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Effect of rapid thermal annealing on texture and properties of pulsed laser deposited zinc oxide thin films

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ABSTRACT

A comparative study on the properties of pulsed laser deposited ZnO thin films as a function of rapid thermal annealing temperature (T_a) is presented. Grazing incidence x-ray diffraction pattern reveals that preferred orientation of the films changes from (002) to (103) as T_a varies from 500 to 800 °C. A clear correlation between grain morphology and texture formation is noticed. Photoluminescence spectra of all films show a strong near-band-edge ultraviolet (UV) emission and the UV emission intensity increases with T_a. Simultaneously, a weak and broad green emission centered at 505 nm corresponds to oxygen vacancies also emerged in the films annealed at $T_a \geq 600$ °C. A significant hysteresis behavior is observed in current–voltage characteristics and attributed to trapping/de-trapping driven effect. It is shown that high resistance state is dominated by space charge limited currents and low resistance state is governed by both Pool–Frenkel (2–5 V) and Schottky emission (0–2 V).

1. Introduction

ZnO thin films and nanostructures are potential candidates for versatile applications in several emerging areas such as integrated optics, piezoelectric devices and spintronics [1,2]. In recent years, much attention has been paid to control the defects in ZnO thin films because their electrical, magnetic and optical properties are known to be strongly depended on defects concentration [3–5]. Recently, it is shown that even un-doped ZnO films show ferromagnetic behavior when defects were introduced by thermal-annealing in flowing argon [3]. Defects at the interface of ZnO/metals cause a resistive switching behavior in ZnO films and make them attractive for non-volatile memories [4]. Intrinsic defects were commonly observed in ZnO films in spite of film growth process. On the other hand, post-annealing treatments are seemed to be an effective way to control the defects and crystalline quality of the films [6,7]. Usually, two kinds of annealing techniques, one is conventional furnace annealing (CFA) and the other is rapid thermal annealing (RTA) were performed. As compared to CFA technique, RTA technique offers shorter cycle time, reduced thermal exposure and a lot of size flexibility [8]. However, the studies of RTA effects on the properties of ZnO thin films are still of great interest.

In this letter, we demonstrate the effect of RTA temperature on the texture, and morphology of pulsed laser deposited ZnO thin films. The effects of defects generated during RTA process on optical and electrical properties are investigated.

2. Experiment

ZnO films with a thickness of ~50 nm were deposited on n-Si (100) substrates by the pulsed laser deposition method using a commercially available ZnO target (99.99% purity from Kurt Lessker). Firstly, the deposition rate was estimated by depositing thick monolayers on glass substrates and calculating the film thickness from the optical transmittance following the 'Envelop method'. Then, ZnO films with a thickness of ≈ 50 nm were deposited on the n-Si (100). The accuracy of this procedure was confirmed earlier by TEM and RBS [9]. The 248 nm line of an excimer laser, with energy of 400 mJ and pulse rate of 5 Hz, was focused onto the target. The films were grown at room temperature in the oxygen partial pressure of 0.01 mbar. Before the deposition, the chamber was first evacuated down to an ambient low pressure of $\approx 3 \times 10^{-6}$ mbar. As-grown films were subjected to the RTA in quartz tube in the presence of nitrogen pressure of 6 mbar. Annealing was performed at different temperatures in the range of 500–800 °C for 60 s. Before performing the annealing, the quartz tube was evacuated to 5×10^{-2} mbar and then nitrogen was introduced into the tube.

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Structural properties were investigated on the basis of grazing incidence x-ray diffraction (GIXRD) patterns. GIXRD measurements were performed employing x-rays of a wavelength $\lambda = 1.54$ Å at the PDIFF-beamline of the ANKA synchrotron facility (Karlsruhe, Germany). Atomic force microscopy (AFM) (Nanoscope IIId system, Digital Instruments) was employed in a semi-contact mode by using an Antimony doped Si cantilever to examine the surface morphology. The force constant of cantilever was 20–80 N/m and the amount of force applied to do the imaging was in the range of 720–2880 N. Photoluminescence (PL) spectra were recorded on a Spex Fluorolog spectrometer in front-face geometry, in spectral range from 350 to 600 nm under a 330 nm excitation from a Xenon lamp. For electrical measurements, the top aluminum (Al) electrodes, having diameter of 1 mm, were deposited by thermal evaporation technique and bottom Al-electrodes were made by electric spark. Current–voltage (*I*–*V*) characteristics of Al/ZnO/n-Si (100)/Al structures have been measured using Keithly electrometer (model no. 605).

3. Results and discussions

GIXRD profiles of the ZnO thin films annealed at different temperatures were shown Fig. 1. GIXRD pattern revealed that all the films had a poly crystalline nature with a hexagonal structure, and demonstrates a strong preferential orientation depending on annealing temperature (T_a). The two major peaks at $2\theta = 34.7 \pm 0.1$ and 63.2 ± 0.1 corresponds to (002) and (103) orientations (JCPDF ♯36-1451). The peak position shifted towards higher angle compared to standard ZnO crystal and attributed to the strain effect and/or presence of defects. In addition, relative intensity $I_{(103)}/I_{(002)}$ significantly increases with increasing T_a. It is observed that the texture of the films changes from (002) to (103) at T_a of 700 °C. Usually, the textured orientation is related to the development of microstructure [10]. Fujimura et al. [11] reported that the (002) orientation has the lowest surface energy. Other orientation has higher surface energy than (002) and requires more thermal energy for its growth. The inclination angles between the planes (002) and (103); (002) and (101); and (002) and (100) were 31.66°, 61.61° and 90° respectively [12]. Since the (103) plane has the lowest inclination angle with (002), it was next possible plane to emerge after (002). Fig. 1 also evidenced that it is possible to grow (103) textured films by annealing at $T_a \geq 700$ °C.

The microstructure of ZnO films was scanned by AFM. As shown in Fig. 2(a)–(d), AFM images reveal significant morphological changes that correspond to T_a. Grain size distribution histograms of corresponding films are shown in Fig. 2(e). Variation of average grain size estimated by the linear intercept method and the root mean square roughness obtained from the thin film surfaces as a function of T_a are shown in Fig. 2(f). As T_a increases from 500 to 600 °C, the grain size increases as excepted. But when T_a gets to 700 °C, the grain size is relatively small. It seems that increasing thermal energy input utilized for texture restructuring as evident in GIXRD rather than grain growth. With further increase of T_a to 800 °C, grain size increases due to the coalescence process. As the grain size increases roughness also increases as shown in Fig. 2(f).

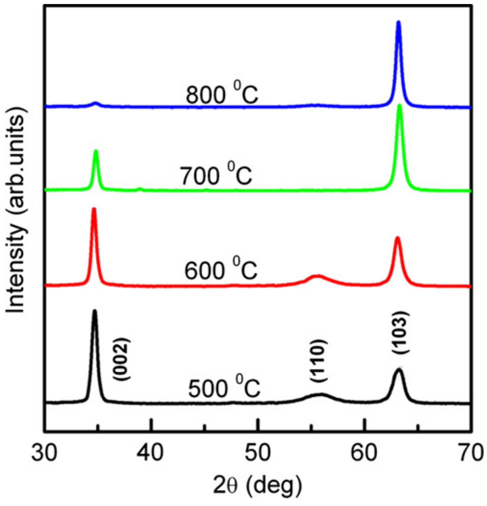

Fig. 1. GIXRD patterns of ZnO thin films annealed at different temperatures.

The effect of T_a on photoluminescence (PL) of ZnO films is shown in Fig. 3. PL spectra of all the films show a strong and sharp UV emission at 378 ± 2 nm corresponding to the near-band-edge (NBE) emission, which is directly related to the crystal quality of ZnO [13]. A narrower PL line width and higher PL intensity with increasing T_a as shown in inset of Fig. 3 is regarded as a clear evidence for the improvement of the crystalline phase. The intensity of the UV emission for the film annealed at 800 °C is 12 times higher than that at 500 °C. This could be due to less number of non-radiative recombination centers like grain boundaries [14]. In addition to strong UV peak, the spectra of the films annealed at $T_a \geq 600$ °C exhibit a weak and broad green emission in the range 400–600 nm with the peak centered at 505 nm. Even though, there is no consistent argument in the literature, on the origin of green emission in ZnO films, its intensity is generally attributed to the density of intrinsic defects such as oxygen vacancy, Zn interstitial and other related defects [14,15]. It is believed that green emissions observed here are probably caused by oxygen vacancies generated in ZnO films during the annealing in nitrogen [3]. However, the green emission increases with increase of T_a as shown in inset of Fig. 3.

Fig. 4 shows current–voltage (*I*–*V*) characteristics of ZnO films annealed at $T_a = 500$ and 700 °C. The voltage was swept from +5 V to −5 V and vice versa. Current flow in the films annealed at 700 °C was higher than that of films annealed at 500 °C. This is due to the presence of oxygen vacancies as it was stated from PL. It is known that structural defects like interstitial Zn ions or oxygen vacancies in ZnO films can contribute by free electrons for electrical conduction, as a result resistivity decreases [16]. Moreover, the presence of oxygen vacancies shifts the Fermi energy level and decreases the resistivity of ZnO films [17]. The resistance estimated from the slope of linear plots in the positive voltage region is 13.2 and 5.5 kΩ for the films annealed at 500 and 700 °C respectively. *I*–*V* characteristics of the films annealed at 700 °C display a good hysteresis behavior with bias voltage in the negative voltage region.

In order to understand the origin of the hysteresis, different conduction models such as space charge limited conduction (SCLC) model, Schottky emission model and Poole–Frenkel emission model are employed. The log–log plot of hysteresis is shown in the inset of Fig. 4. The high resistance state follows the ohmic law ($I \alpha V$) in 0–4 V range and child law ($I \alpha V^2$) in 4–5 V range, which indicates that the main conduction mechanism is SCLC. On the other hand, the low resistance is dominated by the Schottky emission ($Ln\, I \alpha V^{1/2}$) in 0–2 V range and by P–F emission ($(Ln(I/V) \alpha V^{1/2})$) in 2–5 V range. This behavior is consistent with previous reports on the interfacial effects, where the migration of defects causes a resistive switching in heterostructures [18–19]. Therefore, the presence of hysteresis behavior only in films contains defects suggest that the observed hysteresis is due to an electron trapping/de-trapping process by the oxygen vacancies defects localized at the interface of Al/ZnO.

4. Conclusions

In this work, effects of rapid thermal annealing on different properties of ZnO films were highlighted. A good correlation has