

Water-induced degradation in BaTiO₃-based barrier layer capacitors

Wen Chao You · Wan Ping Chen · Wang Xiang ·
Biao Rong Li · Hong Ming Zhou

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Abstract Water-induced degradation in BaTiO₃-based surface barrier layer capacitors (BLCs) were studied through two comparison treatments: in one treatment some BLCs were simply immersed in a 0.01-M NaOH for some time, while in the other treatment, some BLCs were placed in a 0.01-M NaOH solution with their silver electrodes acting as the cathode to electrolyze water. No degradation occurred in the samples that were immersed in the NaOH solution, but for the samples treated by the electrolysis of water, their leakage current was increased by orders of magnitude, their capacitance dramatically decreased, and the dielectric loss dramatically increased at low frequencies. It is proposed that atomic hydrogen generated in the electrolysis of water entered into the barrier layer of the BLCs, increased the concentration of charge carriers by reducing some Ti⁴⁺ to Ti³⁺ in the barrier layer. Much attention should be paid to prevent water-induced degradation in BLCs.

Keywords Barrier layer capacitor · Barium titanate · Degradation · Hydrogen

1 Introduction

Because of their high dielectric constant and high stability, perovskite-type titanates, mainly (Ba,Sr)TiO₃ and its variants, have been the predominant dielectric materials in most commercial ceramic capacitors of large capacitance. To meet the demand of the rapid miniaturization of various electronic circuits, many (Ba,Sr)TiO₃-based ceramic capacitors have adopted a multilayer structure and their volume efficiency has thus been greatly improved. On the other hand, (Ba,Sr)TiO₃ ceramic capacitors of disc shape can also obtain an extremely high capacitance per unit area and effective dielectric constants in the range of 100,000 have been achieved [1]. These are the barrier layer capacitors (BLCs) in which (Ba,Sr)TiO₃ ceramic is semiconducting through sintering in reducing atmospheres. Either a thin layer at the surface is re-oxidized to insulating state by heating in air (surface BLCs) or an insulating layer is formed in the grain boundaries through the diffusion of some metal oxides painted on the surface of the ceramic disc (second-phase BLCs) [2]. The barrier layer is much thinner than the ceramic disc in surface BLCs, or than the grains in second-phase BLCs and very high effective dielectric constants, which are in inverse proportion to the thickness of the barrier, can be obtained. (Ba,Sr)TiO₃-based BLCs have many important applications, especially in various filter circuits, bypass circuits, and coupling circuits.

For many ceramic capacitors, there exists a problem known as resistance degradation, namely, the insulation resistance is steadily decreased when some electric fields are applied over some prolonged periods of time [3]. Resistance degradation is the limiting factor for the lifetime of many ceramic capacitors and extensive investigations have been conducted on it [4]. For BaTiO₃ and SrTiO₃, one origin for the resistance degradation is the reduction

W. C. You · W. P. Chen (✉) · W. Xiang
Department of Physics and Key Laboratory of Acoustic and Photonic Materials and Devices of Ministry of Education, Wuhan University, Wuhan 430072, China
e-mail: wpchen@whu.edu.cn

B. R. Li
Dongguan General Electronic Industry Company,
Dongguan, Guangdong 523062, China

H. M. Zhou
Huazhong Institute of Electro-Optics,
Wuhan 430074, China

reaction of hydrogen generated by the electrolysis of water [5,6]. Hydrogen enters into the lattice of the titanates and a free electron is formed through its ionization. Fortunately, this degradation process is quite slow for them. In this paper, this degradation process has been studied for BLCs and it is found much more serious for BLCs.

2 Experimental

A group of BaTiO₃-based surface BLCs, Model DSC154 M30Y5V, supplied by Guangdong South Hongming Electronic Science and Technology Corporation (Ltd.), China, was used in the present study. The BLCs were 7.0 mm in diameter and 0.25 mm thick, with 6.5-mm diameter silver electrodes coated on the two major surfaces. Two different treatments were applied to the BLCs for comparison. In the first treatment, some samples were immersed in a 0.01-M NaOH solution for some periods of time and then taken out, washed with de-ionized water, and dried. In the second treatment, some BLCs were placed in a 0.01-M NaOH solution and DC voltages were applied between the silver electrodes of the BLCs and a counter Pt electrode in the solution. A detailed description on the experimental setup had been given in a previous paper [7]. The applied DC voltages induced electrolysis of water, with the silver electrodes of the BLCs acting as the cathode and the counter electrode acting as the anode. Hydrogen was evolved on the silver electrodes of the BLCs, and this treatment is hereafter referred to as “electrochemical hydrogen charging”. It highlights the coexistence of water and electricity and has been successfully applied in studying water-induced degradation for many electroceramic components and devices. The DC voltages were removed after some designated periods of time and the samples were taken out, washed, and dried. The frequency spectra of capacitance and dielectric loss of the BLCs were measured on an Agilent 4294 A impedance analyzer. The I–V characteristics of the BLCs were recorded using a Keithley 6517 electrometer/high-resistance meter. A scanning electron microscope STEROSCAN 440 was used for microstructural analyses.

3 Results and discussions

Figure 1 shows a typical SEM micrograph taken for a fractured surface of an as-received BLC. It is evident that almost no pores were present and the BLCs used in this experiment were of a highly dense microstructure. It was difficult for water to permeate into such a dense microstructure. Accordingly, the immersion in the first treatment

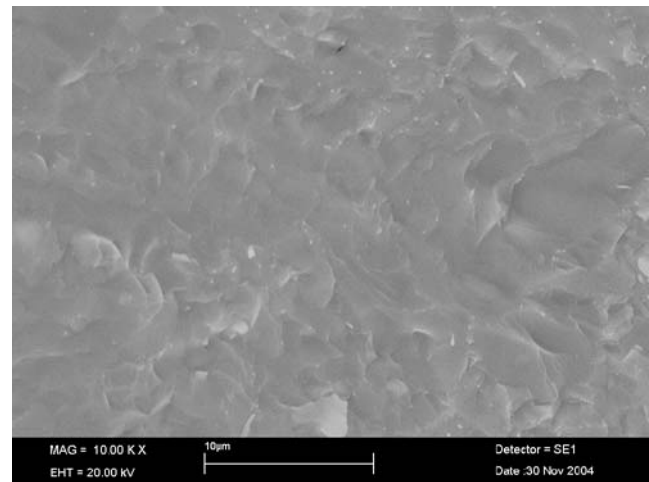


Fig. 1 SEM micrograph taken for a fractured surface of an as-received BaTiO₃-based surface barrier layer capacitor

showed no noticeable influences on the BLCs. Although some BLCs had been immersed in the solution for a prolonged period of 40 h, no discernible changes were observed in the I–V curves or in the frequency spectra of capacitance and dielectric loss that were measured after the samples were cleaned and dried.

Electrochemical hydrogen charging in the second treatment, on the contrary, greatly degraded the properties of the BLCs. Some representative measuring results obtained for an as-received BLC and an electrochemical hydrogen-charging-treated BLC are shown in Figs 2 and 3, respectively. The as-received BLC had a capacitance above 100 nF from 100 Hz to 100 kHz, which was a very big capacitance for its dimension. So the BLCs had a very high effective dielectric constant. The as-received BLC also had a very low leakage current. Of course the measuring voltage was quite low. Surface BLCs have a non-ohmic conduction mechanism. Their resistivity falls dramatically above a certain voltage and their work potential is usually restricted to a few volts [8]. As for the electrochemical hydrogen-charging-treated BLC, a DC voltage of 4.5 V had been applied between its silver electrodes and the Pt electrode in the solution. The cathodic current density was around 0.2 mA/cm² and the hydrogen charging had lasted for 1 h. It can be seen that the electrochemical hydrogen charging had increased the leakage current by about two orders of magnitude, decreased the capacitance by a factor of 4. The dielectric loss was increased by a factor of 7 at 100 Hz, while it was only slightly increased at 100 kHz. In short, the electrochemical hydrogen charging had seriously degraded the BLC and made it failed for its original function. As the solution could not influence the BLCs through permeation, the degradation was obviously related to the electrochemical reactions in the second treatment.

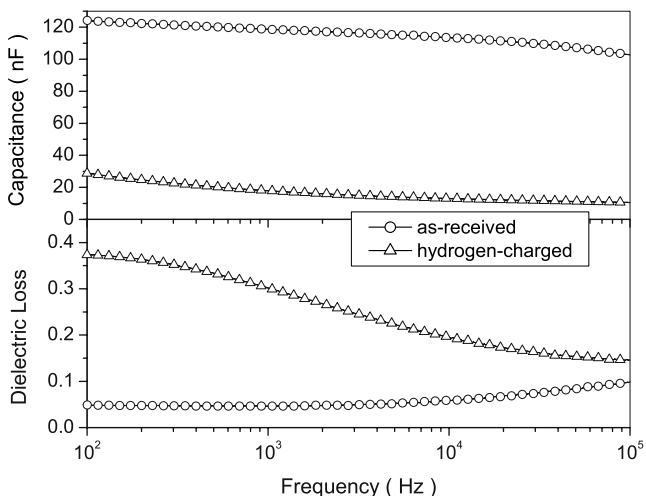
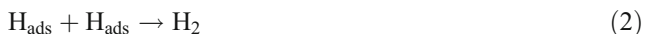


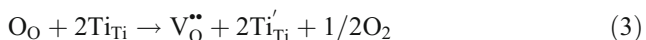
Fig. 2 Frequency spectra of capacitance and dielectric loss of an as-received BaTiO₃-based surface barrier layer capacitor and a BaTiO₃-based surface barrier layer capacitor treated by electrochemical hydrogen charging for 1 h

The evolution of hydrogen on the silver electrodes of the BLCs in the second treatment can be written as:



where H_{ads} represents an adsorbed hydrogen atom. Hydrogen atoms are highly reactive. Although most of them combine with one another and form hydrogen molecules, some of them also react with other matters they encounter in their path. Our previous studies have revealed many room temperature reductions of atomic hydrogen with various oxide materials, which result in serious degradation to the properties of the oxides [5–7]. The reduction of atomic hydrogen must also be responsible for the degradation of the BLCs in this investigation.

BLCs are usually sintered in reducing atmospheres to make the grains semiconducting, which can be expressed as:



where 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 the conductivity of the

grains. For surface BLCs, a subsequent heat-treatment in an oxidizing atmosphere leads to the formation of an insulating barrier layer at the surface, which is reverse to the reaction of Eq. (3). The concentration of Ti_{Ti}' is reduced and the conductivity is decreased accordingly. As we have proposed in our previous works, atomic hydrogen from the electrolysis of water can enter into the lattice of perovskite-type titanates and reduce some tetravalent titanium cations to trivalent titanium cations [5,6]:



In this study, some hydrogen atoms must have diffused into the barrier layer of the BLCs and increased the concentration of Ti_{Ti}' in the barrier layer, so the leakage current was greatly increased and the dielectric loss was obviously increased for the BLCs after electrochemical hydrogen charging. At present, however, we cannot understand why the capacitance of the BLCs was dramatically decreased after the treatment. Such a dramatic decrease in capacitance was not observed in hydrogen-charging-treated BaTiO₃ or SrTiO₃ bulk materials [5,6].

It should be pointed out that, compared with BaTiO₃ and SrTiO₃ bulk materials, BLCs are influenced quite quickly by electrochemical hydrogen charging. It takes a much longer period of time to obtain the same increase (by two orders of magnitude) in leakage current for BaTiO₃ and SrTiO₃ bulk materials through electrochemical hydrogen charging. This must be due to the fact that the barrier layer is just below the electrodes of BLCs and the barrier layer is very thin. Capacitors always operate under some voltages and hydrogen will be deposited on the electrodes when

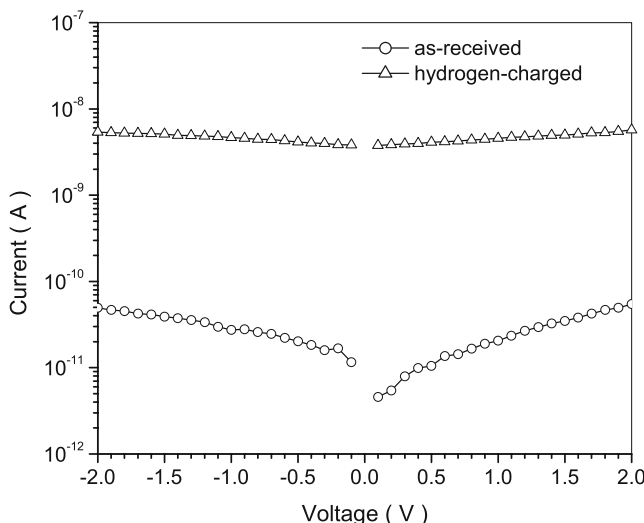


Fig. 3 I–V characteristics of the two samples of Fig. 2

water is present. Much attention should be paid to prevent water-induced degradation in BLCs. Polymer coatings are helpful to prevent the condensation of aqueous vapor on the electrodes of BLCs so they are of great importance to ensure BLCs to operate reliably.

4 Conclusions

For BaTiO₃-based BLCs of a very dense microstructure, their properties were seriously degraded when the electrolysis of water occurred on their silver electrodes: the leakage current was increased by orders of magnitude, their dielectric loss was dramatically increased at low frequencies, and their capacitance was dramatically decreased. It is proposed that atomic hydrogen generated in the electrolysis of water was diffused into the barrier layer of the BLCs and reduced some tetravalent titanium cations to trivalent titanium cations. The concentration of charge carriers was thus increased in the barrier layer, which affected negatively on the properties of the BLCs. This degradation process

is quite quick for BLCs and many efforts should be made to prevent water-induced degradation for BLCs.

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