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Hydrogen-induced degradation in $SrTiO_3$-based grain boundary barrier layer ceramic capacitors

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Abstract

Hydrogen-induced degradation in $SrTiO_3$-based grain boundary barrier layer ceramic capacitors was studied through electrochemical hydrogen charging, in which the capacitors were placed in 0.01 M NaOH solution with hydrogen deposited on their electrodes from the electrolysis of water. The properties of the capacitors were greatly degraded after 0.5 h of treatment: The capacitance was dramatically decreased and the dielectric loss was dramatically increased over the frequency range of 10^2–10^5 Hz, the leakage current was increased by orders of magnitude. It was proposed that atomic hydrogen diffused relatively easily along the grain boundaries and induced a reduction reaction to the grain boundary layer, which resulted in the degradation observed. Hydrogen-induced degradation is more serious in $SrTiO_3$-based grain boundary barrier layer ceramic capacitors than in other ceramic capacitors and great efforts should be made to prevent hydrogen-induced degradation in them.

Keywords: B. Failure analysis; C. Dielectric properties; D. $BaTiO_3$ and titanates; E. Capacitors

1. Introduction

With an extremely low Curie point of −263 °C, $SrTiO_3$ has a relatively low dielectric constant (about 300) with a very small temperature coefficient (−2500 ppm/°C) around room temperature. In recent years, grain boundary barrier layer (GBBL) ceramic capacitors based on $SrTiO_3$ have been successfully developed for many applications. They are attractive in that they largely keep the small temperature coefficient of $SrTiO_3$ while the dielectric constant is increased by two orders of magnitude. This great increase in dielectric constant results from the special microstructure of GBBL capacitors. Through donor-doping and sintering in reducing atmospheres, the grains of $SrTiO_3$-based GBBL capacitors are highly conductive. A slurry of some low-melting point oxides, such as Bi_2O_3 and CuO, is then painted on the ceramic surface and they are diffused along the grain boundaries through a heat-treatment in air at 1000–1100 °C, leading to the formation of an insulating phase in the grain boundaries and an insulating layer in the surface of $SrTiO_3$-based grains. The microstructure of GBBL capacitors is thus composed of semiconductive grains, insulating grain surfaces and an insulating phase in the grain boundaries [1]. The grains of GBBL capacitors act as an electrode and the dielectric layers are confined to the insulating grain surfaces and the insulating phase in the grain boundaries, which are usually defined as grain boundary layer as a whole. The effective dielectric constant of GBBL capacitors is usually estimated according to [2]:

$$\varepsilon \approx \frac{\varepsilon_b d}{t} \tag{1}$$

where d is the grain size; t is the thickness of the grain boundary layer; ε_b is the dielectric constant of the grain boundary layer. The effective dielectric constant of $SrTiO_3$-based GBBL capacitors of X7R type, whose capacitance change is less than ±15% over the temperature range of −55 to +125 °C, can be as high as 20,000 or more.

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As a matter of fact, not only high dielectric properties but also a high stability of the dielectric properties are expected for ceramic capacitors. The limiting factor for the lifetime of many ceramic capacitors is known as resistance degradation, which refers to a steady decrease in insulation resistance of the capacitors when some electric fields are applied over prolonged periods of time [3]. Up to date, a few different mechanisms have been recognized for the resistance degradation in ceramic capacitors, among which an important one is the reduction of hydrogen from the electrolysis of water [4]. As ceramic capacitors always operate under some voltages and water can be formed on the ceramic surface through condensation of H_2O vapor, the reduction of hydrogen may even lead to a sudden failure to ceramic capacitors in service [5]. Presently, an investigation has been conducted on hydrogen-induced degradation in $SrTiO_3$-based GBBL capacitors, which clearly shows that this degradation mechanism is especially important for $SrTiO_3$-based GBBL capacitors.

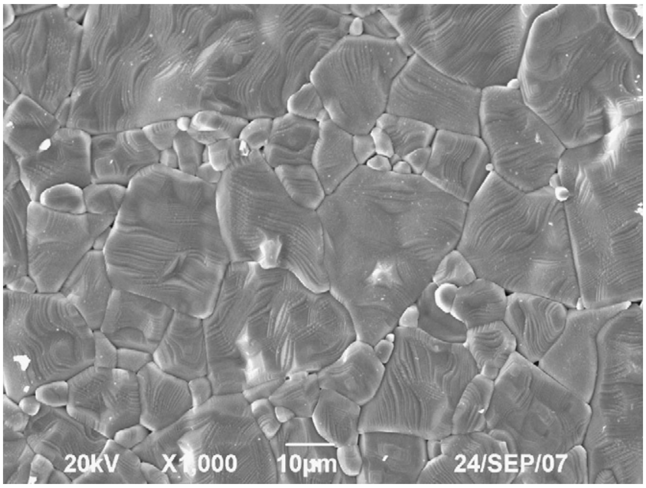

Fig. 1. SEM micrograph taken on the surface of a $SrTiO_3$-based grain boundary barrier layer ceramic capacitor.

2. Experimental

A group of $SrTiO_3$-based GBBL ceramic capacitors, manufactured by Guangzhou Sunrise Electronic Corporation (Ltd.), China, was used in the present study. The capacitors were 2.0 mm × 2.0 mm × 0.2 mm (i.e. 0.8 mm^3) with silver electrode coated on their two major surfaces. Two different treatments were applied to the capacitors for comparison. In the first treatment, some capacitors were immersed in a 0.01 M NaOH solution for some time and then taken out, washed with de-ionized water and dried. In the second treatment, some other capacitors were placed in a 0.01 M NaOH solution and DC voltages were applied between the silver electrodes of the capacitors and a Pt electrode in the solution. The silver electrodes of the capacitors acted as the cathode and hydrogen was evolved on them while oxygen was evolved on the Pt electrode when water was electrolyzed through the applied DC voltages. This treatment is referred to as ‘‘electrochemical hydrogen charging’’ hereafter. After some designated periods of electrochemical hydrogen charging, the capacitors were taken out, washed and dried. The frequency spectra of capacitance and dielectric loss of the capacitors were measured on an Agilent 4294 A impedance analyzer. The *I–V* characteristics of the capacitors were recorded using a Keithley 6517 electrometer/high resistance meter. Both the dielectric and *I–V* measurements were conducted between the two silver electrodes of the capacitors at room temperature (20 °C). A scanning electron microscope JEOL (JSM-6490) was used for microstructural analyses.

3. Results and discussion

Fig. 1 shows a representative SEM micrograph taken on an as-sintered ceramic surface. Though there were many relatively small grains, the major part of the ceramic body was occupied by large grains whose grain size was in the range of 20 μm. According to Eq. (1), these large grains were important for obtaining high effective dielectric constant. It is clear that the capacitors had very dense microstructures. For those samples from the first treatment, no noticeable changes were observed in the frequency spectra of capacitance and dielectric loss or in the *I–V* curves after the capacitors had been immersed in the 0.01 M NaOH solution for dozens of hours. It indicates that the GBBL capacitors were chemically stable against water. Water did not react with the ceramic bodies during the long time of immersion and so the properties of the capacitors exhibited no noticeable changes after the first treatment.

For the capacitors in the second treatment, on the contrary, great changes in properties were observed after electrochemical hydrogen charging. As an example, the results obtained for a capacitor before and after electrochemical hydrogen charging are shown in Figs. 2 and 3, respectively. A 3 V DC voltage had been applied between its silver electrodes and the Pt anode in the NaOH solution and the electrochemical hydrogen charging had lasted for 0.5 h. It can be seen that the as-sintered capacitor showed a very low dielectric loss when compared with that of

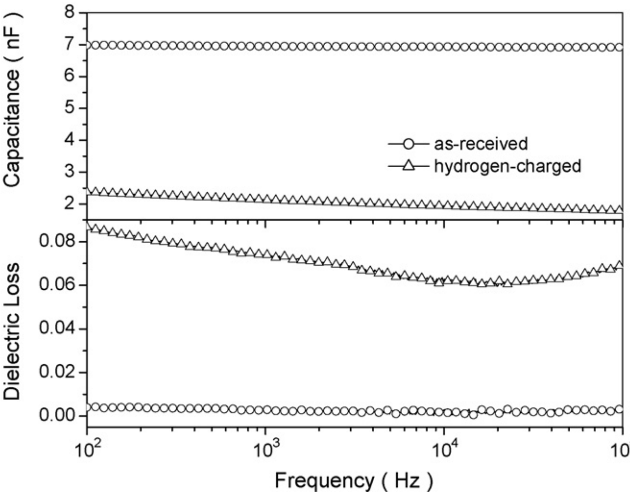

Fig. 2. Frequency spectra of capacitance and dielectric loss of a $SrTiO_3$-based grain boundary barrier layer ceramic capacitor measured as-sintered and after 0.5 h of electrochemical hydrogen charging, respectively.

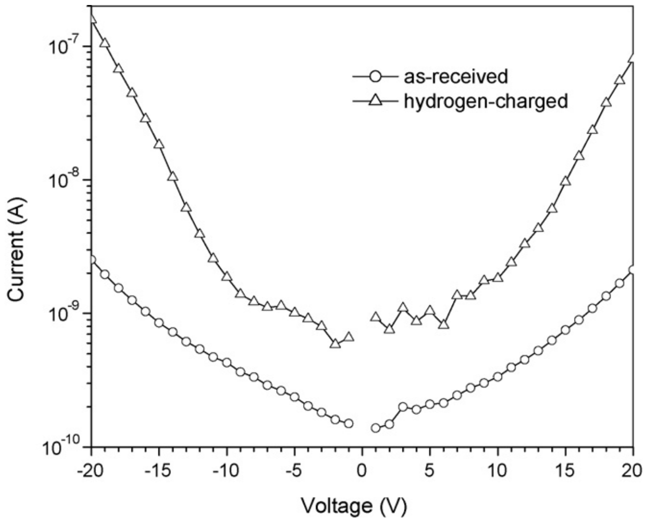

Fig. 3. *I–V* characteristics of a $SrTiO_3$-based grain boundary barrier layer ceramic capacitor measured as-sintered and after 0.5 h of electrochemical hydrogen charging, respectively.

$BaTiO_3$-based barrier layer ceramic capacitors [6] and the large capacitance showed little dispersion over the frequency range of 10^2–10^5 Hz. These dielectric properties together with the small temperature coefficient of capacitance made the capacitors attractive for many applications. Unfortunately, the short time of electrochemical hydrogen charging had seriously degraded the properties. The capacitance was almost decreased by a factor of three and the dielectric loss was increased by nearly two orders of magnitude. At the same time, the leakage current was increased by about two orders of magnitude. Such changes in properties were not acceptable for any practical applications. It should be pointed out that the *I–V* curve of the hydrogen-charged capacitor was quite nonlinear, similar to that of a varistor with a breakdown voltage of 10 V. In fact, $SrTiO_3$-based GBBL capacitors and varistors are very similar in microstructure, namely, semiconducting grains obtained through sintering in reducing atmospheres, an insulating phase in grain boundaries formed through the diffusion of low-melting point oxides during a heat-treatment in oxidizing atmospheres [7]. As the dielectric properties of GBBL capacitors are determined mostly by the grain boundary layer, this degradation should has resulted from changes in the grain boundary layer induced by electrochemical hydrogen charging.

For $SrTiO_3$, the defect chemistry equations of donor-doping and sintering in reducing atmospheres can be expressed by the following equations, respectively:

$$La_2O_3 \rightarrow 2La_{Sr}^{\bullet} + 2e' + 2O_O + \tfrac{1}{2}O_2, \qquad (2)$$

$$O_O \rightarrow V_O^{\bullet\bullet} + 2e' + \tfrac{1}{2}O_2, \qquad (3)$$

where La_2O_3 is an example for donor. Free electrons are generated in both equations so the grains are highly conductive in GBBL capacitors. In the subsequent heat-treatment, the oxidizing atmosphere induces a reaction reverse to Eq. (3) in the surface layer of the grains with some free electrons eliminated. Bi_2O_3 is also diffused into the surface layer of the grains during the heat-treatment. Bi_2O_3 is a donor to $SrTiO_3$ so the donor concentration is greatly increased in the surface layer of the grains. It is well known that there are two kinds of reaction for donor-doping, one is called electron compensation with free electron formed, as expressed by Eq. (2); the other is vacancy compensation with no free electron formed, as shown by the following equation [8]:

$$Bi_2O_3 \rightarrow 2Bi_{Sr}^{\bullet} + V_{Sr}'' + 3O_O \qquad (4)$$

Vacancy compensation occurs at relatively high concentration of donor-doping. So for donor-doping, the conductivity first increases with donor concentration due to electron compensation, reaches a maximum, then decreases quickly with increasing donor concentration due to vacancy compensation. As the donor concentration is greatly increased in the surface layer of the grains, vacancy compensation occurs and its conductivity is decreased. The co-reaction of the oxidizing atmosphere and Bi_2O_3 makes the surface layer of the grains highly insulating, which is important for the dielectric properties of GBBL capacitors. As we proposed in some previous papers, adsorbed hydrogen atom generated by electrochemical hydrogen charging is a strong reductant and it can induce a reduction reaction to $SrTiO_3$ in the following way [4,6]:

$$H_2O + e' \rightarrow OH^- + H_{ads}, \qquad (5)$$

$$H_{ads} \rightarrow H_i^{\bullet} + e', \qquad (6)$$

where H_{ads} represents an adsorbed hydrogen atom, $H_i^{\bullet}$ represents an ionized hydrogen, namely a proton, in an interstitial site. The degradation in the hydrogen-charged GBBL capacitor could be well explained by this reduction. The surface layer of the grains was reduced by hydrogen and free electrons formed according to Eq. (6), which greatly decreased the resistivity of the surface layer and led to the observed increases in dielectric loss and in the leakage current. At the same time, hydrogen may also react with the insulating phase at the grain boudnaries of GBBL capacitors and changed its properties. Previous investigations have shown that some metal oxides can be reduced to metals through elecrochemical hydrogen charging, while hydrogen will enter into the lattice of some other oxides and greatly changes their properties. As the incorporation of hydrogen usually leads to some increase in capacitance of oxides, especially at low frequencies, it is still difficult to understand why the capacitance was dramatically decreased in the hydrogen-charged GBBL capacitor. A similar result had also been observed for $BaTiO_3$-based barrier layer ceramic capacitors [6].

It should be pointed out that electrochemical hydrogen charging induced degradation in the $SrTiO_3$-based GBBL capacitors much more quickly and more seriously than it did to other ceramic capacitors, such as TiO_2-based ceramic capacitors [4]. This is maybe due to the fact that hydrogen could diffuse relatively easily along grain boundaries and the insulating surface layer of the grains of GBBL capacitors was very thin. It will be a great challenge to increase the stability against hydrogen for the further development of GBBL capacitors. On the other hand, some protection measures, such as polymer coatings, should be taken to minimize the amount of water from condensation of aqueous vapor.

4. Conclusions

The properties of $SrTiO_3$-based GBBL ceramic capacitors were quickly and seriously degraded when hydrogen was deposited on their electrode through the electrolysis of water. The capacitance was dramatically decreased and the dielectric loss was dramatically increased over the frequency range of 10^2–10^5 Hz, the leakage current was increased by orders of magnitude. It was proposed that atomic hydrogen diffused relatively easily along the grain boundaries of GBBL ceramic capacitors and induced a reduction reaction to the grain boundary layer, which resulted in the degradation observed. Hydrogen-induced degradation occurs more easily in $SrTiO_3$-based GBBL ceramic capacitors than in other ceramic capacitors and much attention should be paid to prevent hydrogen-induced degradation in $SrTiO_3$-based GBBL ceramic capacitors.

Acknowledgements

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References

[1] I. Burn, S. Neirman, Dielectric-properties of donor-doped polycrystalline $SrTiO_3$, J. Mater. Sci. 17 (1982) 3510–3524.

[2] J.B. Wu, C.W. Nan, Y.H. Lin, Y. Deng, Giant dielectric permittivity observed in Li and Ti doped NiO, Phys. Rev. Lett. 89 (2002) 217601.

[3] R. Waser, T. Baiatu, K.H. Hardtl, dc Electrical degradation of perovskite-type titanates. I. Ceramics, J. Am. Ceram. Soc. 73 (1990) 1645–1653.

[4] W.P. Chen, Y. Wang, J.Y. Dai, S.G. Lu, X.X. Wang, P.F. Lee, H.L.W. Chan, C.L. Choy, Spontaneous recovery of hydrogen-degraded TiO_2 ceramic capacitors, Appl. Phys. Lett. 84 (2004) 103–105.

[5] J.D. Baniecki, J.S. Cross, M. Tsukada, J. Watanabe, H_2O vapor-induced leakage degradation of $Pb(Zr,Ti)O_3$ thin-film capacitors with Pt and IrO_2 electrodes, Appl. Phys. Lett. 81 (2002) 3837–3839.

[6] W.C. You, W.P. Chen, W. Xiang, B.R. Li, H.M. Zhou, Water-induced degradation in $BaTiO_3$-based barrier layer capacitors J. Electroceram., in press.

[7] W.P. Chen, H.L.W. Chan, B.R. Li, Hydrogen-induced degradation in $SrTiO_3$-based ceramic varistors, J. Mater. Sci. 39 (2004) 5543–5545.

[8] J.Q. Qi, W.P. Chen, Y.J. Wu, L.T. Li, Improvement of the PTCR effect in $Ba_{1-x}Sr_xTiO_3$ semiconducting ceramics by doping of Bi_2O_3 vapor during sintering, J. Am. Ceram. Soc. 81 (1998) 437–438.