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Reliability enhancement of zinc oxide varistors using sputtered silver electrodes

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ABSTRACT

Zinc oxide (ZnO) varistors, which are produced by sintering ZnO powder together with small additives of Bi_2O_3, Co_3O_4, Sb_2O_3 and other oxides, are popular ceramic semiconductor devices and widely used in electric circuits and systems as voltage-clamping or surge-arrester owing to their extremely nonlinear current–voltage characteristics. The reliability of ZnO varistors is the most important consideration, and researches are mainly focus on the material properties of ZnO body and the effects of additives, such as ZnO grain size and the surrounding additive-rich insulating barriers. However, the manufacturing of electrodes still remains the traditional silver baking process, and few people investigate the effects of electrodes on the reliability of devices. In this paper, we propose a novel electrodes manufacture process using magnetron sputtering technology, and investigate the reliability of devices comparing to silver baking process. Two groups of samples with diameters of 20 mm were prepared by silver baking and magnetron sputtering process respectively. The nonlinear voltage, nonlinear coefficient, and leakage current parameters were measured by the metal oxide varistor meter typed TTK-168; the energy absorption capacities were measured by a lightning current surge generator with 8/20 μs impulse waves; the adhesive strength of electrodes was measured by a dynamometer; the microstructures of the samples were examined using Scanning Electron Microscope, and the change ratio of nonlinear voltages at an environment of 125 °C after 100 h was chosen as the main reliability parameter. Results show that the sputtered electrodes could improve the reliability of samples by reducing the change ratio from 1.32% to 0.61%, with other parameters exceeding the silver baking samples at the same time. This enhancement is benefit from the good interface between sputtered electrodes and ZnO substrate as well as the low temperature during magnetron sputtering process.

1. Introduction

Zinc oxide (ZnO) varistor, due to its excellent nonlinear characteristics, has been widely used in electric circuits and systems as transient voltage suppression and voltage regulators [1]. It is no exaggeration to say that the performance of varistor determines the reliability of system, therefore, the research on reliability of varistor is significant. A varistor is made from a sintered ceramic material consisting mainly of ZnO powder – together with small additives of Bi_2O_3, Co_3O_4, Sb_2O_3 and other oxides – and formed into cylinders during a sintering process. Then, electrodes are coated on both the end surfaces for electrical contact. Researches are mainly focus on the material properties of ZnO body and sintering process to improve the reliability, such as effects of additives [2], sintering temperature [3], and sintering time [4]. But little attention has been paid to the effects of electrodes on the reliability of varistor.

Traditionally, electrodes of varistor are manufactured by electroless nickel-plating [5], copper electrodeposition, silver baking [6], and aluminum thermal spraying [7]. Nickel has high electric resistance, which will degrade the electrical performance of varistor; both electroless and electrodeposition process are not environmental friendly, and will generate poisonous contaminants; thermal spraying has a risk of explosion accident and needs thick electrodes (~90 μm); silver baking is the mostly used process, but needs baking near 800 °C using silver paste, which always includes lead and is harmful to the operator and environment. Recently, Ake Oberg et al. [7] from ABB AB Corporate Research have adopted magnetron sputtering method to deposition aluminum as electrodes, providing an environment friendly process, and obtained better electrical and mechanical performance owing to the better quality of electrode film. But as we all know, aluminum is easy to be oxidized and has poor welding performance. As Ake Oberg reported, the optimized thickness of aluminum layer needs 25–30 μm.

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In this paper, we propose a three-layer (NiCr/Cu/Ag) sputtered electrodes, instead of a thick single aluminum layer, and investigate the reliability enhancement comparing with those using the traditional silver baking method.

2. Experiment

ZnO ceramics without electrodes were provided by Wanfeng Electronics Co., Ltd. (Kunshan, China). These samples, which the model is 20D681K, have diameter of 19.3–19.7 mm and thickness of 2.50–2.90 mm. Two groups of samples were prepared by silver baking and magnetron sputtering process respectively, and the diameters of deposited electrodes are all 15.5 mm. The silver baking method is the traditional 800 °C process, and the magnetron sputtering process is described as following.

The ZnO ceramics were first washed in deionized water by ultrasonic cleaning about 20 min, then heated in oven-baking at 120 °C for 30 min. Subsequently, the multilayer thin films were deposited on both the end surfaces of substrates by the multi-target magnetron sputtering system, provided by Suzhou Advanced Vacuum Electronic Equipment Co., Ltd. (SAVEE), using metal shadow mask. The magnetron is a rotatable cylindrical structure with target dimension of 1180 × φ72 × φ54 mm, and target materials are NiCr (Ni, 80 wt.%), Cu (99.99 wt.%), and Ag (99.99 wt.%), respectively. The base pressure of sputtering chamber was 3×10^{-3} Pa and the sputtering pressure was 0.5 Pa. Argon (99.999%) was used as the sputtering gas. Detail deposition parameters are shown in Table 1. In this NiCr/Cu/Ag process, NiCr was first deposited as the bottom layer, and then Cu and Ag were deposited sequentially. NiCr provides good adhesion to the ceramic interface; Cu has good conductance and the ability of withstanding high temperature soldering dissolution as well as matches the upper and under layer; Ag is used as protection and welding layer, preventing corrosion and guaranteeing good solder ability. To investigate the effects of NiCr layer, we also carried out an experiment of two-layer electrodes, namely Cu/Ag.

In the experiments, both the mechanical and electrical performances of varistors were investigated. The adhesive strength of electrodes was measured by a dynamometer. The breakdown voltage, nonlinear coefficient, and leakage current parameters were measured by a metal oxide varistor meter typed TTK-168. The energy absorption capacities were measured by a lightning current surge generator (the peak magnitudes of electric current are 3 kA) with 8/20 μs impulse waves. The microstructures of the samples were examined using Scanning Electron Microscope (SEM). For testing the stability and aging characteristic, the varistors were placed in a high temperature environment of 125 °C, and operated at the maximum allowable AC voltage continuously for 100 h. We then measured the nonlinear voltages of before and after the test, and calculate the change ratio as the main reliability parameter of devices.

3. Results and discussions

3.1. Mechanical performance

Adhesive strength is the main mechanical properties of varistor. As mentioned above, dynamometer was used to measure the adhesive strength. Before measurement, a tin drop was soldered with an electrode surface with radius of 1 mm, and a copper wire was then soldered to this drop. Force was applied to the copper wire and measured by a dynamometer. As shown in Fig. 1, the adhesive strength of samples with silver baked electrodes, sputtered NiCr/Cu/Ag electrodes, and sputtered Cu/Ag electrodes is presented respectively. The three-layer electrodes exhibit evidently better adhesion (13.9 MPa) to the substrates than the two-layer electrodes (6.0 Mpa) and the silver baked electrodes (9.7 MPa).

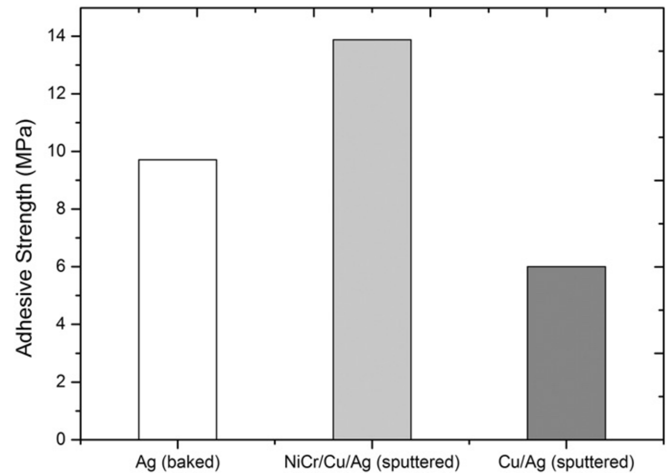

Fig. 1. Comparison of adhesive strength of devices with different electrodes.

According to the magnetron sputtering theory, the firstly sputtered high-energy metal atoms will react with the oxygen at interface and form a chemical bond with the oxide substrate, leading to a good adhesive strength [8]. In our experiments, due to the chemical reaction occurred between the Cr and the ZnO ceramic surface, interface chemical bond enhances the adhesion of Cr in ZnO ceramics surface. According to the reduction ability of metal Cr > Ni > Cu, Cr more easily captures the oxygen in the interface and undergoes chemical reaction, forms chemical bond, so the film adhesion is relatively larger. We use NiCr instead of pure Cr as the first glue layer, because NiCr film has lower residual stresses than Cr film [8] and NiCr is much suitable for manufacture of large rotatable cylindrical targets.

As shown in Table 2, Cr_2O_3 generated at the interface has a similar thermal expansion coefficient with ZnO ceramic, which also is in favor of improving the adhesive strength. For silver baked electrodes, the internal diffusion of Ag and binder leads to the enhancement of the adhesion force with the ZnO ceramics.

3.2. Electrical performance

The nonlinear voltage, nonlinear coefficient, and leakage current parameters are three static electrical parameters of varistor, whereas 8/20 μs impulse wave test is used to represent the dynamic properties of varistor. The ZnO varistor is mainly characterized by nonlinear voltage, which marks the transition from linear to nonlinear mode, and the change of nonlinear voltage before and after 125 °C 100 hour test is always chosen as the main reliability parameter. Nonlinear coefficient is the reciprocal of slope of the current voltage curve, and the greater the value, the better the device. Leakage current is the unwanted small current when varistor acts as an open circuit for normal voltage, and the smaller the value, the better the device. The 8/20 μs test, a pulse current waveform with width of 20 μs and rise time of 8 μs, is

Table 1
List of deposition parameters by magnetron sputtering.

Target material	Sputtering voltage (V)	Sputtering current (A)	Film thickness (nm)
NiCr	450	25	100
Cu	450	25	1700
Ag	450	25	600

Table 2
Thermal expansion coefficients of different materials.

	ZnO	Ag	Cu	Cr_2O_3	Cu_2O
Thermal expansion coefficient (10^{-6}/°C)	6.51	19.5	16.5	6.5	3.5