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Characteristics of ZnO Thin Films Grown on p-type Si and Sapphire Substrate by Pulsed Laser Deposition

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Abstract - ZnO thin films on (100) p-type Si and sapphire substrates have been deposited by a pulsed laser deposition technique using an Nd:YAG laser with a wavelength of 266 nm. The influence of the deposition parameters such as oxygen pressure, substrate temperature and laser energy density on the properties of the grown films was studied. The experiments were performed for substrate temperatures in the range of 200~500^{0}C and oxygen pressure in the range of 100 ~ 700 sccm. All of the films grown in this experiment show strong c-axis orientation with (002) textured ZnO peak. With increasing substrate temperature, the FWHM (full width at half maximum) and surface roughness were decreased. In the case of using sapphire substrate, the intensity of PL spectra increased with increasing ambient oxygen flow rate. We investigated the structural and morphological properties of ZnO thin films using X-ray diffraction (XRD), scanning electron microscopy (SEM) and atomic force microscopy (AFM).

Keywords: Nd:YAG laser, Pulsed Laser Deposition, p-type Si, sapphire, oxygen flow rate

1. Introduction

ZnO has a wide direct band-gap (3.37 eV) with a hexagonal crystal structure ($a = 3.2495 \times 10^{-10}$m, $c = 5.2069 \times 10^{-10}$m) of wurzite and a high exciton binding energy (60 meV), which allows efficient UV emission from the exciton, making it suitable for UV laser-emitting devices [1-2]. Moreover, ZnO is thermally and chemically stable in air. It is an attractive material for many applications, such as in the case of SAW (Surface Acoustic Wave) device, transparent electrode, optoelectronic devices and so on [3-8]. Despite these excellent advantages, the realization of optical devices based on ZnO has not yet been reported, because it is difficult to achieve p-type ZnO films. The properties of ZnO thin films are greatly influenced by not only the grown methods, such as spray pyrolysis, metal organic chemical vapor deposition (MOCVD), laser molecular beam epitaxy (LMBE), reactive thermal evaporation and sputtering, but also the growth and post-treatment parameters, especially thermal annealing [9-14].

Laser technology has drawn considerable interest to the use of lasers for the processing and manufacturing of materials [15], not only making the manufacturing processes simpler and more economical but also providing a unique means of improving the surface properties of materials. The application of laser ablation, laser processing and laser surface treatment have been widely used for the synthesis and characterization of nanomaterials and film deposition [16-18].

The PLD technique has several advantages for the deposition of semiconductor thin films, such as Stoichiometric transfer of material from the target to the substrate, relatively low substrate temperature and less demanding vacuum condition with respect to other more expansive deposition techniques.

Thin films of ZnO grown by PLD, as well as several other deposition techniques, typically exhibit preferred orientation with the c-axis (002) perpendicular to the substrate.

ZnO has generally grown on GaAs, sapphire and Si substrate. But in the case of using GaAs substrate, it is difficult to deposit the films epitaxially due to a different thermal expansion coefficient.

In this study, we have investigated the structural characteristics and surface morphology of ZnO thin films on (100) p-type Si and sapphire substrate with the function of substrate temperature and partial oxygen pressure using a 4th harmonic Nd:YAG laser .

2. Experiment

A Quantel BrillantB Q-swithced 4th harmonic Nd:YAG laser (λ=266 nm) with a fluence of about 0.2 J/cm^2 and a repetition rate of 10 Hz has been used to deposit ZnO thin films. The laser beam pulse width was 3.5 ns, and the pulse repetition rate was 10 Hz. The chamber was evacuated initially to 10^{-6} Torr with the oil diffusion pump, and then gaseous O_2 was introduced to various flow rates using a

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mass flow controller (MFC). After the deposition was completed, the film was spontaneously cooled to room temperature using injected O_2 gas.

Targets used in this study to deposit thin films were prepared from High Purity Chemicals Inc. with a purity of 99.99%. The p-type (100) Si and sapphire substrates were 40 mm away from the target at variable temperatures of 200 ~ 500^{0}C during deposition. The target was rotated at a constant speed of about 4 rpm for the laser beam to be irradiated on a different area.

Prior to the film growth, the substrates were cleaned to remove organic particles in an ultrasonic bath with acetone and methanol for 10 minutes, respectively, and then dried by an N_2 gun.

Films were characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), and atomic force microscopy (AFM).

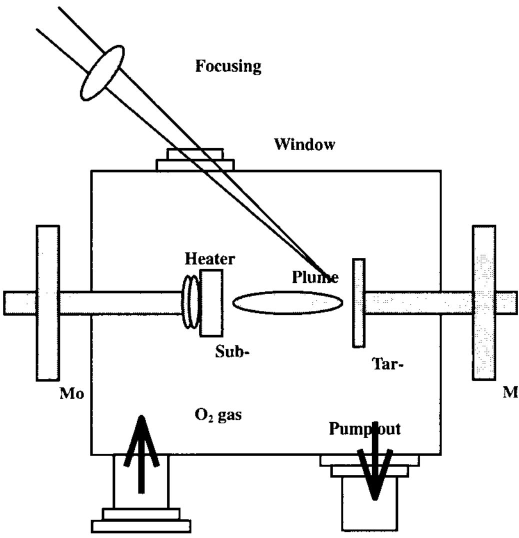

Fig. 1 A schematic illustration of the Pulsed Laser System

3. Results and Discussion

The role of oxygen flow rate, substrate temperature, and laser fluence on the deposited ZnO thin film quality was mainly assessed by investigating the position and FWHM value of the (002) XRD reflection line. In this experiment, the optimum substrate temperature and laser fluence was 400^{0}C and 0.2 J/cm^2, respectively. Also, the optimum oxygen flow rate was 300 sccm. Fig. 2 shows the full width at half maximum (FWHM) value of the rocking curve of (002) peaks of the PLD ZnO thin films in the 2θ mode deposited on p-type (100) Si substrate with structural characteristics as functions of deposition oxygen flow rate and deposition temperature. The ZnO films were grown with c-axis orientation. The (002) and (101) diffraction peak of the ZnO films deposited at substrate temperature of 200^{0}C were prominent. In the XRD spectra, the (101) peak related to the oxygen deficiency appears at around the (002) peak. This indicates insufficiency of thermal energy, which is needed to combine zinc and oxygen with stoichiomety. At above 400^{0}C the FWHM value inclined to increase. It is thought that the crystallinity of ZnO thin film was decreased due to excessive contents of zinc with a melting temperature of 423^{0}C comparing to that of oxygen.

The (002) textured film must be formed in an effective equilibrium state giving enough surface mobility to impinge atoms under the condition of substrate temperature above 200^{0}C. A tiny (400) peak and a couple of peaks belonging to the p-type Si substrate can also be seen. As shown in Fig. 2 (a), with increasing substrate temperature, the FWHM value is decreased signifying that the crystallinity of ZnO thin films is improved with increasing substrate temperature. The FWHM value of 2θ values was related to the grain size of the film. The smaller the FWHM value means the larger the grain size, and the better crystal quality of the entire film. In the vicinity of 300 sccm of oxygen flow rate, as shown in Fig. 2 (b), a more uniform distribution of the various constituents of the ablation plasma with a beneficial effect on the grown film quality can be assured. However, an oxygen flow rate that is too high can drastically reduce the deposition rate and degrade the film quality. The FWHM value of the deposited ZnO thin films below oxygen flow rate of 300 sccm is inclined to decrease. However, above 300 sccm it is increased. In general, an improvement of crystallinity under relatively low oxygen partial pressure is caused by quantitative increment of oxygen radical and reduction of porosity inside the film. In this case, abundant oxygen radical occurred by reaction of ambient oxygen in the vicinity of the laser irradiated target surface, resulting in an improvement of crystallinity. It has been suggested that a relatively high oxygen pressure can ensure a more uniform velocity distribution of the various constituents of the laser plume with a beneficial effect on the grown film quality. However, oxygen pressure (> 400 sccm) that is too high can drastically reduce the deposition rate and slow down the incoming atoms and radical to energies where the surface mobility is too low to promote high-quality crystallinity [19].

Fig. 3 (a) and (b) show the SEM photographs of ZnO thin films grown by PLD. Fig. 3 (a) exhibits a rough surface morphology of ZnO thin film deposited at 200^{0}C. The surface has porosity caused by oxygen deficiency and insufficiency of thermal energy to combine zinc and oxygen. In Fig. 3 (b), the ZnO film seems to be smooth and contains uniform grains.

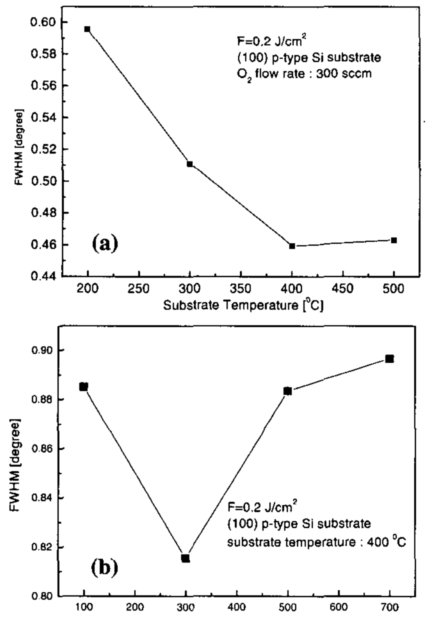

Fig. 2 The FWHM value of ZnO (002) rocking curves as functions of oxygen flow rate (a) and substrate temperature (b) (Laser fluence=0.2 J/cm^2)

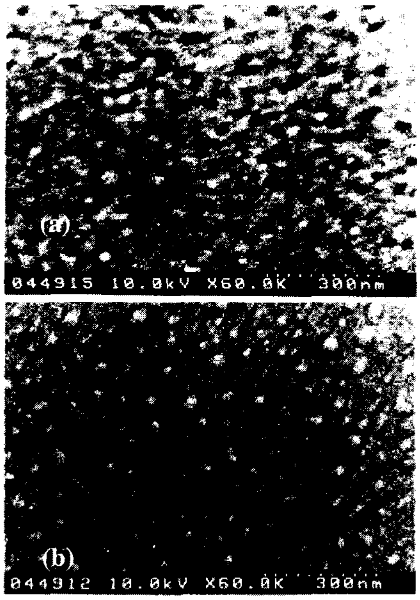

Fig. 3 The SEM photographs of ZnO thin films deposited on p-type (100) Si at substrate temperature of (a) 200^{0}C (b) 400^{0}C (Laser fluence=0.2 J/cm^2, O_2 flow rate = 300 sccm)

The influence on substrate temperature is summarized in two ways. First, high substrate temperature can offer more kinetic energy for mobility of particles on the surface to achieve better crystalline growth. It helps Zn and O to combine with a proper composition. Second, the supply of thermal energy to substrate can accelerate the reaction of oxygen ambient and the substrate, resulting in the increase of deposition rate. On the other hand, at extremely high laser fluence such as 0.8 J/cm^2, the ablation plume occupied with a relatively large and irregular particle or radical could not reach the substrate. So films were hardly deposited, which was clear from AFM and PL measurements. The optimal laser fluence to ablate the target with crystallinity was 0.1 through 0.2 J/cm^2.

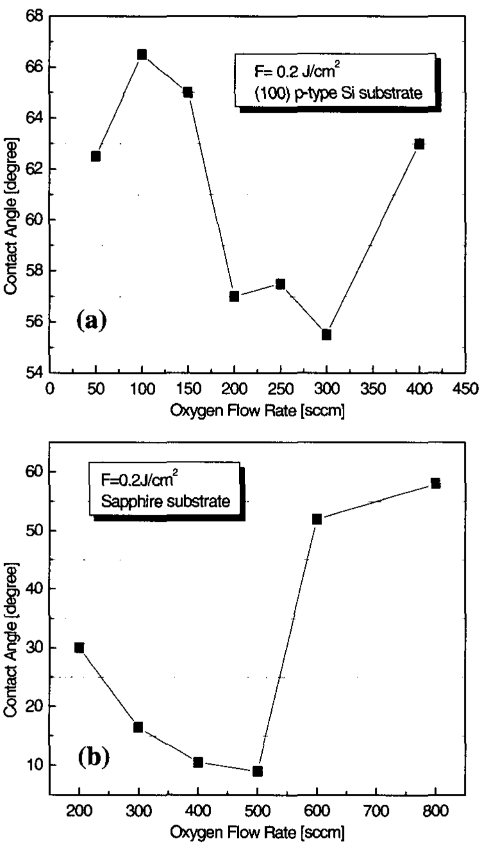

Fig. 4 The graphs showing the alteration of contact angle as a function of the oxygen flow rate the ZnO thin films deposited on (100) p-type Si (a) and sapphire substrate (b). (Laser fluence=0.2 J/cm^2, substrate temperature=400^{0}C)

Fig. 4 represents the alteration of contact angle of the deposited ZnO thin films on both substrates. Contact angle is closely related to surface adhesion. Generally, contact angle is inversely proportional to surface adhesion. Therefore, the ZnO thin film having small contact angle is well adhered to the substrate. As mentioned before, the FWHM of the deposited ZnO thin film on (100) p-type Si has a minimum value at the oxygen flow rate of 300 sccm. At 300 sccm, the contact angle is the smallest value of 55° and it corresponds to the result of FWHM. In the case of using sapphire as a substrate, it has a minimum contact angle at oxygen flow rate of 500 sccm. It is well known that ZnO displays three major PL peaks: a UV near-band-edge emission peak at around 380 nm, a green emission peak at approximately 510 nm and a red emission peak at around 650 nm. Moreover, it is accepted that the green and red emissions are associated with the deep level formed by oxygen vacancies or interstitial Zn [20].

Fig. 5 exhibits the photoluminescence (PL) spectra of ZnO thin films deposited on sapphire substrate at different oxygen flow rates. The ZnO thin films display intensive green emission PL peaks as shown. Both UV and red emission peaks with high intensity were not obtained in this experiment. It is thought that this PL peak with deep level emission was related to the concentration of the inner defects. This indicates that annealing is required to achieve the high quality ZnO thin film. Also, the intensity of PL spectra amplified with increasing ambient oxygen flow rate. The peak is slightly red-shifted at a higher oxygen flow rate (above 500 sccm). The red shift has been preciously reported and is attributed to a shift in the origin of the PL from P_2 band to P band [21].

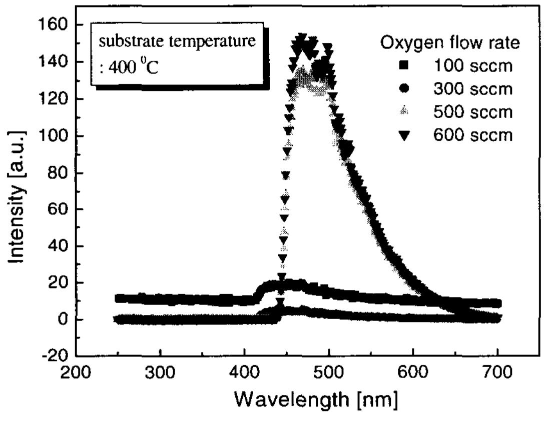

Fig. 5 Photoluminescence spectra obtained from ZnO thin films deposited on sapphire substrate with a function of oxygen flow rate (Laser fluence=0.2 J/cm^2, substrate temperature=400^{0}C)

4. Conclusions

The ZnO thin films were deposited on p-type (100) Si and sapphire substrates using a 4th harmonic Nd:YAG laser. All of the films grown in this experiment showed strong c-axis orientation with (002) textured ZnO peak as the result of XRD measurement. With increasing substrate temperature, the FWHM and surface roughness were decreased. However, above 500^{0}C the surface roughness was increased somewhat due to difficulty in combining zinc and oxygen with stoichiomety. Moreover, at a fixed substrate temperature of 400^{0}C the crystallinity of ZnO thin films deposited at oxygen flow rates less than 300 sccm was improved. The FWHM of the deposited ZnO thin films on (100) p-type Si has a minimum value at the oxygen flow rate of 300 sccm. At 300 sccm, the contact angle is the smallest value of 55° and it corresponds to the result of FWHM. Above 300 sccm, with increasing the oxygen flow rate, it is decreased. In the case of using sapphire as a substrate, the intensity of PL spectra increased with increasing ambient oxygen flow rate.

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