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High c-axis preferred orientation ZnO thin films prepared by oxidation of metallic zinc

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ABSTRACT

Thin films of zinc oxide were grown on glass substrates by thermal oxidation. The metallic zinc films were thermally oxidized at different temperatures ranging from 300 to 600 °C to yield ZnO thin films. The structural property of the thin films was characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The X-ray diffraction measurements showed that the films oxidized at 300 °C were not oxidized entirely, and the films deposited at 600 °C had better crystalline quality than the rest. When the oxidation temperature increased above 400 °C, the films exhibited preferred orientation along (002) and high transmittance ranging from 85% to 98% in vis–near-infrared band. Meanwhile, the films showed a UV emission at about 377 nm and green emission. With the increasing of oxidation temperature, the intensity of green emission peak was enhanced, and then decreased, disappearing at 600 °C, and the case of UV emission increased. Furthermore, a strong green emission was observed in the film sintered in pure oxygen atmosphere.

1. Introduction

Transparent conductive oxide films have been used extensively as transparent electrodes in flat panel displays and solar cells [1–3] such as In_2O_3, SnO_2 and ZnO. Among them, ZnO is an attractive material for transparent electrode. In general, electrical and optical progress of ZnO transparent electrode can be improved by oxygen partial pressure [4], substrate temperature [5,6] and others. Despite there is an enormous interest in ZnO deposition, thermal oxidation is one of the techniques, which has been paid very little attention to although with its obvious simplicity until recently. There have been only a few reports in the literature devoted to the deposition of ZnO by thermal oxidation, which investigated the effects of annealing temperature [7–9], the heating rate [10,11] and the oxygen pressure [12] during oxidation progress. But in these studies, the ZnO thin films did not possess preferred orientation. Gao et al. [13] reported that the ZnO films with (100) preferred crystal orientation were fabricated by thermal oxidation of amorphous ZnS films.

In this paper, the metallic zinc films with high preferred orientation was deposited at room temperature by using laser molecular beam epitaxy (LMBE), then the ZnO thin films with 002 preferred crystal orientation were fabricated by thermal oxidation of metallic zinc at different temperatures ranging from 300 °C to 600 °C, whose structural and optical properties were investigated.

2. Experimental details

Zinc films were grown on glass substrates at room temperature by laser molecular beam epitaxy (LMBE). The purity of zinc target was 99.99%. Prior to deposition, the system was evacuated to a base pressure of 2×10^{-7} Pa. The space between the target and the substrate was about 5 cm. Ablation of the target was achieved using UV KrF excimer laser source (248 nm). The laser fluence of 350 mJ/cm^2 and repetition rate of 5 Hz was chosen during the films deposition. Before successive deposition event, the pure zinc target surface was cleaned by applying 2000 laser pulses, and 9000 subsequent laser pulses were applied in order to deposit one pure zinc film. Then the deposited zinc films were annealed at temperature ranging from 300 °C to 600 °C in the air to obtain ZnO films, and the oxidation time was 1 h. The optical thickness of ZnO films was 430–712 nm.

The crystalline structure of the ZnO films was characterized by X-ray diffraction (XRD) technique with Cu-$K\alpha$ radiation ($\lambda = 0.15406$ nm). The optical thickness was measured at room temperature with M-2000VI Ellipsometer of J.A. Woollan Co., Inc. The morphology of ZnO films was characterized by scanning electronic microscopy (SEM). Photoluminescence (PL) spectra were measured at room temperature with Edinburgh Instruments FLS920 type spectrofluorophotometer. The excitation wavelength was chosen as 325 nm, and a 450 W Xe-lamp was used as the exciting light source.

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3. Results and discussion

3.1. Structural properties

In Fig. 1, the XRD patterns of the zinc and zinc oxide films annealed in the air with various annealing temperature are shown. This figure shows that one diffraction peak 002 of zinc film (36.48°) is observed, indicating that zinc film forms the close-peaked hexagonal structure. As zinc films are annealed in the air, there occurs a structural change. A strong diffraction peak positioned at 34.48° appears corresponding to the 002 diffraction peak of ZnO with wurtzite structure. With thermal oxidation temperature increasing, the intensity of diffraction peak increases. It is noted that a sharp and narrow peak at 36.40° is observed which is corresponding to the 002 diffraction peak of metallic zinc or the (101) diffraction peak of ZnO. We believe that the origin of this diffraction peak is from the recrystallization of metallic zinc, because the peak is too sharp. It indicates that zinc films cannot be oxidized entirely at 300 °C, and this result corresponds to the reports of Rusu [14] and Dhananjay [15]. The full width at half maximum (FWHM) of 002 diffraction peak for ZnO films is 0.4243°, 0.3364° and 0.3102° for the films sintered at 400, 500 and 600 °C respectively. As we all know that the narrowest the FWHM is, the best the crystal quality is. So the film sintered at 600 °C has the best crystal quality. In order to analyze the diffraction pattern clearly, the XRD pattern in logarithmic scale is shown in Fig. 1b, and a very weak diffraction peak at about 31° is observed which corresponds to 100 diffraction peak of ZnO with wurtzite structure. The zinc film has better preferential orientation than others' work [7,9,13]. Furthermore, the rocking curves of ZnO films which are normalized are shown in Fig. 1c. It is obvious that the ZnO film sintered at 600 °C has the smallest FWHM values.

In order to investigate whether the oxidation time is too short to make zinc oxidized entirely, the zinc films have been annealed at 300 °C for 10, 30, 60 and 120 min respectively. The result of XRD is shown in Fig. 2. As can be seen, the diffraction peaks exhibit little change, which indicates that the films cannot be oxidized entirely at 300 °C even the annealing time is 120 min. The intensity ratio between the diffraction peaks of 002 for zinc oxidation and zinc films is shown in the inset of Fig. 2. The calculated values of ratio are 0.84, 0.69, 1.30 and 1.40 respectively. It indicates that the annealing time has an effect on the degree of oxidation. However, the oxidation degree reveals little change with annealing time increasing from 60 to 120 min. At low temperature, oxygen atoms have no enough energy to enter the underlayer of zinc films, which causes the lack of oxygen atoms in the zinc film. With the oxidation temperature increasing, the degree of oxidation is improved.

Fig. 3 shows the SEM images of the ZnO films oxidized in the oxidation temperature in the range of 300–600 °C. The

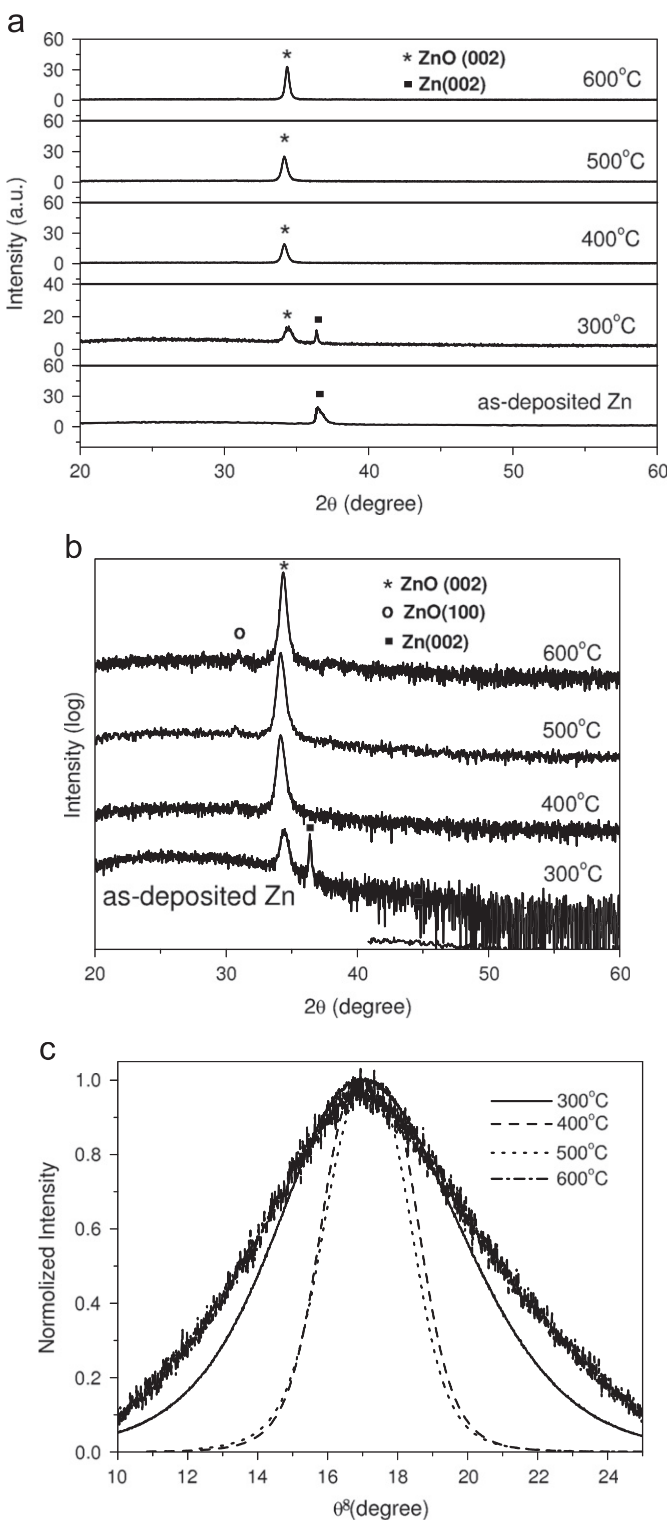

Fig. 1. The XRD patterns of as-deposited Zn and ZnO films with different oxidation temperatures (a) in a.u.; (b) in logarithmic scale; (c) rocking curves.

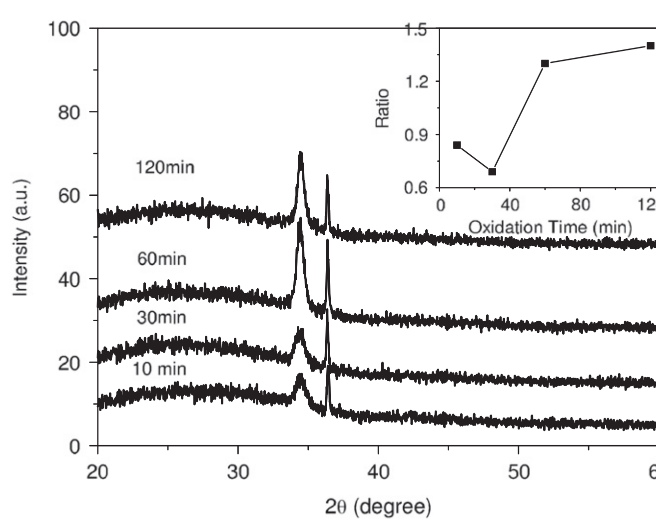

Fig. 2. The XRD patterns of ZnO films with different oxidation time. The inset is the ratio between the intensity of (002) diffraction peaks for zinc oxidation and zinc films.