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Varistor performance of nanocrystalline Zn–Bi–O thin films prepared by reactive RF magnetron sputtering at room temperature

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Abstract

The Zn–Bi–O films were deposited by reactive radio frequency magnetron sputtering in oxygen atmosphere from ZnBi alloy target (wt% ratio Zn:Bi = 9:1) on glass substrate at room temperature. The XRD patterns show that the films deposited on tin-doped indium oxide/glass substrates were nanocrystalline. The microstructure of Bi-doped ZnO films was studied by scanning electron microscopy in combination with energy dispersive X-ray spectroscopy. All the obtained layers had varistor-type non-linear current–voltage (*I–V*) characteristics with low breakdown voltage varying from few tenths of a volt to few volts.
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1. Introduction

ZnO-based varistors are strongly nonlinear resistors whose conductivity increases by several orders of magnitude when a characteristic voltage is exceeded. Therefore, they are used as surge arresters in power transmission and as transient voltage suppressors for the protection of electronic devices. Nowadays, due to considerable growth of PC equipment and telecommunication networks there is a need to develop low-voltage (battery operating regions of 3–12 V) surface mountable thin layer or multilayer varistors. External protection is required at system inputs and outputs to eliminate electrical overstress damages caused especially by electrostatic discharges. Doped zinc oxide has drawn much interest in another area as potential blue and UV light–emitting diodes (LED) and lasers [1,2] or transparent conducting oxide (TCO) electrodes [3] in optoelectronics, gas sensors [4–6], piezoelectric devices [7]. ZnO films have been grown by many methods including sol–gel process [8], chemical vapour deposition (CVD), molecular beam epitaxy (MBE), metal organic chemical vapour deposition (MOCVD) [9] and pulse laser deposition [10]. However, the magnetron sputtering method [11] has several attractive

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advantages, for example low substrate temperature (down to room temperature) and good adhesion of the film on the substrate. Large-area films of well-controlled compositions can be deposited economically and with a growth rate which is high enough for thick films and low enough for ultra-thin films by changing the sputtering rate.

The main goal of this investigation was the characterization of structural and electrical properties of semi-amorphous nanocrystalline Bi-doped ZnO thin films deposited on tin-doped indium oxide (ITO)/glass substrate at room temperature having non-linear *I–V* characteristics with low breakdown voltage. However, there is little information about the actual conduction mechanism in such nanocrystalline varistor thin-film structures. Also the electronic properties of their grain boundaries are not well understood since conventional techniques are not well adapted to such small structures.

2. Experiments

The Zn–Bi–O films were deposited by reactive radio frequency (RF) magnetron sputtering in pure oxygen from ZnBi alloy target (wt% ratio Zn:Bi = 9:1). The two substrate materials were Corning glass with deposited transparent and conducting ITO layer and quartz glass. Additional ITO layers were used as measuring electrode. The sputtering chamber was evacuated with a rotary and oil diffusion pumps below 6.65×10^{-5} hPa. The oxygen gas pressure during sputtering was changed in the region of 6.65×10^{-3}–8.0×10^{-2} hPa in this experiment. Total RF power was varied from 100 to 800 W. The target–substrate distance was fixed at 40 mm. The substrate holder was not heated or cooled during the film deposition. The achieved film growth rate in pure oxygen at fixed energy density released at the sputtered target ($P = 18\,\mathrm{W/cm^2}$) was about 10 nm/min [12]. The deposited films were transparent with slightly yellowish tint. Film thickness was measured by a quartz crystal thickness monitor during deposition. The thickness of the investigated films was varied from 0.3 to 4 μm.

The crystal structure of the films was determined by X-ray diffraction (XRD), using a DRON-3 diffractometer with CuKα radiation. The surface morphology was observed with a Philips 515 scanning electron microscope (SEM) coupled with energy dispersive X-ray spectroscopy (EDS) and LEO 1530 field emission SEM. *I–V* characteristics of obtained specimens were measured using a Keithley 617 programmable electrometer/voltage source by scanning the DC voltage at a speed of 0.1–1 V/min until the current flowing through the specimens reached 1 mA. These measurements were carried out at room temperature.

3. Results and discussion

The surface morphology of a typical Zn–Bi–O thin-film (0.3 μm thickness) deposited on ITO/glass substrate at room temperature is shown in Fig. 1. The surface of the deposited layer looks very smooth, however includes several big grains (about 0.1–1 μm) on top of the surface which are Bi-rich phase, because these entities all appear white in SEM backscattered electron compositional images. EDX analyses indeed showed that they consist of mainly bismuth oxide (wt% ratio Zn:Bi = 27:73). The average concentration of metals in the film is Zn:Bi = 79:21 (wt% ratio). This could be a consequence of non-stoichiometric

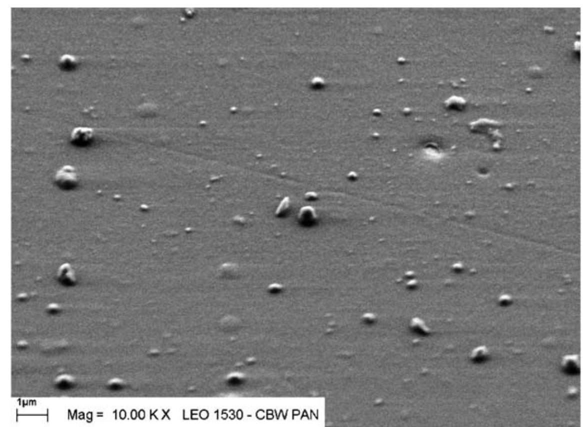

Fig. 1. SEM micrographs of a Zn–Bi–O thin film (thickness = 0.3 μm) deposited by magnetron sputtering on ITO/glass substrate.

sputtering of metal alloy target when high RF power was applied. The continuous film must have very fine grains at the nanometer range and the grains are very tightly packed together, because there are no visible boundary regions.

It is well known that the crystal growth of ZnO films prepared by RF sputtering is greatly influenced by the surface crystallinity, morphology of substrates and surface roughness [13]. Crystallinity of ZnO thin films depends also on the Ar/O_2 gas concentration. Using pure oxygen as the sputtering gas a low crystalline film was obtained. But even then an amorphous thin layer is observed at the ZnO/glass interface and polycrystalline ZnO, that is not oriented, is observed on the amorphous layer. A *c*-axis orientation is observed on most upper layers [13]. Deposition of films on non-heated substrates always create a conditions for formation of a semi-amorphous structure of the layers.

Fig. 2a shows the XRD pattern of a Zn–Bi–O thin film grown at room temperature on an ITO/glass substrate (thickness about 0.3 μm and RF power of 320W). This film shows highly nanocrystalline structure (low intensity of (1 0 0) peak of ZnO). Well-observable diffraction peaks are only from the mixed-oriented polycrystalline ITO layer (2 2 2)/(4 0 0)/(4 4 0). For comparison, Figs. 2b and c show XRD curves of thicker Zn–Bi–O films (4 μm thickness) on bare quartz glass deposited using an RF power of 320 and 430W, respectively. The thick layers deposited on quartz have higher proportion of nanocrystalline fraction of ZnO phase with respect to the thin film on ITO/glass substrate. There is no typical (0 0 2) orientation (i.e. the *c*-axis of the film is perpendicular to the substrate plane) for layers deposited with low RF power (Fig. 2b). Only when the RF power increases the (0 0 2) peak of ZnO appears (Fig. 2c).

The underlying reason for the formation of semi-amorphous ZnO at low substrate temperature is the reduced mobility of the zinc–oxygen cluster by virtue of lower kinetic energy. Several process parameters affect the kinetic energy of sputtered clusters on the substrate: substrate temperature, sputtering power, (which determines the energy of the sputtered particles as it leaves the target), sputtering gas pressure and target–substrate distance, (which determine the number of collisions with gas molecules and subsequent energy loss). High sputtering energy, low sputtering gas pressure, and a small target–substrate distance increase the kinetic energy of sputtered atoms on the substrate. On the other hand, these process parameters increase the gas bombardment, which serves to degrade the crystallinity of Zn–Bi–O films. Thus on the film surface, there is a trade-off between sputtering energy, substrate temperature, sputtering gas pressure and target–substrate distance to achieve a polycrystalline or semi-amorphous film with the desired electrical or optical properties.

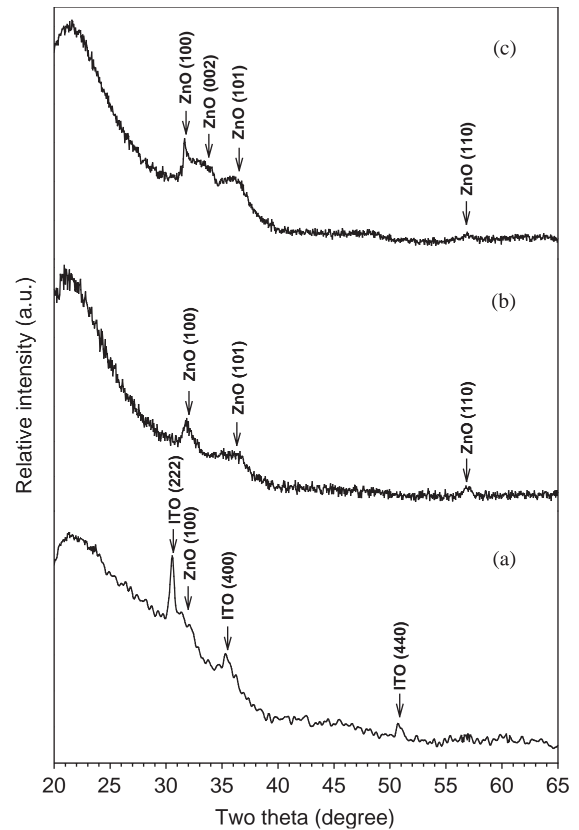

Fig. 2. Measured XRD spectra of 0.3 μm thick Zn–Bi–O films deposited on ITO/glass (a) and bare quartz glass with 4 μm thickness and RF powers of 320 W (b) and 430 W (c), respectively.

The measured *I–V* characteristics of 0.3 μm thick amorphous Zn–Bi–O films are shown in Fig. 3 for subsequent measurement cycles. The

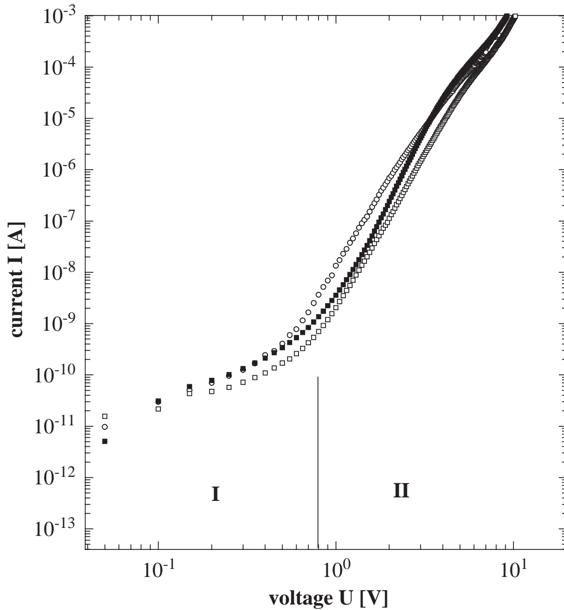

Fig. 3. I–V characteristics of 0.3 μm thick Zn–Bi–O layers deposited on ITO/glass at room temperature for subsequent measuring cycles.

varistor layer was deposited on ITO/glass substrates at $p_{O_2} = 2.6 \times 10^{-2}$ hPa oxygen pressure and RF power density $P = 3.5\,\mathrm{W\,cm^{-2}}$. Transition voltage for this layer is $U_t = 0.8$ V. There are two distinct voltage region. At lower voltage region below $U < U_t$ (region I in Fig. 3) this layer behaves as typical dielectric material with low leakage current. Above $U > U_t$ (region II in Fig. 3) conducting current significantly increases. This region appears as normal operation region of a varistor.

The I–V characteristic of varistor layers can be represented by a power low $I = kV^{\alpha}$, where α is the nonlinear coefficient, I is the current flow flowing through it, V is the voltage across the sample, and k is a constant. For present thin film varistor the nonlinear coefficient is $\alpha = 7$.

4. Conclusions

Bi-doped ZnO films made by reactive RF magnetron sputtering on glass substrate at room temperature have been studied. All the obtained films had strongly non-linear current–voltage characteristics. It was observed from XRD that thin film deposited on an ITO/glass substrate has nanocrystalline structure. Furthermore, SEM revealed that the films are very smooth with some big grains (Bi-rich phase) on top of the layer. These films have varistor-type current–voltage characteristics with low breakdown voltage varying from few tenths of a volt to several volts and the non-linearity coefficient α from 5 to 15, depending on the layer thickness.

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