

## Hydrogen-induced degradation in SrTiO<sub>3</sub>-based ceramic varistors

W. P. CHEN, H. L. W. CHAN

*Department of Applied Physics and Materials Research Center, The Hong Kong Polytechnic University, Hong Kong, People's Republic of China*  
E-mail: apchenwp@polyu.edu.hk

B. R. LI

*Dongguan General Electronic Industry Company, Dongguan 523062, Guangdong Province, People's Republic of China*

Varistors, namely variable resistors, are applied in various electronic circuits and electric power systems to limit voltage surges by making use of their highly voltage-sensitive resistivity. Among the several types of practical varistors, ZnO-based ceramic varistors are usually the most widely used [1]. In recent years, however, more and more attention has been paid to other types of varistors, such as SrTiO<sub>3</sub>-based ceramic varistors. Compared to ZnO-based ceramic varistors, SrTiO<sub>3</sub>-based ceramic varistors are very popular for their relatively low switch voltages [2]. As a matter of fact, the operating voltages of many electronic circuits are quite low and the varistors in them should have low switching voltages. As they find more and more applications, the reliability of SrTiO<sub>3</sub>-based ceramic varistors becomes an important concern.

For ZnO-based ceramic varistors, it was found that the current leakage is largely increased by the reduction of hydrogen generated in nickel electroplating and electroless nickel plating [3]. Nickel acts as a barrier to protect the silver electrode of ZnO chip varistors from dissolution while soldering surface mounting. Hydrogen-induced degradation also occurs in in-service ZnO-based varistors when hydrogen is generated by the electrolysis of water condensed from environmental moisture [4]. In this study, we investigated hydrogen-induced degradation in SrTiO<sub>3</sub>-based ceramic varistors, which shows that the ambient-temperature reduction of hydrogen is also an important cause for the degradation of SrTiO<sub>3</sub>-based ceramic varistors.

Several SrTiO<sub>3</sub>-based ceramic varistors were used in the investigation. The ring-shaped varistors were 0.90 mm thick with an inner and outer radius of 3.4 and 5.3 mm, respectively. The two major surfaces of the rings were coated with silver electrode. Two different treatments were applied to the varistors for comparison. In the first treatment, some samples were immersed in a 0.01 M NaOH solution for some time then taken out, washed with de-ionized water, and dried. In the second treatment, some varistors were placed in a 0.01 M NaOH solution and DC voltages were applied between the silver electrodes of the varistors and a counter electrode in the solution. The silver electrodes of the varistors acted as the cathode and the counter electrode acted as the anode. Electrolysis of water occurred due

to the applied DC voltages and hydrogen was evolved on the silver electrodes of the varistors, so this treatment is hereafter referred to as "electrochemical hydrogen charging". The DC voltages were removed after some designated periods of time and the samples were taken out, washed and dried. The I–V characteristics of the varistors were measured using a Keithley 6517 electrometer/high-resistance meter. The frequency spectra of capacitance and dielectric loss of the varistors were measured using an Agilent 4294 A impedance analyzer. A scanning electron microscope STEROSCAN 440 was used for microstructural analyses.

A representative SEM micrograph taken from the surface of a varistor is shown in Fig. 1. It is clear that the varistor was of a very dense microstructure. No noticeable changes were observed in the properties of the varistors after being immersed in the 0.01 M NaOH solution for 100 hrs. This indicates that the varistors were very stable in water and that water did not influence the varistors through permeation, which is in agreement with the microstructural observation.

For the samples with the second treatment, on the other hand, great changes were observed in the I–V characteristics and in the frequency spectra of capacitance and dielectric loss, which are shown in Figs 2 and 3. For the hydrogen-charged varistor, a 4.5 V DC voltage had been applied between its silver electrode and the anode in the 0.01 M NaOH solution. The cathodic current density was around 0.4 mA/cm<sup>2</sup> and the hydrogen charging lasted for 30 min. It is well known that a high nonlinearity of I–V curve is of great importance for the application of varistors. In the hydrogen-charged varistor, however, the nonlinearity has been greatly decreased and the difference between the I–V curves measured by increasing and decreasing voltage is quite large. The dielectric loss has also been obviously increased, especially in the low frequency region. These results clearly show that electrochemical hydrogen charging causes serious degradation in SrTiO<sub>3</sub>-based ceramic varistors. The degradation of SrTiO<sub>3</sub>-based ceramic varistors is different from that of ZnO ceramic varistors. For ZnO ceramic varistors, electrochemical hydrogen charging greatly increases the current leakage below the switching voltage, while the nonlinearity of I–V curve and the switching voltage almost remain unchanged [4].

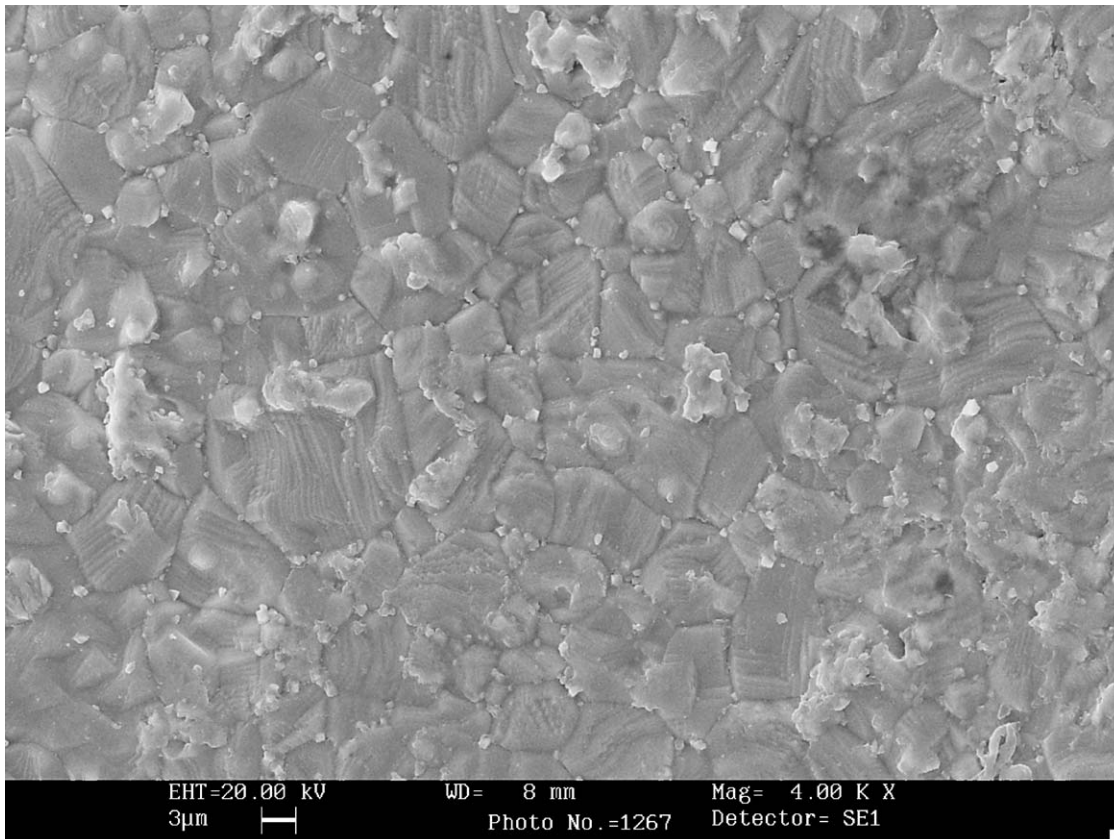


Figure 1 SEM micrograph taken from the surface of a SrTiO<sub>3</sub>-based ceramic varistor.

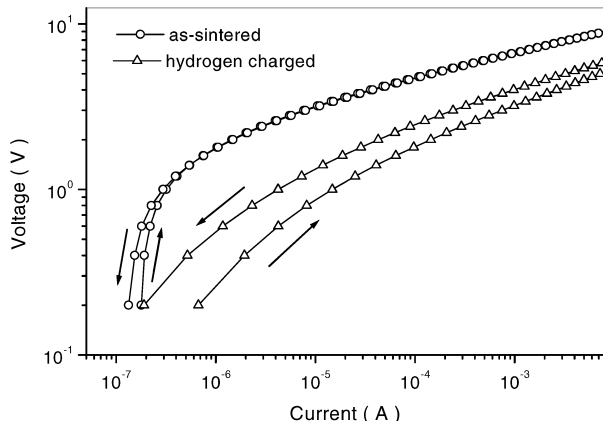


Figure 2 I-V characteristics of an as-sintered SrTiO<sub>3</sub>-based ceramic varistor and a hydrogen-charged SrTiO<sub>3</sub>-based ceramic varistor.

As we pointed out in our previous papers, hydrogen charging is actually a kind of ambient-temperature reduction treatment [4]. Some adsorbed hydrogen atoms generated by the electrolysis of water diffuse into the ceramics and react with them, though most of them combine with one another to form hydrogen molecules. The degradation of SrTiO<sub>3</sub>-based ceramic varistors also results from the reduction of hydrogen. During the fabrication of SrTiO<sub>3</sub>-based ceramic varistors, sintering is carried out in a reducing atmosphere to increase the conductivity of SrTiO<sub>3</sub>-based grains. It is well known that SrTiO<sub>3</sub> is semiconducting after heat-treatment in reducing atmospheres. Hydrogen charging should not have any adverse effects on the grains of SrTiO<sub>3</sub>-based ceramic varistors. However, some low-melting oxides,

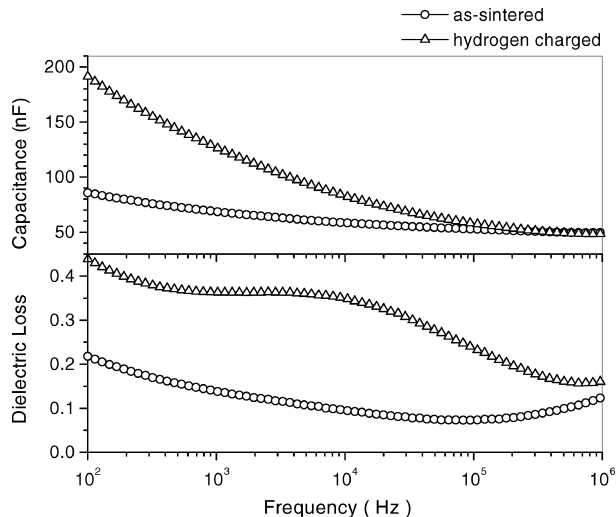


Figure 3 Frequency spectra of capacitance and dielectric loss of an as-sintered SrTiO<sub>3</sub>-based ceramic varistor and a hydrogen-charged SrTiO<sub>3</sub>-based ceramic varistor.

such as mixtures of PbO + Bi<sub>2</sub>O<sub>3</sub> + B<sub>2</sub>O<sub>3</sub>, are always doped in oxidizing atmospheres after sintering to form insulating potential barriers in the grain boundaries [5], which is important for the nonlinearity of I-V curves. Hydrogen must have some reduction reaction with the insulating potential barriers so that the nonlinearity of I-V curves is greatly decreased after the treatment. The presence of insulating potential barriers helps the varistors to have a relatively low dielectric loss, though the grains themselves are semiconducting. The obvious increase in the capacitance and in the dielectric loss of

the varistors after hydrogen charging must also be due to the reaction of hydrogen with the insulating potential barriers.

Varistors always operate under some voltages, indicating that electrolysis of water will occur when water is present, such as from condensation of environmental moisture, and hydrogen-induced degradation will occur. It is important for varistors to have a polymer coating. However, SrTiO<sub>3</sub>-based ceramic varistors are mainly used to protect electronic circuits, in which surface mounting technology (SMT) is becoming more and more important. SMT requires that components must be fabricated as chips and no polymer coating can be used, so more attention should be paid to hydrogen-induced degradation for SrTiO<sub>3</sub>-based chip varistors. On the other hand, electroless nickel plating is often used to form ohmic contact electrode for SrTiO<sub>3</sub>-based ceramic varistors [5]. Previous researches have shown that hydrogen generated in electroless nickel plating will also diffuse into ceramics and induce some reduction at room temperature [6]. This work indicates that hydrogen-induced degradation should also be taken into consideration when electroless nickel plating is applied to SrTiO<sub>3</sub>-based varistors.

In summary, hydrogen generated in electrolysis of water induces obvious degradation in SrTiO<sub>3</sub>-based ceramic varistors in that the nonlinearity of I–V curves is greatly decreased, and the dielectric loss and the capacitance are considerably increased. It is proposed that atomic hydrogen evolving from electrolysis of water diffuses into SrTiO<sub>3</sub>-based varistors

and has some ambient-temperature reduction influence on the insulating potential barriers in the grain boundaries. Extra attention should be paid to this hydrogen-induced degradation for SrTiO<sub>3</sub>-based chip varistors and when electroless nickel plating is applied to form ohmic contact electrodes for SrTiO<sub>3</sub>-based disc varistors.

### Acknowledgments

This work was supported by the Postdoctoral Research Fellowship Scheme and the Center for Smart Materials of the Hong Kong Polytechnic University. We thank Dr. Zhuang Yan of Guangzhou Sunrise Electronic Co. (Ltd.) for providing SrTiO<sub>3</sub>-based ceramic varistors.

### References

1. D. R. CLARKE, *J. Amer. Ceram. Soc.* **82** (1999) 485.
2. T. R. N. KUTTY and V. RAVI, *Appl. Phys. Lett.* **59** (1991) 2691.
3. W. P. CHEN, S. G. LU and H. L. W. CHAN, *Mater. Sci. Eng. B* **99** (2003) 70.
4. W. P. CHEN and H. L. W. CHAN, *J. Amer. Ceram. Soc.* **85** (2002) 1625.
5. T. R. N. KUTTY and S. PHILIP, *Mater. Sci. Eng. B* **33** (1995) 58.
6. W. P. CHEN, L. T. LI and Z. L. GUI, *J. Mater. Res.* **12** (1997) 877.

*Received 31 October 2003  
and accepted 21 April 2004*