Microstructure and electrical properties of La$_2$O$_3$-doped ZnO-based varistor thin films by sol-gel process

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Abstract: Microstructure and electrical properties of La$_2$O$_3$-doped ZnO-Bi$_2$O$_3$ thin films prepared by sol–gel process have been investigated. X-ray diffraction shows that most diffraction peaks of ZnO are equal, and the crystals of ZnO grow well. Scanning electron microscopy and atomic force microscopy results indicate that the samples have a good structure and lower surface roughness. The nonlinear $V$–$I$ characteristics of the films show that La$_2$O$_3$ develops the electrical properties largely and the best doped content is 0.3% lanthanum ion, with the leakage current of 0.25 mA, the threshold field of 150 V/mm and the nonlinear coefficient of 4.0 in detail.

Key words: zinc oxide; varistor; film; sol-gel process; electrical properties; microstructure

1 Introduction

ZnO thin films are doped or fabricated into a multilayered structure with Bi$_2$O$_3$ and other metal oxides [1–2], such as CoO, MnO, Sb$_2$O$_3$ and Cr$_2$O$_3$. They exhibit highly nonlinear voltage–current ($V$–$I$) characteristics and are widely used as surge absorbers in electronic circuits, devices and electrical power systems to protect against dangerous over-voltage surges.

The nonlinearity of ZnO thin films is considered to be the grain boundary phenomenon where a barrier to majority charge carriers (electrons) exists in the depletion layers of the adjacent grains, and the electrical properties are affected strongly by the secondary phases [3]. To increase the threshold voltage, it is necessary to decrease the average size of the ZnO grains. It is clear that the addition of the rare-earth element decreases the diameter of ZnO grains and increases the varistor voltage [4–7]. The traditional rare-earth oxide in ZnO-Bi$_2$O$_3$-based varistor ceramics have been used to improve the electrical characteristics of ZnO varistors, but the nonlinearity of ZnO varistor becomes bad [8]. There are some better results that other researchers got from ZnO thin films. MISTA et al [9] prepared Zn-Bi-O thin films by reactive RF magnetron sputtering at room temperature, with the nonlinear coefficient $\alpha$ from 5 to 15 for different layer thicknesses. JIANG et al [10] prepared ZnO-Bi$_2$O$_3$ thin films by sol-gel method, and these ZnO-based ceramic films have the electrical properties of nonlinear voltage lower than 5 V and nonlinear coefficient of 20 at 750 °C. HUANG et al [11–12] prepared ZnO-based ceramic by novel sol-gel process, the nonlinear voltage was 2–10 V, the nonlinear coefficient ($\alpha$) was 3–22. The highest nonlinearity coefficient with nonlinear voltage of 4 V could be achieved at 750 °C by the films with a thickness of 2 μm. Actually, the electrical properties of La$_2$O$_3$-doped ZnO thin films have never been reported. Therefore, we conducted the experiments to investigate the microstructure and electrical properties of La$_2$O$_3$-doped ZnO thin films this time.
In this work, we use the sol-gel process to produce ZnO-Bi₂O₃ thin films, because sol-gel process is very easy to realize the doping in the period of preparation of the films. There are several additives of metal oxides doping in the starting materials which is inexpensive. The microstructure and the crystal phases of the films were studied using X-ray diffraction (XRD), scanning electron microscopy (SEM) and atomic force microscopy (AFM) analysis and the properties of the ZnO based films for using as varistors were discussed on the basis of the measurements of V–I characteristics.

2 Experimental procedures

ZnO-based thin films were deposited on silicon substrates by novel sol-gel process using the following procedures. The sols were prepared by zinc acetate dehydrate (Zn(CH₃COO)₂·2H₂O) (99.9%, Analytical reagent), dopants such as Bi(NO₃)₃·2H₂O, Mn(CH₃COO)₂·2H₂O, La(NO₃)₃ and the solvents ethylalcohol [13]. According to the different doping amounts of lanthanum ion (0, 0.1%, 0.2%, 0.3 %), we labeled samples as QD0, QD1, QD2, QD3, respectively. Zn(CH₃COO)₃·2H₂O and the dopants were firstly dissolved in ethylalcohol by the addition of diethanolamine and glacial acetic acid, making the concentration of Zn(CH₃COO)₂ be 0.5 mol/L. The dopants solution was added to the zinc acetate solution in such a way that the final composition of ZnO, Bi₂O₃, MnO was in the relative molar ratio of 99:0.5:0.5. The different amounts of La(NO₃)₃ were added to make the resultant solutions which were stirred at room temperature for more than 2 h to yield a clear, stable and homogeneous sol.

At the same time, the silicon substrates are cleaned by the ultrasonic wave washing machine for several times. After the sol has been aged for 24 h, the ZnO-based thin films were prepared on the silicon substrates by repeated dip-coating at room temperature, with the substrate dipping time of 1 min. After each deposition, the films were heated in air at 400 °C for 10 min. After 15 layers had been deposited, the films were then subjected to annealing in air at 750 °C for 1 h. And then they were allowed to cool inside the furnace.

The V–I characteristics of ZnO-based ceramic films were investigated with a V–I source/measure unit (CJP CJ1001). The nominal varistor voltages (Vₘ) at 0.1 and 1.0 mA were measured, and the threshold voltage Vₜ (Vₜ=Vₘ/d, where d is the thickness of the sample). The nonlinear coefficient α (α=1/log(Vₜ/V₁mA/Vₘ/1mA)) was determined. The leakage current (Iₗ) was measured at 0.75 Vₘ (1 mA) [14–20]. XRD of the ZnO-based thin films was measured by X-ray diffractometer (Rigaku D/max 2550 X-ray) with Cu Kα radiation [21–23]. The surfaces of the films were observed via AFM (Solver P47). The microstructures of the films were observed by SEM (HITACHIs-4800).

3 Results and discussion

Figure 1 shows X-ray diffraction patterns of ZnO films doped lanthanum ion with 0, 0.1%, 0.2 % and 0.3%, respectively. It can be seen that most diffraction peaks are equal. The growth characteristics of crystal phase and para-crystal phase are not influenced with the additional La₂O₃. And the diffraction peaks of La₂O₃ were not found in Fig. 1, we consider that the amount of La₂O₃ is too little to be found. The results of JIANG et al [24] also proved the correctness of our conclusion.

Figure 2 shows the three dimensional AFM images of ZnO thin films which are fabricated by dip-coating method. From these images, it can be found that the undulate surface of the thin film consists of massif-like ZnO aggregates with average grain sizes of 55 to 105 nm and continuous accumulation of particles, the sample QD1 has the biggest average grain size about 105 nm, the samples QD0, QD2 and QD3 have the similar average grain sizes among 55 to 65 nm, and local surfaces are even and neat. The whole samples have lower surface roughness with 3.5 nm, 4.9 nm, 3.6 nm and 6.3 nm, respectively. Such differences should be reflected in the electrical properties.

The SEM micrographs in Fig. 3 show the microstructure of the films prepared by sol-gel process after annealing in air at 750 °C for 1 h. The grain shape of ZnO doped by La₂O₃ makes no significant change. All micrographs show the evidence of the films with an average size clearly below the micron. These micrographs also show those differences observed in the films, that is, compared