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Grain growth behaviour of ZnO-based multilayer varistors

Shu-Ting Kuo, Wei-Hsing Tuan *

Department of Materials Science and Engineering, National Taiwan University, Taipei 106, Taiwan

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Abstract

In the present study, a model multilayer structure composing of seven Bi_2O_3-doped ZnO layers and AgPd inner electrodes is prepared. The Bi_2O_3-doped ZnO bulk specimens are also prepared for comparison purpose. The size of ZnO grains in the multilayer specimens is smaller than that in the bulk specimen. Furthermore, the size of ZnO grains in the multilayer specimens decreases with the decrease of layer thickness. Microstructure analysis demonstrates that the Bi_2O_3-rich liquid phase wets not only the ZnO grains but also the AgPd electrodes.

Keywords: ZnO; Varistor; Microstructure-final; Firing; Multilayer

1. Introduction

Due to the unique nonlinear *I–V* characteristics of ZnO–Bi_2O_3-based ceramics, they are applied as varistors to protect electronic devices against voltage surges.[1–4] Many 3C appliances nowadays are operated with rechargeable batteries. The voltage provided by the batteries is low. The multilayer varistors (MLV) are therefore developed for such low voltage applications. For multilayer components, the choice of inner electrode is important to their cost and performance. Previous study indicated that precious metal Pt is chemically inert to ZnO–Bi_2O_3-based ceramic.[5] Metallic Pt can therefore be used as the inner electrode for MLV. Since the layer thickness is small in MLV, the growth of ZnO grains is constrained by the limited space available between the Pt inner electrodes.[5]

The cost of Pt is very high. The 70%Ag–30%Pd alloy is now considered as the material for inner electrode. The basic requirement on inner electrode is its ability to co-fire with ZnO-based ceramics in air at elevated temperatures. For low voltage applications, the layer thickness between inner electrodes has to be small. The grain growth behaviour within a small space is not the same as that in the bulk specimen.[5,6] For example, the grain growth behaviour in multilayer specimen[5] and in thin film[6] is different from that in a bulk specimen. Furthermore, previous studies indicated that Bi_2O_3 could react with Pd at elevated temperatures.[7,8] Such reaction may affect the grain growth behaviour within the inner electrodes. However, the grain growth behaviour within AgPd inner electrodes has not been investigated before. In the present study, the grain growth behaviour of Bi_2O_3-doped ZnO grains within AgPd inner electrodes is thus investigated.

2. Experimental

A high-purity ZnO and 5 wt% Bi_2O_3 were mixed with solvents and binders first. The tape with a thickness of 20 μm was then prepared by tape casting. The AgPd (70%Ag–30%Pd) paste was deposited onto the green tape by screen printing. Laminating different numbers of green tapes made a multilayer structure with various thicknesses from 20 to 140 μm. To facilitate the comparison, the layers with different thickness were all built into one component. The schematics of the electrode configuration are shown in Fig. 1. The laminates were then cut into a size of 1.85 mm (length) × 0.95 mm (width) × 0.75 mm (thickness). All specimens were firstly fired from room temperature to 400 °C in air for 1 h using a heating rate of 1 °C/min to remove the organics. After the binder burnout stage, the sintering was performed in air at 900–1100 °C for various times. Several bulk specimens with the same composition were also prepared for comparison purpose. The thickness of the bulk specimens was around 3 mm. In order to prevent the evaporation of Bi_2O_3 during sintering, the specimens were sintered in a powder bed which composition was the same as that of the specimens.[9]

In order to carry out the microstructure analysis, the specimens were ground with SiC abrasive papers and polished with 0.05 μm Al_2O_3 particles. The specimens were etched with

* Corresponding author. Tel.: +886 2 33663899.
E-mail address: tuan@ntu.edu.tw (W.-H. Tuan).

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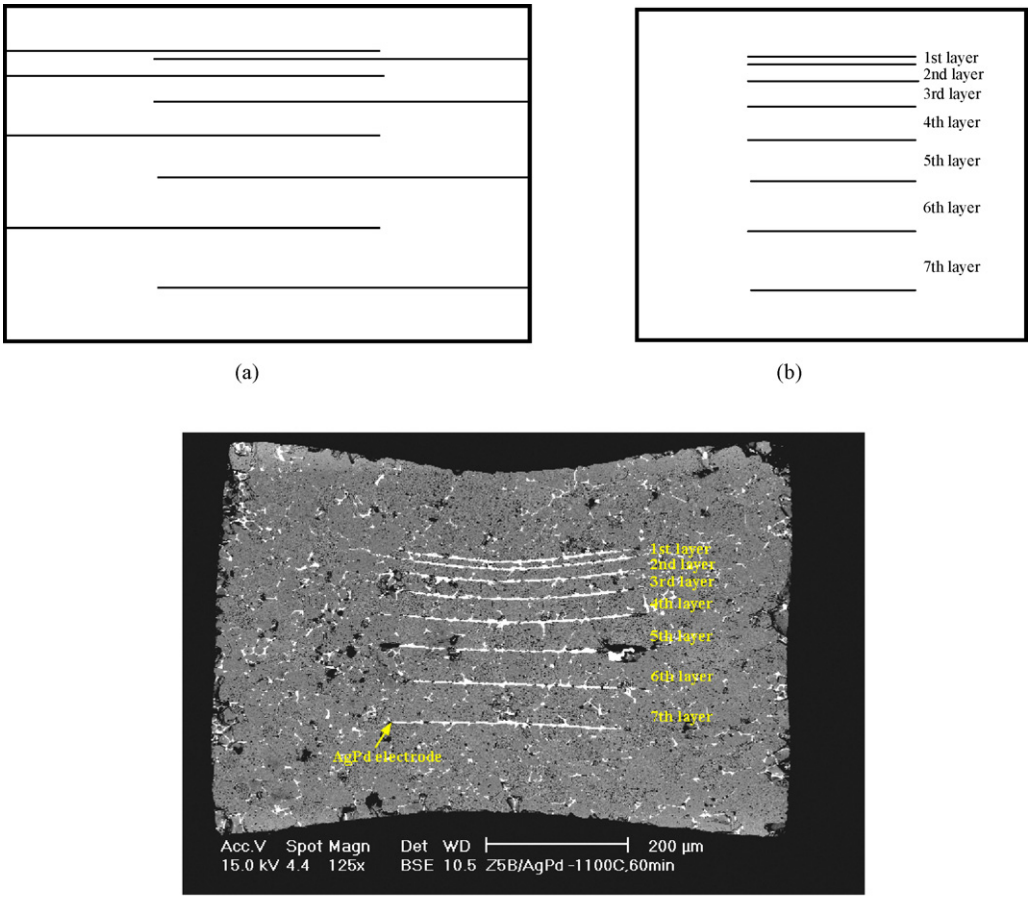

Fig. 1. (a) Side view and (b) cross-section for the electrode configuration of an MLV. (c) Cross-section of a typical ZnO–Bi_2O_3/AgPd MLV specimen after sintering at 1100 °C for 60 min.

dilute hydrochloric acid. The microstructures were observed by using scanning electron microscopy (SEM, XL-30, Philips Co., Netherlands). The size of ZnO grains was determined by applying an image analysis technique.[5] By assuming that each grain is spherical in shape, the size of ZnO grains was estimated. The composition analyses were carried out by using electron probe micro-analyzer (EPMA, Model JAX-8200, JOEL, Japan). Phase analysis of the sintered specimens was characterized with a synchrotron X-ray source (Beam-line 17B1, National Synchrotron Radiation Research Center, Hsinchu, Taiwan). Before the phase analysis, several multilayer specimens were mounted together into resin then ground to expose the cross-sections. The synchrotron X-ray beam was then spotted at the cross-sections of the specimens to carry out the phase analysis.

3. Results

Fig. 1(c) shows the cross-section of one typical MLV specimen after sintering at 1100 °C for 60 min. There are seven ceramic layers in the MLV specimen. The layer thickness varies from 8 to 55 μm after sintering. The volume shrinkage at the middle of the MLV specimen is larger than that at the two ends. Fig. 2 shows the XRD pattern of the MLV specimens after

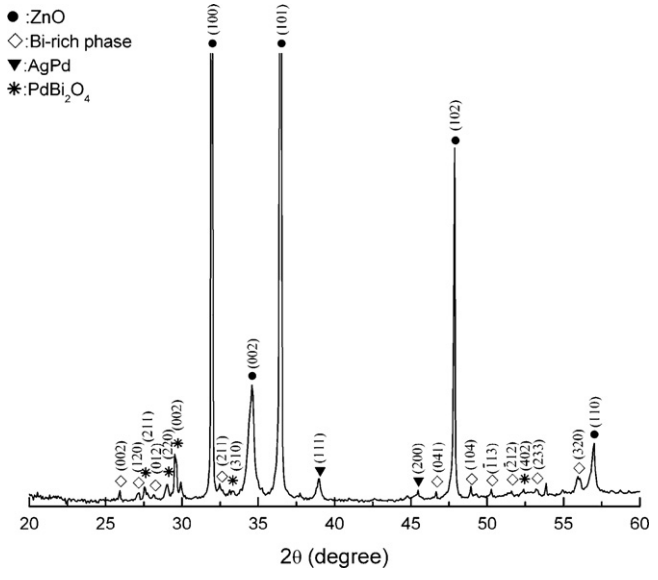

Fig. 2. XRD pattern of the ZnO–Bi_2O_3/AgPd MLV specimen after sintering at 1100 °C for 60 min.