induces an obvious degradation in the capacitors, the degraded properties exhibit a strong dependence on time, and the degradation is gradually recovered through an aging process without any thermal treatment. This indicates that hydrogen-induced defects are only metastable in TiO<sub>2</sub>-based ceramic capacitors at room temperature, in contrast to hydrogen-induced defects in many other oxides.

The composition and sintering of the TiO<sub>2</sub>-based temperature-compensating ceramic capacitors used in the present investigation were reported in another paper.<sup>9</sup> The capacitors were 0.70 mm thick and 7.5 mm in diameter, with a 4.5 mm diameter silver electrode on one surface and a 5.5

mm diameter silver electrode on the other surface. Some capacitors were placed in a 0.01 M NaOH solution and dc voltages were imposed between the silver electrode of the capacitors and an anode in the solution. The electrolysis of water occurred because the applied dc voltages and hydrogen evolved on the silver electrode of the capacitors. This treatment is hereafter referred to as hydrogen charging. The dc voltages were disconnected after designated periods of time and the capacitors were taken out, cleaned with de-ionized water and dried. An Agilent 4294A impedance analyzer was used to measure the frequency spectra of capacitance and dielectric loss of the capacitors. The current density-voltage (J-V) characteristics of the capacitors were measured through a Keithley 6517 electrometer/high resistance meter. Polished rutile (001) single crystals  $(10\times10\times0.5 \text{ mm}^3 \text{ in})$ size) have been used for studying the reaction mechanism between hydrogen and TiO2. A 3 mm diameter silver electrode was fired onto a corner of a rutile single crystal for hydrogen charging. Fourier-transform infrared (FTIR) absorption spectra were obtained with a Nicolet's Magna-TRTM 750 FTIR spectrometer by measuring the transmittance spectroscopy. Raman spectra were recorded through a Jobin-Yvon T6400 instrument, with an Ar<sup>+</sup> laser source of 514 nm wavelength and an incident power of 100 mW.

SEM analysis revealed that the capacitors were very dense in microstructure. Some samples had been immersed in the NaOH solution for 100 h. After washing and drying, it was found that the immersion had no noticeable influence on the properties of the capacitors. By contrast, changes were observed in both the appearance and properties of those samples treated by hydrogen charging. The as-sintered samples were yellowish in color. The blank ceramic surface gradually changed to bluish—gray and finally to blue—black as hydrogen charging proceeded. Associated with the color change were dramatic increases in dielectric loss and in leakage current of the capacitors. Similar to the blank ceramic surface of TiO<sub>2</sub> capacitors, the blank part of the rutile single crystal with a 3 mm silver electrode on a corner also changed

a) Electronic mail: apchenwp@polyu.edu.hk

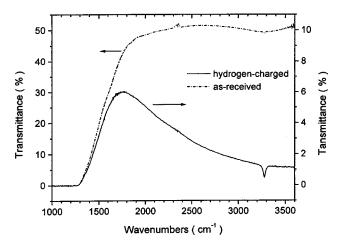


FIG. 1. Room temperature Fourier-transform infrared (FTIR) absorption spectra of an as-received rutile single crystal and a hydrogen-charged rutile single crystal.

to blue-black after hydrogen charging and the transparency was greatly decreased. The FTIR absorption spectra for an as-received rutile single crystal and the hydrogen-charged rutile single crystal are shown in Fig. 1. Hydrogen charging had been conducted for 80 h with the application of a 6 V dc voltage and a cathodic current density of 0.5 mA/cm<sup>2</sup>. The FTIR absorption spectra were taken at 60 h after hydrogen charging. One can see that for the hydrogen-charged sample, the transmittance had been greatly decreased above 1300 cm<sup>-1</sup> and there is a significant absorption peak around the wavenumber of 3280 cm<sup>-1</sup>. This is a characteristic absorption for interstitial hydrogen identification. 10 So it is direct evidence that hydrogen has been incorporated into the TiO2 lattice at an ambient temperature by means of electrochemical hydrogen charging. It is well known that Ti<sup>4+</sup> can be reduced to Ti<sup>3+</sup>. Therefore, the reaction between hydrogen generated by the electrolysis of water and TiO<sub>2</sub> capacitors can be expressed as

$$H_2O + e^- \rightarrow OH^- + H_{ads},$$
 (1)

$$H_{ads} + H_{ads} \rightarrow H_2$$
, (2)

$$H_{ads} + Ti_{Ti} \rightarrow H_i^{\bullet} + Ti_{Ti}',$$
 (3)

where  $H_{ads}$  represents an adsorbed hydrogen atom,  $H_i^{\bullet}$  represents an ionized hydrogen in an interstitial site and  $Ti'_{Ti}$  represents a trivalent titanium in the lattice site of a tetravalent titanium. The electron in  $Ti'_{Ti}$  is weakly bonded and is easily activated to the conduction band, which results in great increases in dielectric loss and in leakage current.

The spontaneous recovery of hydrogen-induced degradation in TiO<sub>2</sub> capacitors is shown by a representative sample in the following. The capacitor had been treated by hydrogen charging for 12 h, with the application of a 4.5 V dc voltage and a cathodic current density of around 0.3 mA/cm<sup>2</sup>. To measure the time dependence, the moment when the sample was disconnected from the dc voltage was taken as the starting point of aging. After cleaning and drying, the sample was kept at 20 °C for both aging and measuring. Figure 2 shows the frequency spectra of capacitance and dielectric loss of the capacitor measured at different aging times. It is clear that the spectra depend greatly on aging time. For the as-sintered capacitor, the capacitance is about 24.9 pF from 1 kHz to 1

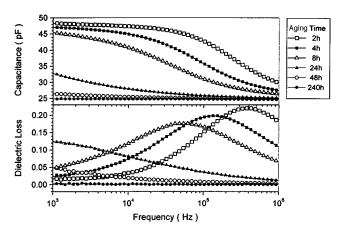


FIG. 2. Frequency spectra of capacitance and dielectric loss for a hydrogen charging degraded TiO<sub>2</sub>-based ceramic capacitor measured at various aging times

MHz and the dielectric loss is very low over this frequency range. For the degraded capacitor, at the early stages of aging, the capacitance has obviously increased, and it decreases with increasing testing frequency; the dielectric loss has also greatly increased and a peak appears in its frequency spectrum. The increase in capacitance must be due to the incorporated hydrogen atoms. They ionize and form dipoles that make a noticeable contribution to the polarization, especially in the low frequency region. It is interesting to note that the spectra of capacitance and dielectric loss both change systematically with aging time. As aging proceeds, the dielectric loss peak moves to the low frequency side and the peak height decreases; finally, the dielectric loss becomes very small over the testing frequency range. The change in the capacitance-frequency curve with aging time is also very clear. Roughly speaking, the slope of the curve decreases as the aging time increases, until the capacitance becomes independent of frequency. After 240 h of aging, the capacitor exhibits the same capacitance and dielectric loss versus frequency characteristics as that of the capacitor before electrochemical hydrogen charging; i.e., the dielectric properties recovered after 240 h of aging.

The J-V characteristics of the capacitor also exhibited a strong dependence on time, as illustrated in Fig. 3. According to the J-V curve measured after 1 h of aging, the leakage current density of the degraded capacitor is more than three orders of magnitude larger than that of the as-sintered

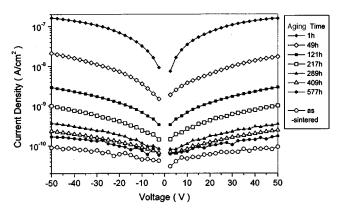


FIG. 3. J-V characteristics for a hydrogen charging degraded  $TiO_2$ -based ceramic capacitor measured at various aging times.

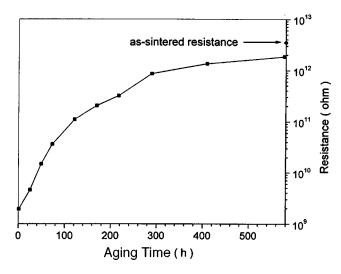


FIG. 4. The relationship between the resistance and aging time for a hydrogen charging degraded TiO<sub>2</sub>-based ceramic capacitor.

capacitor. But as aging time increases, the difference gradually narrows. The relationship between resistance (calculated from the J-V curves at the voltage of -50 V) and aging time is shown in Fig. 4. It can be seen that the decreased insulation resistance increases monotonously to approach that of the as-sintered capacitor. The recovery is fast at the early stage of aging, but becomes slower as aging time increases. After 577 h of aging, the resistance reaches about 50% of that before hydrogen charging.

It should be pointed out that the darkened color induced by hydrogen charging fades gradually in the course of aging. Together with the recovery observed in various properties, it is reasonable to assume that the concentration of the defects (interstitial hydrogen in this case) responsible for the degradation decreases as aging time increases. A possible mechanism is expressed as

$$2H_{i}^{\bullet} + 2Ti_{Ti}^{\prime} \rightarrow 2Ti_{Ti} + H_{2}. \tag{4}$$

It is assumed that interstitial hydrogen ions are metastable in TiO2-based ceramics. As a matter of fact, the characteristic FTIR absorption peak for the O-H stretch mode, which is around 3500 cm<sup>-1</sup>, <sup>10,11</sup> cannot be seen in Fig. 1 for the hydrogen-charged rutile single crystal. Figure 5 shows the Raman spectra for an as-received rutile single crystal and for the hydrogen-charged rutile single crystal of Fig. 1. The vibration modes of three peaks are 240 cm<sup>-1</sup> (disorder and second order scattering); 451 cm<sup>-1</sup> ( $E_g$ ); 610 cm<sup>-1</sup> ( $A_{1g}$ ). 12 There is no noticeable change for the three modes between the two samples; no special Raman scattering peak for the O-H stretch mode, which was located around 3700 cm<sup>-1</sup>, <sup>1,13</sup> was observed for the hydrogen-charged crystal, either. These results suggest that incorporated hydrogen does not form an O-H bond with oxygen ion in rutile, which may explain why hydrogen is only metastable in the rutile lattice. A similar result had been reported for LiNbO<sub>3</sub> and LiTaO<sub>3</sub>, <sup>10</sup> in which hydrogen corresponding to the FTIR absorption peak of 3280 cm<sup>-1</sup> is also only metastable. On the other hand, when incorporated hydrogen forms an O-H bond with an oxygen ion, such as in Pb(Nb,Zr,Ti)O<sub>3</sub>, <sup>14</sup> it shows a higher stability and it is driven out only at some elevated temperatures.

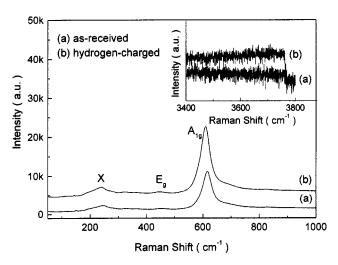


FIG. 5. Raman spectra for an as-received rutile single crystal and for the hydrogen-charged rutile single crystal of Fig. 1.

To summarize, this study clearly shows that hydrogen generated by the electrolysis of water is incorporated in the TiO<sub>2</sub> lattice and induces an obvious degradation in TiO<sub>2</sub>-based ceramic capacitors. Through an aging process, however, the degradation vanishes gradually as the various degraded properties systematically return to their original values. It is proposed that the degradation results from the reduction of titanium and the formation of interstitial hydrogen. These hydrogen-induced defects are only metastable in the TiO<sub>2</sub> lattice, and their disappearance results in the recovery. Hydrogen-induced defects exhibit different stabilities between TiO<sub>2</sub> and many other oxides. It is imperative to build up a systematic understanding on the reactions between hydrogen and metal oxides.

<sup>&</sup>lt;sup>1</sup>S. Aggarwal, S. R. Perusse, C. W. Tipton, R. Ramesh, H. D. Drew, T. Venkatesan, D. B. Romero, V. B. Podobedov, and A. Weber, Appl. Phys. Lett. **73**, 1973 (1998).

<sup>&</sup>lt;sup>2</sup>N. Poonawala, V. P. Dravid, O. Auciello, J. Im, and A. R. Krauss, J. Appl. Phys. 87, 2227 (2000).

<sup>&</sup>lt;sup>3</sup>J. H. Ahn, P. C. McIntyre, L. W. Mirkarimi, S. R. Gilbert, J. Amano, and M. Schulberg, Appl. Phys. Lett. 77, 1378 (2000).

<sup>&</sup>lt;sup>4</sup>W. P. Chen, L. T. Li, Y. Wang, and Z. L. Gui, J. Mater. Res. **13**, 1110 (1998).

<sup>&</sup>lt;sup>5</sup> W. P. Chen, H. L. W. Chan, F. C. H. Yiu, K. M. W. Ng, and P. C. K. Liu, Appl. Phys. Lett. **80**, 3587 (2002).

<sup>&</sup>lt;sup>6</sup> W. P. Chen, X. P. Jiang, Y. Wang, Z. Peng, and H. L. W. Chan, J. Am. Ceram. Soc. **86**, 735 (2003).

<sup>&</sup>lt;sup>7</sup> J. D. Baniecki, J. S. Cross, M. Tsukada, and J. Watanabe, Appl. Phys. Lett. 81, 3837 (2002).

<sup>&</sup>lt;sup>8</sup>J. Im, O. Auciello, A. R. Krauss, D. M. Gruen, R. P. H. Chang, S. H. Kim, and A. I. Kingon, Appl. Phys. Lett. **78**, 1162 (1999).

<sup>&</sup>lt;sup>9</sup> W. P. Chen, Y. Wang, X. X. Wang, J. Wang, and H. L. W. Chan, Mater. Chem. Phys. 82, 520 (2003).

<sup>&</sup>lt;sup>10</sup> P. Baldi, M. P. De Micheli, K. El Hadi, S. Nouh, A. C. Cino, P. Aschieri, and D. B. Ostrowsky, Opt. Eng. 37, 1193 (1998).

<sup>&</sup>lt;sup>11</sup> X. L. Tong, M. Zhang, A. Yariv, A. Agranat, R. Hofmeister, and V. Leyva, Appl. Phys. Lett. **69**, 479 (1996).

<sup>&</sup>lt;sup>12</sup> J. Arbiol, J. Cerda, G. Dezanneau, A. Cirera, F. Peiro, A. Cornet, and J. R. Morante, J. Appl. Phys. **92**, 853 (2002).

A. R. Krauss, A. Dhote, O. Auciello, J. Im, R. Ramash, and S. Aggarwal, Integr. Ferroelectr. 27, 1191 (1999).

<sup>&</sup>lt;sup>14</sup> S. Aggarwal, S. R. Perusse, C. J. Kerr, R. Ramesh, J. T. Evans, Jr., L. Boyer, and G. Velasquez, Appl. Phys. Lett. 76, 918 (2000).

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