ELSEVIER

Ceramics International 33 (2007) 1137–1140

CERAMICS
INTERNATIONAL

www.elsevier.com/locate/ceramint

Short communication

Degradation of $SrTiO_3$-based ceramic varistors induced by water and ac voltages

J.Q. Sun [a], W.P. Chen [a,b,*], W. Xiang [a], W.C. You [a],
Y. Zhuang [c], H.L.W. Chan [b]

[a] *Department of Physics and Key Laboratory of Acoustic and Photonic Materials and*
Devices of Ministry of Education, Wuhan University, Wuhan 430072, China
[b] *Department of Applied Physics and Materials Research Center,*
The Hong Kong Polytechnic University, Hong Kong, China
[c] *Guangzhou Sunrise Electronic Corporation (Ltd.), Guangzhou, Guangdong 510335, China*

Received 6 December 2005; received in revised form 15 January 2006; accepted 9 March 2006

Abstract

A comparison experiment was conducted in which some $SrTiO_3$-based ceramic varistors were simply immersed in a 0.01 M NaOH solution for some periods of time while other varistors were immersed in the solution with a 50 Hz ac voltage applied between the electrodes of the varistors and a counter electrode in the solution. Though the simple immersion showed no noticeable influence on the varistors, those varistors treated with the application of the ac voltage were greatly degraded in their properties. It was proposed that the degradation resulted from the collaborated reactions of atomic hydrogen and oxygen generated in the ac voltage-induced electrolysis of water with the insulating potential barriers of the varistors. It is important to prevent water-induced degradation in $SrTiO_3$-based ceramic varistors operating under ac voltages.

Keywords: E. Varistor; Degradation; Electrolysis of water; Strontium titanate

---

1. Introduction

ZnO-based ceramic varistors are widely applied to protect various electrical circuits, whose voltage can be as high as tens of kilovolts such as in electrical power distribution networks. On the other hand, however, ZnO varistors face some limitations for low-voltage applications in electronic circuits. The switching voltage of an individual grain boundary in ZnO ceramic varistors was found to be ~3.5 V [1], indicating that ZnO varistors can be only a few grains thick to be used in electronic circuits whose components and devices usually operate under voltages of 3–12 V. Such a small number of grains between the electrodes of ZnO ceramic varistors greatly decrease the nonlinearity of the *I–V* characteristics and lower the reliability of the varistors. So many efforts have been made to develop low-voltage varistors based on other materials, among which $SrTiO_3$-based ceramic varistors have been successfully commercialized [2]. With not only low switching voltage but also large capacity, $SrTiO_3$-based ceramic varistors possess a compound function of varistors and capacitors and have found excellent applications as electro-magnetic compatibility (EMC) components of spark elimination and noise absorption over wide frequency ranges. For various types of varistors, there exists a common problem known as degradation, namely their leakage current increases steadily with time when some dc or ac voltages are applied. So one of the major challenges for the continuing development of varistors has been to increase their reliability, and to understand degradation origins under all circumstances is the first step toward this goal. In a previous work, we found that water leads to serious degradation in $SrTiO_3$-based ceramic varistors in the presence of a dc voltage, and the reduction reaction of hydrogen generated by the dc voltage-induced electrolysis of water was proven to be responsible for it [3]. Water, or moisture, is a basic environmental factor that cannot be neglected. Up to date, little information is available regarding the influence of water on

---

[*] Corresponding author at: Department of Physics and Key Laboratory of Acoustic and Photonic Materials and Devices of Ministry of Education, Wuhan University, Wuhan 430072, China. Tel.: +86 27 6131 2396; fax: +86 27 6875 2697.

E-mail address: chenwp66@yahoo.com (W.P. Chen).

0272-8842/$32.00 © 2006 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2006.03.005

$SrTiO_3$ varistors when ac voltages are applied. It is well known that in most cases $SrTiO_3$ varistors operate under ac voltages, it is imperative to know how water influences $SrTiO_3$ varistors in the presence of ac voltages.

2. Experimental

A group of commercial $SrTiO_3$-based ceramic ring varistors (Model SRA-090, Guangzhou Sunrise Electronic Corporation (Ltd.), Guangzhou, China) was used in the experiment. The varistors were rings 1.0 mm thick with an inner and outer radius of 3.4 and 5.3 mm, respectively. Three separate identical silver electrodes were coated on one major surface of the rings and the varistors were designed for use in dc micro-motors for spark elimination and noise absorption. However, for the convenience of measurement, a modification was made to the varistors used in this investigation. The two major surfaces of the rings were fully coated with silver as electrodes. Two different treatments were applied to the varistors for comparison. In the first treatment, some samples were just immersed in a 0.01 M NaOH solution for some time and then taken out, washed and dried; while in the second treatment, some varistors were immersed in a 0.01 M NaOH solution and a 50 Hz ac voltage was applied between the silver electrodes of the varistors and a counter Pt electrode in the solution. The amplitude of the ac voltage was adjusted through a transformer in the circuit. The solution was maintained at 20 °C and was stirred using a magnetic agitator throughout the treatment. A detailed description about the experimental set-up has been given in a previous paper [4]. The ac voltage was removed after designated periods of time and the varistors were taken out, washed and dried. The frequency spectra of capacitance and dielectric loss of the varistors were measured on an Agilent 4294 A impedance analyzer. A Keithley 6517 electrometer/high-resistance meter was used to record the *I–V* characteristics of the varistors. Microstructural analyses were conducted on a scanning electron microscope STEROSCAN 440.

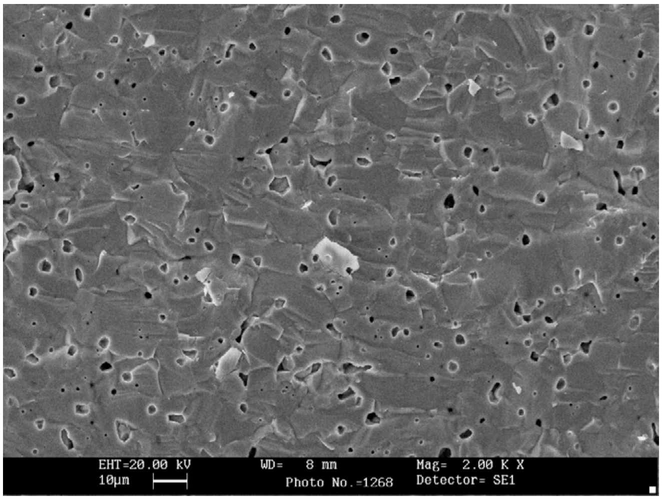

Fig. 1. SEM micrograph taken for a fractured surface of an as-received $SrTiO_3$-based ceramic varistor.

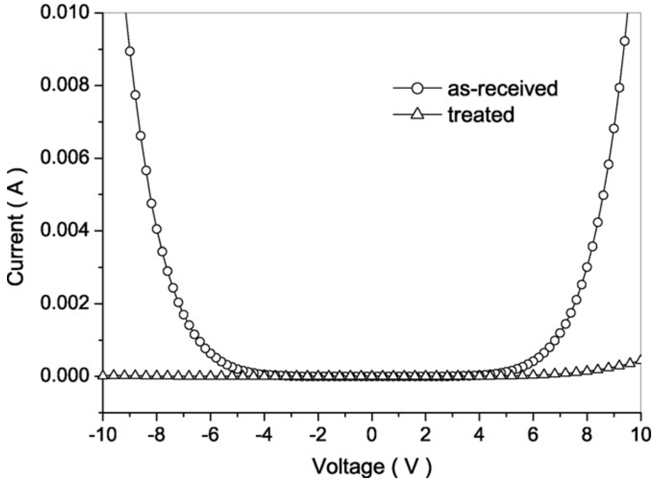

Fig. 2. *I–V* characteristics of an as-received $SrTiO_3$-based ceramic varistor and a $SrTiO_3$-based ceramic varistor treated by 50 Hz ac voltage-induced electrolysis of water for 60 min.

3. Results and discussions

For the samples from the first treatment, no noticeable changes were observed in the *I–V* curves or in the frequency spectra of capacitance and dielectric loss even after the varistors had been immersed in the 0.01 M NaOH solution for 24 h. A typical SEM micrograph taken for a fractured surface of an as-received $SrTiO_3$-based ceramic varistor is shown in Fig. 1. It is evident that only some very small and isolated holes can be observed in the micrograph. Such a dense microstructure must have prevented the solution from permeating into the varistors in the first treatment so their properties were not affected.

For those samples from the second treatment, on the contrary, great changes were observed in the *I–V* characteristics and in the frequency spectra of capacitance and dielectric loss. Figs. 2 and 3 show some representative results obtained for an as-received varistor and a varistor from the second treatment, respectively. The latter one had been treated in the second

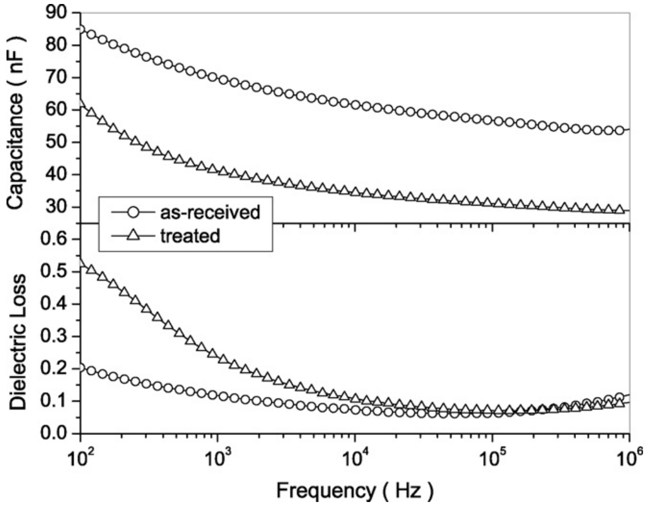

Fig. 3. Frequency spectra of capacitance and dielectric loss of the two samples in Fig. 2.

treatment for 60 min through applying a 50 Hz ac voltage between its silver electrodes and the counter electrode in the 0.01 M NaOH solution. V_{p-p} of the ac voltage was 45 V and I_{rms} in the circuit was around 12 mA. It can be seen that the as-received varistor exhibited a highly nonlinear *I–V* curve with a switching voltage around 6 V. This high nonlinearity in *I–V* curve was of great importance for the application of the varistors. While for the treated varistor, this nonlinearity almost disappeared completely and the current remained very small over the whole measuring range from −10 to +10 V. With such a totally different *I–V* characteristic, the treated varistor obviously could not fulfill any functions that had been initially designed for it. The influence of the second treatment on the varistors was also clearly reflected in the frequency spectra. Compared with the as-received varistor, the treated varistor approximately showed a one-third decrease in capacitance over the frequency range from 10^2 to 10^6 Hz, and a 1.5 times increase in dielectric loss at 10^2 Hz. As the immersion in the first treatment showed no noticeable effect on the varistors, the influence of the second treatment must have resulted from the electrochemical reactions induced by the applied ac voltage.

It is well known that $SrTiO_3$-based ceramic varistors are composed of semiconducting $SrTiO_3$ grains and some low-melting oxides (such as mixtures of $PbO + Bi_2O_3 + B_2O_3$) as insulating potential barriers in the grain boundaries. The semiconducting $SrTiO_3$ grains are formed through sintering in reducing atmospheres while the low-melting oxides are always doped in oxidizing atmospheres after sintering [5]. Oxidizing atmospheres are important for the formation of the potential barriers. However, it was found that the potential barriers in $SrTiO_3$ varistors can be easily weakened through the reduction of hydrogen generated by a dc voltage-induced electrolysis of water, resulting in a great increase in the leakage current and an obvious decrease in the nonlinearity of the *I–V* curve [3]. It was suggested that some adsorbed hydrogen atoms must have reacted with $SrTiO_3$ varistors though most of them combined one another to form hydrogen molecules to evolve at the cathode during the electrolysis of water. Of course an ac voltage-induced electrolysis of water is different from a dc voltage-induced electrolysis of water. Both hydrogen and oxygen were deposited simultaneously on the silver electrodes of the varistors in the second treatment of this experiment. As we have pointed out in some previous works, in ac voltages-induced electrolysis of water, some adsorbed hydrogen atoms and oxygen atoms will react with other materials they meet though most of them form hydrogen molecules and oxygen molecules to evolve at the electrodes. Previous investigations have shown that for oxide materials, the oxidation of atomic oxygen usually does not compensate for the reduction of atomic hydrogen. As a matter of fact, adsorbed hydrogen atoms and oxygen atoms usually collaborate to result in an obvious decrease in capacitance and a considerable increase in dielectric loss [6], which were also observed for the $SrTiO_3$ varistors in this study. So the changes in the properties of the $SrTiO_3$ varistors must have resulted from the collaborated reactions of hydrogen and oxygen. As the grains are semiconducting in all types of varistors, their dielectric properties are mainly decided by the insulating potential barriers in the grain boundaries. So the changes in the capacitance and in the dielectric loss of the varistors from the second treatment implied that the insulating potential barriers had been affected seriously, which should be responsible for the disappearance of the nonlinearity in the *I–V* curves of the treated varistors. For TiO_2-based ceramic capacitors, hydrogen generated by dc voltages-induced electrolysis of water increases their leakage currents by many orders of magnitude, while the collaborated reactions of hydrogen and oxygen from ac voltages-induced electrolysis of water actually lead to no increase in the leakage current at all [4]. Obviously this difference was also observed for the $SrTiO_3$-based ceramic varistors. In fact, for the varistors from the second treatment in this experiment, the leakage current above the switching voltage has been greatly decreased, contrasting sharply with that of $SrTiO_3$-based ceramic varistors reduced by hydrogen from dc voltages-induced electrolysis of water [3].

For most commercial ZnO ceramic varistors of disk shape, a polymer coating is usually adopted to prevent any presence of water on their surface. However, the $SrTiO_3$-based ceramic varistors in this investigation were designed for applications in dc micro-motors and they could not be protected through any polymer coating. Much attention should be made to ensure them to work in a dry environment. If some water is present on them accidentally, it is important to turn off the power source first to prevent the occurrence of the electrolysis of water. Of course, it is best to improve the stability of the varistors against the influence from electrolysis of water induced by dc or ac voltages and this is an important task for the further development of various types of varistors.

4. Conclusions

For $SrTiO_3$-based ceramic varistors of a very dense microstructure, water caused serious damages to their properties through ac voltages-induced electrolysis of water. The nonlinearity of the *I–V* curve was greatly decreased, the capacitance was obviously decreased and the dielectric loss in low frequencies was considerably increased. It is proposed that the insulating potential barriers of the varistors were seriously affected by the collaborated reactions of atomic hydrogen and oxygen generated in ac voltages-induced electrolysis of water and the properties of the varistors were thus greatly changed. Much attention should be paid to prevent water-induced degradation to $SrTiO_3$-based ceramic varistors operating under ac voltages.

Acknowledgement

This work has been supported by the Centre for Smart Materials of the Hong Kong Polytechnic University (Project: 1-A302).

References

[1] D.R. Clarke, Varistor ceramics, J. Am. Ceram. Soc. 82 (1999) 485–502.

[2] T.R. Kutty, V. Ravi, Varistor property of *n*-$BaTiO_3$ based current limiters, Appl. Phys. Lett. 59 (1991) 2691–2693.

[3] 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.

[4] W.P. Chen, Y. Wang, X.X. Wang, J. Wang, H.L.W. Chan, Water-induced dc and ac degradations in TiO_2-based ceramic capacitors, Mater. Chem. Phys. 82 (2003) 520–524.

[5] T.R.N. Kutty, S. Philip, Low-voltage varistors based on $SrTiO_3$ ceramics, Mater. Sci. Eng. B 33 (1995) 58–66.

[6] W.P. Chen, H.L.W. Chan, Degradation of ZnO ceramic varistors induced by water and AC voltages, Jpn. J. Appl. Phys. 43 (2004) 701–702.