

Preparation of ZnO thin films on various substrates by pulsed laser deposition

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Abstract

The structural and optical properties of ZnO thin films deposited on Si (1 0 0), silica glass, α -Al₂O₃ (0 0 0 1) and Corning 7059 glass substrates by pulsed laser deposition have been studied. We have investigated the dependence of film properties on deposition conditions such as an ambient oxygen gas pressure (P_{O_2}) and a substrate temperature (T_s). XRD, AFM and photoluminescence (PL) measurements were used to characterize the grown films. The ZnO thin films deposited on various substrates under optimized condition of $P_{O_2}=0.67$ Pa and $T_s=550$ °C were highly *c*-axis (0 0 2) orientated. The ZnO thin film deposited on α -Al₂O₃ (0 0 0 1) substrate under optimal condition emitted ultra-violet PL at approximately 395 nm by optically pumped excitation (355 nm) at a power of 466 kW/cm².

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1. Introduction

Zinc oxide (ZnO) is one of the wide bandgap (3.37 eV) semiconductor materials. Therefore ZnO seems to have potentials for optical applications such as ultraviolet (UV) laser, blue light-emitting diodes and phosphorescent display. It is essential for these applications that the binding energy of the exciton is much larger than the thermal energy at room temperature (RT: 26 meV). ZnO has the exciton binding energy of approximately 60 meV at RT and is larger than those of ZnSe (22 meV) and GaN (25 meV) that have been widely used [1]. Furthermore, because ZnO thin films are highly *c*-axis oriented, self-textured ZnO thin films can be synthesized on various semiconductor substrates [2,3]. Recently, UV and green–yellow photoluminescence (PL) emissions from ZnO thin films deposited by various techniques have been investigated by optical excitation [4–8].

The pulsed laser deposition (PLD) method suits for growing high quality thin films at a relatively low T_s . Furthermore, by changing the P_{O_2} , the particles in the

films are easily controlled. We have prepared ZnO thin films on four different substrates (Si (1 0 0), silica glass, α -Al₂O₃ (0 0 0 1) and Corning 7059 glass) at various P_{O_2} and T_s by the PLD. In this paper, we have investigated the effect of structural and optical properties of ZnO thin films on P_{O_2} , T_s and substrate materials.

2. Experimental

A detailed description of PLD system are provided elsewhere [9]. The KrF excimer laser (248 nm, 25 ns, 10 Hz) was irradiated with the fluence of 2 J/cm² to the ZnO target for deposition period of 15 min. The film thickness was measured by a surface profile measuring system. The ZnO film thickness was varied from 242 to 1520 nm depending on the deposition conditions. The deposition rate was estimated by the film thickness divided by the number of laser pulses. The P_{O_2} was varied from 6.67×10^{-3} to 26.7 Pa and the T_s was in the range from RT to 700 °C. The ZnO thin films were grown on Si (1 0 0), silica glass, α -Al₂O₃ (0 0 0 1), and Corning 7059. Since the substrates were cleaned with ethanol using the ultrasonic cleaner, the surface of Si (1 0 0) substrate was covered with a thin oxidized layer. In order to verify the reproducibility of the present

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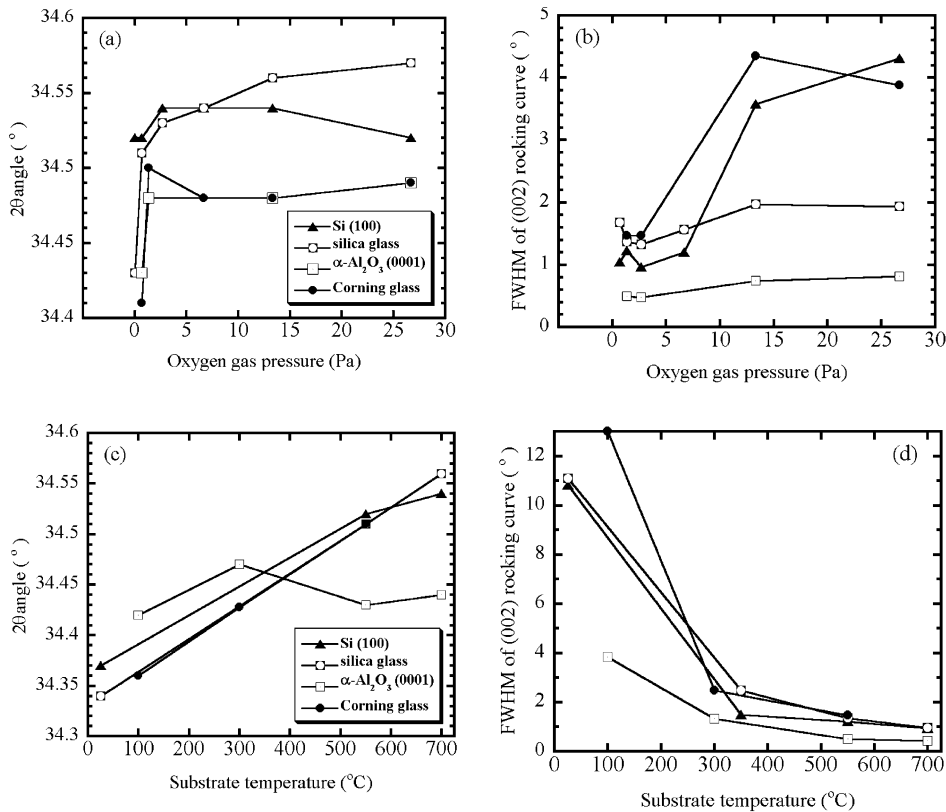


Fig. 1. XRD results of ZnO thin films deposited at various P_{O_2} ($T_s = 550$ °C constant) and T_s ($P_{O_2} = 0.67$ Pa constant). (a) (0 0 2) peak angle of θ - 2θ scan vs. P_{O_2} ; (b) FWHM of (0 0 2) rocking curve vs. P_{O_2} ; (c) (0 0 2) peak angle of θ - 2θ scan vs. T_s and (d) FWHM of (0 0 2) rocking curve vs. T_s .

experiment we have prepared ZnO thin films twice under above-mentioned deposition conditions.

The structural properties of the grown films were investigated using a XRD with a Cu K α ($\lambda = 1.5406$ Å) source and an AFM. For the PL measurement, an area of $\phi = 1$ mm of the sample was irradiated by the third harmonic light (355 nm, 3 ns, 10 Hz) of a Nd:YAG laser. In order to investigate PL vs. the excitation intensity, a power density of the excitation laser was controlled using the concave and convex lenses, and the PL emission spectra were taken using a spectrometer equipped with an ICCD camera.

3. Results and discussion

For the whole range of deposition parameters used in this experiment, the XRD of all ZnO thin films showed c -axis orientation, exhibiting only the (0 0 2) and (0 0 4) diffractions. Fig. 1a and b show the (0 0 2) peak angles and the FWHM of (0 0 2) rocking curve of the ZnO thin films deposited on different substrates at various P_{O_2} , respectively. The (0 0 2) 2θ angles increase rapidly near $P_{O_2} = 1.33$ Pa, and these are almost constant over 6.67 Pa. The 2θ angles of (0 0 2) peak are related to the c -axis length of films. The stoichiometric ZnO target

used in this study showed $2\theta = 34.47^\circ$ (c -axis lattice constant = 5.200 Å). At lower P_{O_2} , the (0 0 2) 2θ angles of the films deposited on the different substrates are almost the same as the value of the ZnO target. On the other hand, at higher P_{O_2} , the c -axis length becomes short compared with lower P_{O_2} because oxygen atoms were incorporated into lattices. The FWHM of the rocking curve indicates the crystal quality of the grown plane with higher precision than that obtained by the θ - 2θ scan method. The FWHMs of (0 0 2) rocking curves also increased with the P_{O_2} for all samples. The surface energy of the (0 0 2) orientation takes minimum in the ZnO crystal, and then in order to grow a c -axis oriented ZnO crystal, it is important that the particles ablated from the target have still energy at the substrate surface. We investigated on the plasma plume state during the deposition in previous paper [9]. It is found that the ambient oxygen gas reacts with particles ablated from the target. The ZnO (0 0 2) orientation is easily formed by the particles having the higher energy near the substrate surface at lower P_{O_2} of 1.33 Pa. Since at higher P_{O_2} than 6.67 Pa the energy of particles decreases due to collisions with the ambient gas, the formation of the highly (0 0 2) oriented ZnO film is suppressed. Fig. 1c and d show the dependence of the T_s on crystalline

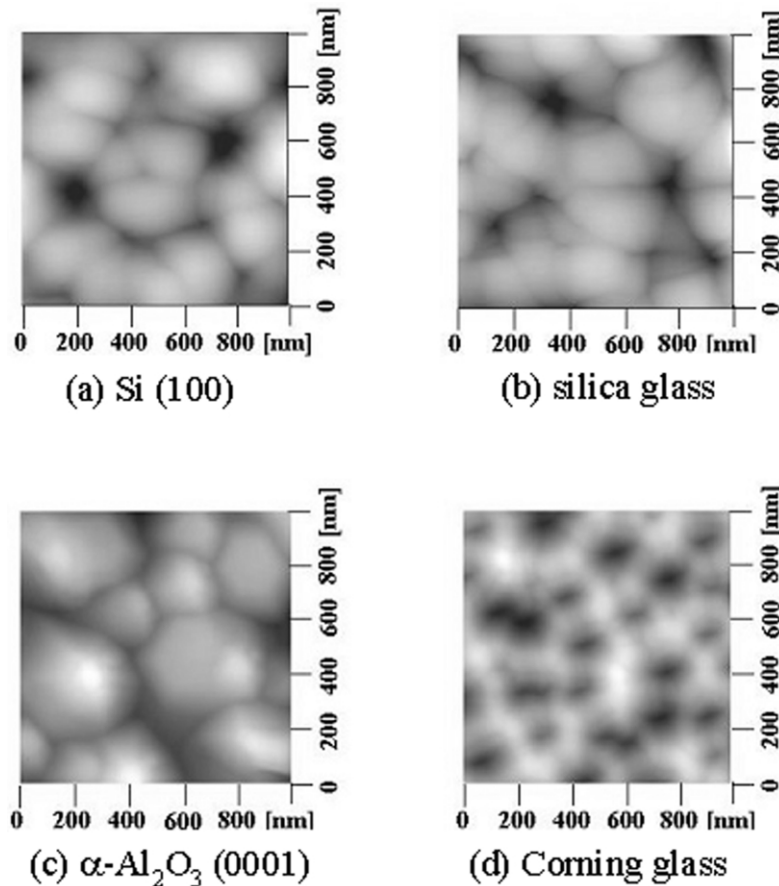


Fig. 2. AFM images of ZnO deposited on (a) Si (1 0 0); (b) silica glass; (c) α -Al₂O₃ (0 0 0 1) and (d) Corning glass substrates at temperature of 550 °C and oxygen gas pressure of 0.67 Pa.

properties same as (a) and (b). The (0 0 2) peak angles increase with T_s except for α -Al₂O₃ (0 0 0 1). This is due to the reason that amount of the oxygen incorporation into lattices may increase at higher T_s . Another reason is considered to be the strain in the film due to the difference in thermal expansion coefficients (TEC) between the ZnO and the substrate. TEC is $4 \times 10^{-6}/\text{K}$ for ZnO and approximately $2 \times 10^{-6}/\text{K}$ for SiO₂. TEC of Si (1 0 0) single crystal covered with oxide layer of a few nanometer is assumed to have almost the same value as SiO₂ [10]. When the substrate with the deposited film is cooled down the T_s after deposition, the internal stress of ZnO a - b plane will be larger stress than that of the substrate due to the TEC difference. As the result, 2θ angle tends to shift toward higher angle, that is, the c -axis lattice constant decreases with increase of the T_s . However, for the ZnO thin films deposited on α -Al₂O₃ (0 0 0 1), the (0 0 2) 2θ angles are almost independent of the T_s because the TEC mismatch between the ZnO and α -Al₂O₃ (0 0 0 1) ($4.5 \times 10^{-6}/\text{K}$) is smaller than that of SiO₂. As shown in Fig. 1d the FWHMs of (0 0 2) rocking curve decrease with increase of the T_s . This shows that the T_s strongly affects

the crystal orientation of the grown film. At the higher T_s , the thermal energy of the substrate can supply enough energy necessary to form the (0 0 2) orientation. As a result, the films prepared at the higher T_s show a good crystalline quality. It is found that P_{O_2} from 0.67 to 1.33 Pa and T_s from 550 to 700 °C give the good orientation films. As for dependence of the ZnO film crystallinity on the substrate material, the FWHM of ZnO (0 0 2) rocking curve of the film deposited on α -Al₂O₃ (0 0 0 1) under the optimum condition is narrower than that for the other substrates, and the (0 0 2) 2θ angle is close to the value of the ZnO bulk in spite of large lattice mismatch (18%) between ZnO and α -Al₂O₃ (0 0 0 1). This result shows that highly oriented ZnO thin films can be easily grown on a single crystal substrate rather than other amorphous substrates. In above discussion, effects of the film thickness on crystalline quality should be considered. In this paper, however, in order to clarify the fundamental phenomena in the film growth, we have only studied the deposition process and film properties in the wide range of the film thickness.

We investigated the morphology of the film surface using AFM. Fig. 2 shows AFM images of ZnO thin

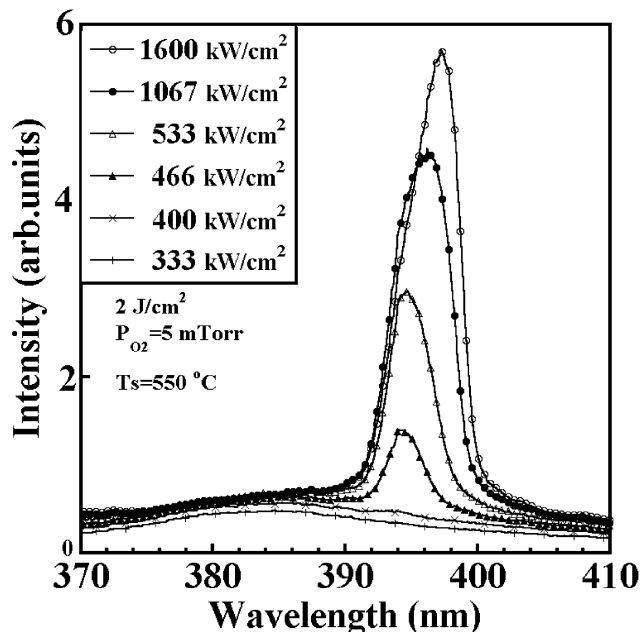


Fig. 3. Dependence of PL spectra on the pumping power.

films deposited on different substrates under optimum deposition condition. The ZnO thin film on α -Al₂O₃ (0 0 0 1) has hexagonal grains with irregular size. The roughness increases with P_{O_2} below 6.67 Pa. When the P_{O_2} exceeds 13.3 Pa, the roughness becomes small and the grain becomes large. These tendencies agree with the result on ZnO films prepared by PLD method [8]. For the T_s , both the roughness and the grain increase with the T_s , because the T_s helps to activate and enhance the migration of grains.

Generally PL emission spectrum from ZnO consists of UV component at approximately 380 nm due to the transition from the conduction band to the valence band and green–yellow emission at approximately 510 nm due to the transition between the donor level and the acceptor level. However, the green–yellow emission spectra were too weak to recognize in this study, because defects in the ZnO was relatively small. In a previous paper, it was demonstrated that the green emission could not detect due to low defect states in the films [12]. Fig. 3 shows PL spectrum obtained from the ZnO thin film deposited on α -Al₂O₃ (0 0 0 1) under optimum deposition conditions. Below the pumping power of 400 kW/cm², weak and broad emissions centered at approximately 382 nm were observed, which are attributed to the spontaneous emission from the free exciton. At the pumping power over 466 kW/cm², the emission peak at approximately 395 nm appeared. This PL spectrum with longer wavelength than that of the spontaneous free exciton emission peak abruptly increases with the pumping power. This rapid increase is due to the

exciton–exciton scattering process, in which one of two excitons obtains energy from the other and scatters into a higher exciton state. The ZnO thin films deposited on α -Al₂O₃ (0 0 0 1) showed the strong increase of stimulated emission, while the other films grown on amorphous substrates showed only a single broad emission at approximately 382 nm even at the high pumping power. The threshold for the stimulated emission at approximately 395 nm is 466 kW/cm² in this PL measurement. The thresholds for the stimulated emission are different depending on deposition methods. Epitaxial films with the hexagonal nano-crystal grown on Al₂O₃ (0 0 0 1) using laser MBE method have a threshold of 24 kW/cm² [11]. The threshold of 380 kW/cm² was reported for polycrystalline films deposited on the amorphous quartz substrates by PLD, while ZnO thin films grown on the glass by the same method showed the high threshold of 2387 kW/cm² [8,12]. The difference of the threshold depends on the methods of the film growth and the measurement of PL emission spectra. In practical optical applications small threshold of the stimulated emission is preferable.

4. Conclusion

ZnO thin film deposition using PLD is discussed. The high quality ZnO thin films were obtained under the deposition condition (2 J/cm², 0.67 Pa, 550 °C). The PL spectrum at approximately 395 nm of the ZnO thin films deposited on α -Al₂O₃ (0 0 0 1) rapidly increased at the pumping power over 466 kW/cm². The results in the experiment will provide information on deposition conditions, for the higher quality films and fabrication of the optoelectronic devices.

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