Electroplating-induced degradation in ZnO ceramic varistors

W. P. CHEN*
Department of Physics, Wuhan University, Wuhan, Hubei 430072, P. R. China
E-mail: chenwp66@yahoo.com

H. L. W. CHAN
Department of Applied Physics and Materials Research Center, The Hong Kong Polytechnic University, Hong Kong, P. R. China

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In recent years, more and more electronic products are being fabricated through a new assembly method called surface mounting technology (SMT), in which various components and devices are mounted directly onto tracks on a substrate. Compared with the traditional assembly method, in which components and devices are mounted by soldering their leads through holes in the circuit boards, SMT provides considerable improvements in reliability, volume efficiency and process automation. Components and devices have also experienced much evolution in configuration to meet up with the rapid development of SMT. For various components, the biggest change must have been in the termination electrode. The termination electrode for most ceramic components used in the traditional assembly is silver, which can be easily formed through firing of silver paste. However, silver termination electrode is not suitable for chip components used in SMT as silver will be dissolved in solder during mounting. Now a three-layer termination electrode, namely Ag/Ni/Sn–Pb, is widely adopted for many kinds of chip components, in which nickel acts as a barrier layer to prevent Ag from dissolution and Sn–Pb improves solderability of the electrode. Ag layer is still formed through firing of silver paste, while Ni and Sn–Pb layers are usually formed through electroplating. Electroplating is an ideal technology for mass production.

As electroplating is applied to more and more ceramic components, it is found that electroplating sometimes induces serious degradations to the properties of some components. In fact, electroplating has become a bottleneck for these components to be used as chip components in SMT. A well-known example for these components is ZnO-based ceramic varistors. With highly nonlinear I–V characteristics, ZnO varistors are widely used to prevent voltage surges in electrical power systems and electronic circuits. For those varistors used in electronic circuits protection, there is an increasing demand for them to be fabricated as chip varistors, i.e., Ag/Ni/Sn–Pb termination electrode should be used. However, the leakage current of the varistors is increased by orders of magnitude after electroplating if no special protection is adopted. In practice, layers of a different ceramic material are pre-coated and co-fired with ZnO varistors to prevent the influence of electroplating [1]. At present, a fundamental understanding about the influence of electroplating on ZnO ceramic varistors is still lacking. When they studied electroplating-induced degradation in $Pb(Mg_{1/3}Nb_{2/3})O_3$-based multilayer ceramic capacitors (MLCCs) and (Ba, Pb) TiO_3-based thermistors, Chen and co-workers found that the ambient-temperature reduction of hydrogen generated in electroplating plays a vital role in the degradation process [2, 3]. In $Pb(Mg_{1/3}Nb_{2/3})O_3$-based ceramic, Nb^{5+} and Pb^{2+} are partially reduced to Nb^{4+} and metallic Pb at ambient temperature by atomic hydrogen, which results in a dramatic decrease in insulation resistance [4]. Now we have conducted an investigation to study the influence of electroplating on ZnO varistors in depth, which shows the reduction of hydrogen is also the main factor causing the electroplating-induced degradation in ZnO ceramic varistors.

A group of commercial ZnO-based ceramic varistors (Model TNRG330K, Nippon Chemi-Con Corporation, Japan) was used in the experiment. They were pellets of 7.25 mm in diameter and 0.9-mm thick. The varistors were coated with 6.0-mm diameter silver electrode on both surfaces and the switch voltage was 33 V. After being cleaned with acetone and de-ionized water, the varistors were put in the barrel of a barrel-electroplating machine to electroplate with nickel on the silver electrode in a nickel sulfamate-based solution. Many steel balls were placed in the barrel as conduction media. The composition of the electroplating solution and some processing parameters are listed in Table I. After electroplating, the varistors were taken out, washed with de-ionized water and dried. The I–V characteristics of the varistors were recorded using a Keithley 237 DC source/measure unit. The frequency spectra of capacitance and dielectric loss were measured on an Agilent 4294 A impedance analyzer. A scanning electron microscope STEROSCAN 440 equipped with an EDX detector was used for microstructural and compositional analyses.

The EDX analysis results show that the varistors had a composition of ZnO + 0.8 mol% Bi_2O_3 + 1.3 mol%

* Author to whom all correspondence should be addressed.

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TABLE I Nickel electroplating process parameters

Nickel sulfamate (g/l)	60
$NiCl_2$ (g/l)	15
Boric acid (g/l)	40
pH	4.5
Temperature (°C)	55
Cathodic current density (A/m^2)	100

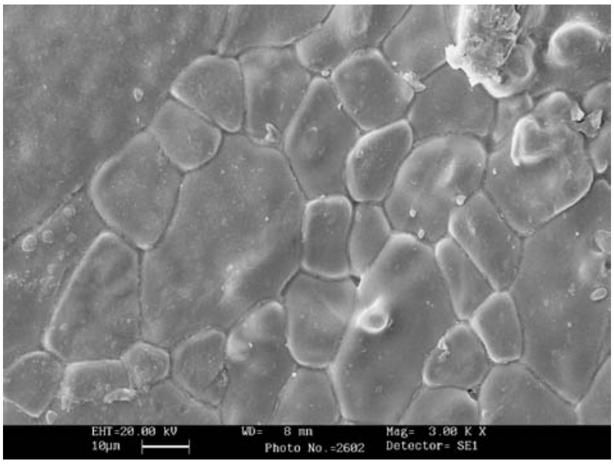

Figure 1 SEM micrograph taken for a fractured surface of a ZnO ceramic varistor.

CoO + 0.6 mol% MnO_2. Bi_2O_3, CoO and MnO_2 are commonly doped in ZnO-based varistors to increase the nonlinearity and stability of I–V characteristics and the varistors used in this investigation were representative of ZnO-based ceramic varistors. An SEM micrograph of the surface of a varistor is shown in Fig. 1. It is clear that the varistors had a very dense microstructure, which should prevent permeation of plating solution in the varistors. For reference, some varistors had been immersed in the plating solution at 55 °C but no DC voltages were applied for electroplating. The immersion had no noticeable influences on the I–V characteristics of the varistors, as shown by that of a representative varistor, Sample B in Fig. 2. Sample B had been immersed in the plating solution for 60 min. It can be seen that its I–V curve was very close to that of an as-received varistor, Sample A. The I–V curve remained unchanged for those samples immersed in the plating solution for even longer periods of time. It indicates that the varistors were very stable against the plating solution and the solution did not influence the varistors through permeation, which is in agreement with the microstructural observation.

For those varistors treated by electroplating, it was found that nickel was deposited not only on the silver electrode but also on the blank ceramic surface of the varistors. In our previous work, we found that ZnO ceramics is reduced to metallic zinc in the surface at ambient temperature by hydrogen generated from electrolysis of water and the following reaction mechanism has been proposed [5]:

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

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

$$2H_{ads} + ZnO \rightarrow Zn + H_2O, \quad (3)$$

where H_{ads} represents adsorbed hydrogen atom. It has been supposed that some hydrogen atoms react with ZnO though most of them combine with one another to form hydrogen molecules to evolve. Atomic hydrogen is highly reactive and this explains why ZnO is reduced to Zn at ambient temperatures. With hydrogen molecules ZnO can only be reduced at some elevated temperatures [6]. It is well known that hydrogen is also deposited in the course of electroplating. We believe that the same reduction also occurred to the ceramic surface of ZnO varistors during electroplating. Metallic zinc was formed in the surface first and Ni was then deposited on zinc. Nickel deposited on the side surface of the varistors connected electrically the opposite silver electrodes of the varistors and had been removed before further analyses were conducted. The I–V measurement results obtained for two representative samples, Samples C and D are also shown in Fig. 2. They had been electroplated with nickel for 20 and 40 min,

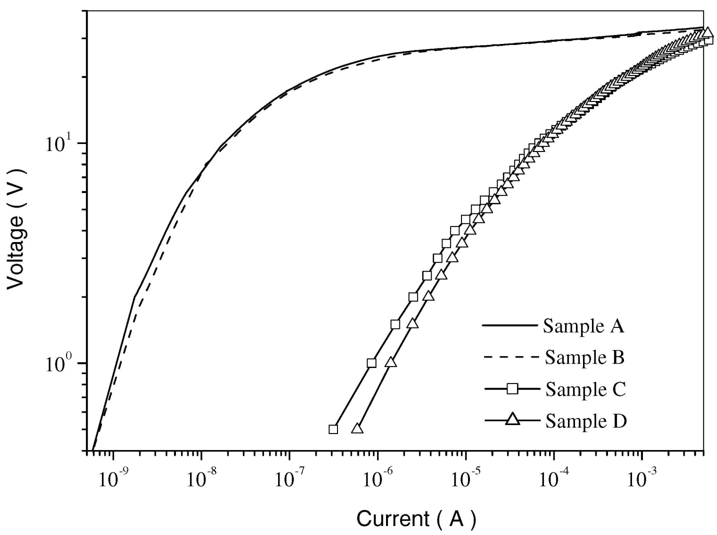

Figure 2 I–V characteristics of ZnO varistors with different treatments. Sample A: as-received; Sample B: immersed in 55 °C nickel plating solution for 60 min; Samples C and D: electroplated with nickel for 20 and 40 min, respectively.

respectively. It is clear that their leakage current was increased by orders of magnitude and their nonlinearity was greatly decreased. So electroplating had resulted in serious degradation in the varistors. As the plating solution did not influence the varistors through permeation, this degradation was obviously related to the electrochemical reactions in electroplating. It is well known that the properties of ZnO-based ceramic varistors depend greatly on redox. Oxidizing atmospheres are necessary for the sintering of ZnO-based ceramic varistors. Some researchers proposed that the nonlinearity of I–V characteristics of ZnO varistors is strongly related to the amount of oxygen in the grain boundaries [7]. Serious degradation will occur when ZnO varistors are heated in reducing atmospheres [8]. A previous research has shown that hydrogen generated by electrolysis of water can reduce ZnO varistors at ambient temperatures and greatly increase the leakage current [9]. It is reasonable to assume that the electroplating-induced degradation in the I–V curve of the varistors has also resulted from the reduction of hydrogen. Hydrogen generated in electroplating not only reduced the surface of ZnO varistors and made nickel deposit on the blank ceramic surface of the varistors, but also diffused into the interior of the varistors and greatly influenced the I–V characteristics. The influence must have been very quick in the early stage and then gradually slowed down with increasing time of electroplating. So there was not a large difference between the I–V characteristics of Samples C and D whereas the difference in time of electroplating was twice between them.

The influence of electroplating was also reflected in the frequency spectra of capacitance and dielectric loss of the varistors, as shown in Fig. 3. As the blank ceramic surface around the silver electrode of the ZnO varistors had been metallized in electroplating, the electrode area was increased and the capacitance of Samples C and D was obviously larger than that of Sample A. ZnO ceramic varistors are generally considered to contain conducting ZnO grains and potential barriers localized at the grain boundaries that are responsible for varistor action. The commonly used additives, such as Bi_2O_3, CoO and MnO_2, are mostly concentrated at the grain boundaries to form the potential barriers. The intergranular insulating potential barriers make the varistors show a relatively low dielectric loss in the low frequency region, which can be seen from the dielectric loss-frequency curve of Sample A in Fig. 3. Electroplating, however, lead to a dramatic increase in the dielectric loss in the low frequency region. So Samples C and D had relatively high dielectric losses in the low frequency region, indicating that the insulating potential barriers in the grain boundaries were weakened after electroplating. The degradation in I–V characteristics of Samples C and D was obviously related to this change in the potential barriers, which must have resulted from the reduction of hydrogen. As it should be relatively easy for hydrogen to diffuse along grain boundaries, it explains why the interior of ZnO ceramic varistors was also so seriously influenced after electroplating.

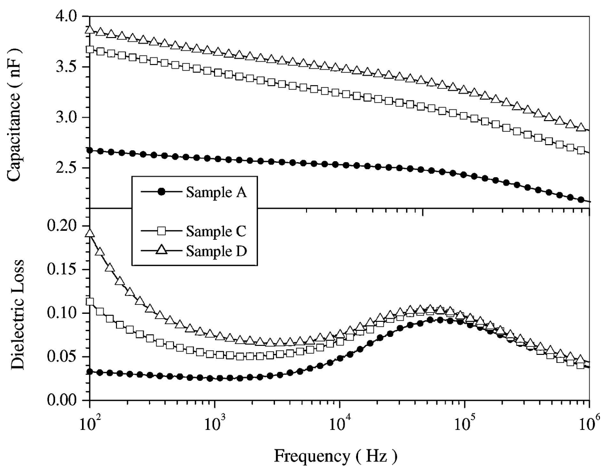

Figure 3 Frequency spectra of capacitance and dielectric loss of ZnO varistors with different treatments. Sample A: as-received; Samples C and D: electroplated with nickel for 20 and 40 min, respectively.

For metals and alloys, electroplating-induced degradation, namely hydrogen-embrittleness, is well known and extensive researches have been conducted to minimize this degradation [10]. For electroceramic components, our present investigation shows that electroplating can also result in serious degradation through the reaction of hydrogen. The influence of hydrogen is sometimes twofold. On the one hand, hydrogen causes undesired metallization on the blank ceramic surface of the components, which sometimes can only be overcome through coating a different ceramic material on the surface of the components [1]. On the other hand, the reduction of hydrogen degrades the electrical properties of the components. In many cases, reduction is harmful for the properties of oxides-based ceramic components. Efforts should be made to prevent the reduction of hydrogen in electroplating.

In summary, for ZnO ceramic varistors with dense microstructure, though the influence from permeation of plating solution can be avoided, electroplating exerts a twofold influence on the varistors: undesired metallization on the blank ceramic surface and degradation in electrical properties of the varistors. The influence can be well explained by the reduction reaction of atomic hydrogen generated in electroplating. Atomic hydrogen reduces ZnO to Zn in the surface of the varistors and nickel is deposited on Zn subsequently. Hydrogen also diffuses into the interior of the varistors and weakens the potential barrier at the grain boundaries of the varistors, which causes great increases in the leakage current and the dielectric loss of the varistors.

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