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Effects of Oxygen Pressure on the Crystalline of ZnO Films Grown on Sapphire by PLD Method

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We studied the effects of oxygen pressure on the crystallinity of ZnO films. ZnO films on sapphire(001) substrates were deposited by the pulsed laser deposition (PLD) technique and were grown at various oxygen pressures ranging from 5 mTorr to 150 mTorr to investigate the effect of ambient O_2 pressure on the structural properties of the films. We found that the lattice constant along the *c*-axis and the crystallinity of ZnO films were sensitive to the O_2 pressure.

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I. INTRODUCTION

Recently, ZnO films have drawn global attention due to their potential in many applications such as transparent conducting oxide electrodes, thin film gas sensors, solar cells, luminescence materials, hetero-junction laser diodes *etc.* [1–4]. Many researchers have considered ZnO as a promising material for ultraviolet and blue light-emitting diodes (LED) and laser diodes (LD). The exciton binding energy of ZnO at room temperature is 60 meV higher than that of well-known blue emission material GaN (28 meV). This property of ZnO is particular promising because it may allow more efficient lasing at room temperature. There have been reports of success in optical-pumping lasing in epitaxial ZnO thin films which have further stimulated interest in ZnO materials [5,6]. Also, we can grow a good quality ZnO film at temperatures ranging from 500 °C to 600 °C [7]. This temperature range is hundreds of degrees lower than the growth temperatures of GaN [8].

ZnO thin films can be grown by various deposition techniques which include pulsed laser deposition (PLD), chemical vapor deposition (CVD), molecular beam epitaxy (MBE) and vapor phase epitaxy (VPE). Among these techniques, the PLD is a promising technique for deposition of ZnO thin film. The advantages of PLD method are the ability to reproduce the target composition under appropriate conditions, an inherently clean process, a significant degree of parameter freedom, and the ability to deposit multi-layers of different materials. It is also possible to control the bandgap of ZnO by alloying with MgO. Stable Mg doped ZnO (MZO) ternary alloys with a bandgap up to ∼6 eV have been fabricated. Also, multi-layer deposition of MgO/ZnO forms tunable bandgap energy materials [9].

In order to develop a high-quality ZnO film for a device application, it is necessary to clarify the roles and the effects of additives, surface morphology with structural mismatch [10] and the different conditions of growth such as ambient O_2 pressure and deposition temperature in the PLD method [11]. This will result in different surface morphology and crystallinity suitable for the different applications. The effect of O_2 pressure on the crystallinity of ZnO film has been previously studied by several authors. Kim *et al.* have suggested that the lattice spacing of ZnO film increased as the oxygen ambient pressure increased [12]. Shan *et al.* have also studied the quality of ZnO film with different oxygen ambient pressures which are much higher than the oxygen pressure which we used in our study [13]. They reported that the structure of ZnO film is not sensitive to the ambient oxygen pressure. Although considerable progress has been made in recent years, the effect of the oxygen ambient pressure on the ZnO film crystallinity is still the subject of controversy.

In this paper, we report the effect of O_2 pressure on the crystallinity of ZnO films fabricated on sapphire(001) substrates by the PLD technique. X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) measurements are performed to evaluate the O_2 pressure effects on the properties of ZnO films.

II. EXPERIMENTS

A series of ZnO films were grown on Al_2O_3(001) substrates by using a PLD technique. A pulsed KrF excimer

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laser (Lambda physik COMPex 102, 248 nm and pulse duration of 20 ns) was operated at a pulse rate of 5 Hz and was focused through a 30 cm focal length lens onto a rotating target at a 45° angle of incidence. In the chamber of the PLD system, there are three rotatable target holders on one carousel and one rotatable substrate holder. The substrate holder is usually located at the opposite position to one of the target holders.

The ZnO target was fabricated by following conventional ceramic powder procedure (cold pressing). It was sintered for 24 hours at 1000 °C in air in an electric furnace. The sapphire substrate was cleaned in an ultrasonic cleaner with acetone and ethylalcohol for 20 minutes before being loaded on the holder.

The substrates were positioned 4 cm away from the target and 1 cm off from the center to avoid direct exposure to the plume. The chamber was initially evacuated to 2.0×10^{-6} Torr and was kept at the desired pressure with oxygen gas during the deposition. The growth temperature was held constant at 500 °C by four halogen lamps. X-ray diffraction measurements were performed at the 5C2 beamline of the Pohang Light Source. The incident X-rays were monochromated to 1.24173 Å. An X-ray photoelectron spectroscopy (XPS) analysis was performed with the Escalab 250 XPS spectrometer after etching of samples for 200 seconds.

III. RESULTS AND DISCUSSION

We investigated structural properties of ZnO films grown at various O_2 pressures by using XRD. XRD spectra of ZnO film are displayed in Figure 1. The ZnO film was deposited at a substrate temperature of 500 °C under fixed 5-mTorr oxygen pressure and was annealed at 900 °C for 3 hours. Figure 1(a) and (b) show $\theta \sim 2\theta$ scan and ϕ scan results of ZnO film. As can be seen in Figure 1(a), the 2θ peak position of the film is at 27.5°, which corresponds to the bulk ZnO(002) 2θ peak position. The data in Figure 1(b) indicate that six-fold symmetry is formed in the in-plane of the film. These results imply that a clear hexagonal ZnO(002) structure was formed on Al_2O_3 substrate.

Figure 2 shows XRD spectra of ZnO films grown at oxygen pressure of 5, 50, 75, 100 and 150 mTorr. As can be seen in Figure 2, the peak position shifted to a higher value as the oxygen pressure increased; *i.e.*, the lattice constant along the *c*-axis decreased as the oxygen pressure increased. As marked in Figure 2 as a vertical solid line, $q_z = 2.41354$ Å^{-1} corresponds to the *c*-axis lattice constant of bulk ZnO(002) d =2.603 Å. Therefore, the results in Figure 2 imply that the *c*-axis lattice constant of grown ZnO films is larger or smaller than that of bulk ZnO(002) when the ambient oxygen pressure is lower or higher than 75-mTorr. This result indicates that the lattice constant of the film is sensitively influenced by the ambient oxygen pressure during the film growth. It seems that our results are different from those in previous studies. Kim *et al*. [12] found that the lattice constant increased as the ambient oxygen pressure increased. Also, Fan *et al*. [14] and Zhao *et al*. [15] found that the crystallinity of ZnO film improved with the oxygen ambient pressure. They argued that the improved crystallinity of ZnO film with higher oxygen pressure mainly originated from the kinetics of the atomic arrangement during the deposition process. However, in our experiment, we found that the crystallinity of the film started to degrade when the oxygen pressure was higher than the optimum pressure, due to O-H defect formation. The extra oxygen seems to more easily bond to remaining hydrogen

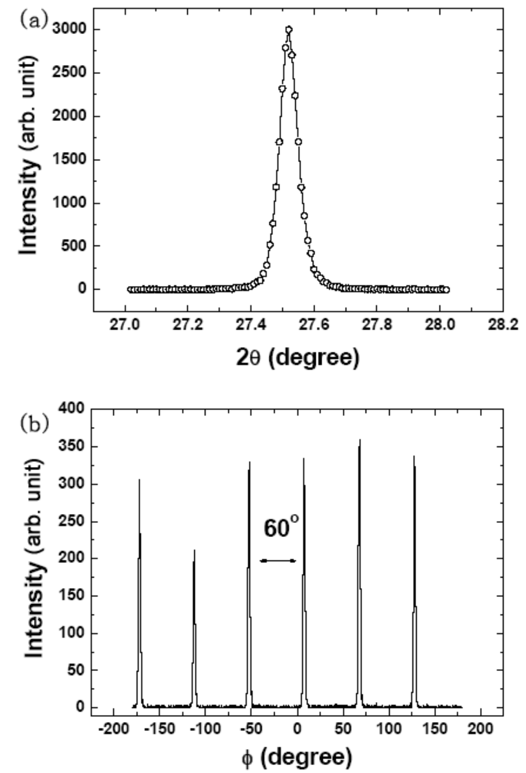

Fig. 1. XRD spectra of ZnO film deposited on sapphire(001) substrate by PLD method. (a) θ-2θ scan, and (b) ϕ scan.

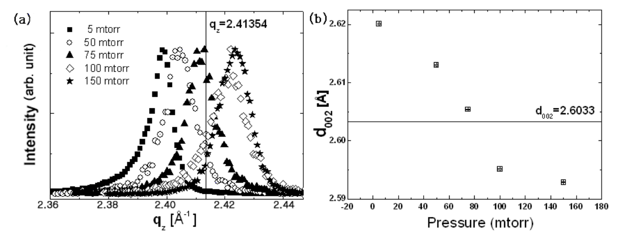

Fig. 2. (a) Longitudinal XRD spectra of ZnO films with different oxygen pressure. The peak intensities were normalized and the bulk value of q_z is indicated by a vertical line. (b) Oxygen-pressure-dependent lattice constant, d_{002}.

Table 1. Atomic concentration of ZnO films.

Pressure	Zn2p (1021.3 eV) (%)	O1s (529.8 eV) (%)	O1s′ (531.7 eV) (%)	O1s/Zn2p	O1s′/Zn2p	O1s′/O1s
5 mTorr	54.00	40.72	5.28	0.754	0.097	0.129
100 mTorr	54.06	39.60	6.34	0.732	0.117	0.160

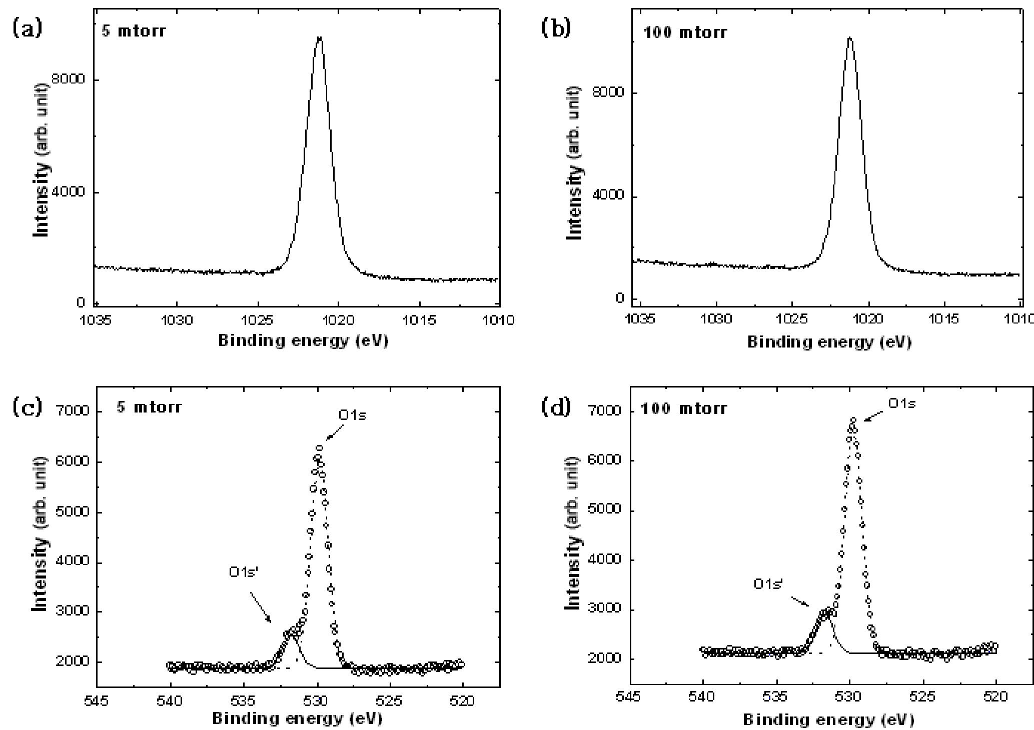

Fig. 3. XPS spectra of ZnO films. (a) and (b) show the ZnO 2p peak of the films grown with 5 mTorr and 100 mTorr oxygen pressures, respectively. (c) and (d) show the O1s peak of the films grown with 5 mTorr and 100 mTorr oxygen pressures, respectively.

in the chamber than to Zn atoms. Recently, Chris and Van de Walle found from their first-principles study that the lowest energy state for H^+ at the bond-centered position forms an O-H bond which can be regarded as a new type of dopant atom [16]. In general, O-H bonds can be formed in the growth chamber after growth, due to collisions with remaining H_2O molecules.

We were also able to perceive that the bulk value of q_z could be obtained when the films were grown in the oxygen pressure range from 75 mTorr to 100 mTorr. Film crystallinity can be affected by the kinetics of atomic arrangements during deposition [12, 13]. For a high-crystallinity film, simply stated, there must be sufficient time for deposited atoms to undergo surface diffusion to thermodynamically stable sites before being covered by the next layer of atoms [12]. As reported, the average energy of atoms in a PLD plume is in the order of 10 eV and the average energy is usually degraded by collisions with the ambient gas for pressures above 10 mTorr [17]. Therefore, in PLD, the energy of the deposition flux can be controlled by means of the pressure of the ambient gas.

Figure 3 shows XPS spectra of ZnO films. Incident energy of an X-ray photoelectron is 1486.6 eV. The Zn 2p peak and O 1s peak of the ZnO were calibrated by the carbon C 1s peak (284.68 eV). Figure 3(a) and (b) show that the binding energy of Zn 2p peak is about 1021.3 eV. There is no appreciable change in chemical states of Zn in ZnO films. Figure 3(c) and (d) show the spectra of the O 1s in ZnO films. O 1s peak which is related with Zn-O bonding has a pronounced shoulder at higher binding energies, besides the typical O 1s peak. Lu *et al.* [18] showed that this additional peak, marked O 1s′, is formed due to the presence of O-H groups of ZnO. O 1s peak and O 1s′ peak are located at 529.8 eV and 531.7 eV, respectively. Hydrogen is very difficult to remove from the crystal growth environment. It also forms a strong bond with oxygen and must be an impurity that

is unintentionally incorporated [16].

The atomic percentage of zinc and oxygen in ZnO film grown under 5 mTorr and 100 mTorr oxygen pressures were summarized in Table 1. The atomic percents of Zn and O were calculated from the integrated intensity of the XPS peaks. As we can see in Table 1, the ratios of the O 1s peak to O 1s′ peak for 5 mTorr and 100 mTorr conditions were 0.129 and 0.160, respectively. ZnO films grown under 100 mTorr oxygen pressure have more O 1s′ state than ZnO films grown under 5 mTorr oxygen pressure.

In the rocking curves of the ZnO(002) films (not shown in this paper), the FWHMs of the films grown under 5 mTorr and 100 mTorr oxygen pressure were 0.391° and 2.189°, respectively. This result indicates that the quality of film grown under 5 mTorr oxygen pressure is better than that under 100 mTorr. Also, the ratio of O 1s′/O 1s was larger in the film grown under 100 mTorr oxygen pressure. It was reported that the O 1s′ component in XPS measurements was due to the O-H bonding in ZnO films. Those O-H bonds can exist on the surface, since hydrogen atoms in ZnO are known to behave as shallow donors [16,19,20]. However, our results show that O-H bond as a defect does not influences only on the surface but also influences below the surface by the etching process before XPS measurement. Therefore, we speculate that this defect can affect the interaction between Zn and O, and that it can decrease the Zn-O bond length along the *c*-axis.

IV. CONCLUSIONS

We studied the effect of oxygen pressure on the crystallinity of ZnO(002) films grown on sapphire(001) substrate by a PLD method. We found in XRD experiments that the q_z value in as-grown films was the same as that in the bulk ZnO films when the ambient oxygen pressure was from 75 mTorr to 100 mTorr. When the oxygen pressure was higher than 100 mTorr, the crystallinity of the film started to deteriorate. These results were consistent with the results from XPS and X-ray rocking measurements. We speculate that the deterioration of crystallinity causes a decreasing lattice constant because ZnO film grown at oxygen pressure higher than 100 mTorr contains more O-H defects.

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