Thin Solid Films 414 (2002) 170–174

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Effect of the growth temperature on ZnO thin films grown by plasma enhanced chemical vapor deposition

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Received 10 April 2001; received in revised form 10 December 2001; accepted 21 May 2002

Abstract

A preferred oriented (0 0 2) ZnO thin films have been grown on Si (1 0 0) substrate via plasma enhanced chemical vapor deposition using diethylzinc and carbon dioxide as reactant sources. In this paper, the dependence of the quality of the ZnO thin film on the growth temperature is studied. A polycrystalline ZnO thin film with a *c*-axis-orientated wurtize structure is obtained at a growth temperature of 230 °C. X-ray diffraction shows that the full width at half maximum (FWHM) of (0 0 2) ZnO, located at 34.42°, is approximately 0.26°. A pronounced exciton absorption peak is observed in the absorption spectrum. The photoluminescence (PL) spectra show a strong ultraviolet (UV) band emission approximately 3.26 eV with a weak emission related to deep-level defects, implying that the ZnO thin films are nearly stoichiometric. The FWHMs of the PL spectra become narrower with increasing growth temperature. The origin of the UV band is from free exciton recombination, testified by the temperature dependent PL spectra in the range of 81–581 K.

PACS: 81.15.Gh; 78.66.Hf; 78.70.Ck; 78.55.Et

Keywords: Zinc oxide; Plasma processing and deposition; Luminescence; Organometallic vapor deposition

1. Introduction

ZnO is a wide direct band gap semiconductor with a large exciton binding energy of 60 meV at room temperature. It has several applications such as device for surface acoustic waves, ferro-electric memories, transparent windows for a solar cell and in the blue-ultraviolet (UV) optical emission devices. Recently the UV emission of ZnO at room temperature has been paid a great attention since this may provide storage with higher density information [1]. To obtain high quality ZnO thin films a variety of techniques have been applied such as molecular beam epitaxy [2,3], metal-organic chemical vapor deposition [4], magnetron controlled sputtering [5,6] and pulsed laser deposition [7,8]. In this paper plasma enhanced chemical vapor deposition (PECVD) is employed to prepare ZnO thin films from mixtures of diethylzinc (DEZ) and carbon dioxide (CO_2).

ZnO thin films can be prepared at low temperatures, even at room temperature, by PECVD using DEZ and CO_2. This will avoid impurity redistribution at high temperature which reduce the different thermal expansion between epilayer and substrate, and make it possible for ZnO thin films to be prepared on organic optoelectronic materials. In order to look for the optimal temperature for growth of ZnO thin films, the dependence of the quality of thin films on substrate temperature, ranging from 300 to 550 K is studied by X-ray diffraction (XRD) optical absorption (OA) spectrum and photoluminescence (PL) spectra analysis. A preferred oriented ZnO thin films on Si substrate are obtained at 503 K. To our knowledge, there are few papers dealing with the growth of ZnO thin films on a Si substrate [9–11], and in particular, the growth of ZnO thin film on a Si substrate via PECVD.

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PII: S0040-6090(02)00491-1

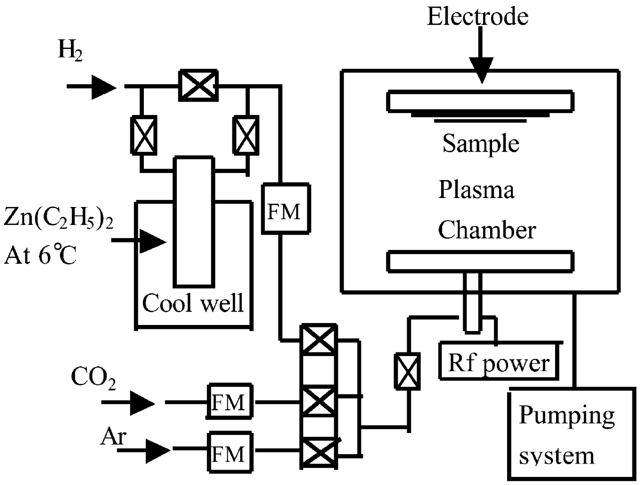

Fig. 1. Schematic diagram of the PECVD.

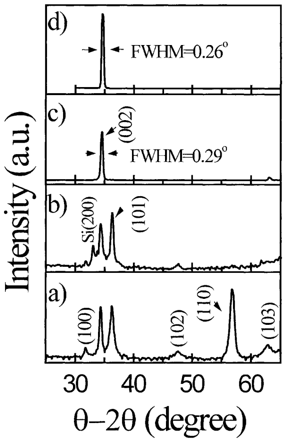

Fig. 2. XRD patterns of the ZnO thin films grown on Si (1 0 0) substrates prepared at different growth temperature: (a) 373 K; (b) 413 K; (c) 443 K; (d) 503 K.

2. Experimental procedure

ZnO thin films are grown by PECVD from a mixture of DEZ and CO_2 gas. Fig. 1 shows a schematic diagram of the PECVD system. The gas flow rates are controlled by different gas flowmeters. The DEZ source is packed in a steel cylinder cooled well to 6 °C by a CW-1 type fine controlled temperature semiconductor device. The high pure hydrogen is used as carrier gas for carrying DEZ source into the reactive chamber. CO_2 does not react with DEZ at room temperature, and can be blended adequately with DEZ before they enter the plasma chamber. The Si substrates are chemically treated by a standard Radio Corporation of America Cleaning process [12]. The background pressure is less than 4×10^{-4} Pa. Sequentially argon and hydrogen are filled into the plasma chamber. After the Si substrate is heated, radio frequency (rf) power is launched into the chamber. The argon and hydrogen plasmas generated by the rf in the plasma chamber to clean the Si surface. The substrate temperature is measured by a copper–constantan thermocouple.

Generally the quality of ZnO thin films depends strongly on the substrate temperature [13,14]. To demonstrate this dependency and to optimize the experimental parameters, a set of samples were prepared with different substrate temperatures. Typical growth conditions are listed in Table 1.

The crystalline quality of the ZnO layers is examined by XRD using a rotating anode X-ray diffractometer using CuKα1 radiation of $\lambda = 1.54$ Å. The OA spectrum is measured by an UV-360 Recording Spectrophotometer (Shimadzu) at room temperature. A deuterium lamp was the light source with the wavelength range of 200–460 nm. The signals were detected by a R_{456}-type photoelectric multiplier with a high resolution of 0.1 nm. The PL spectra are measured using an UV Labran Infinity Spectrophotometer, excited by a continuous He–Cd laser at 325 nm with a power of 50 mW. The temperature dependent PL spectra are obtained using the 325 nm line of a He–Cd laser and a PL microprobe measurement system (J-Y company, French). Measurements below room temperature were taken in the range of 81–581 K by placing the sample cells in a cryogenic unit.

3. Results and discussion

Fig. 2a–d shows the XRD of the ZnO thin films prepared by PECVD at different substrate temperatures with a fixed gas flow rate ratio of $Zn(C_2H_5)_2$ to CO_2 of 4:5. For the sample A which was prepared at 373 K,

Table 1
Deposition conditions of ZnO thin films

Sample	Substrate temperature (K)	(rf) Power (W)	GFRR of $Zn(C_2H_5)_2$ to CO_2	Gas flow rate of argon (sccm)
A	373	35	4:5	4
B	413	35	4:5	4
C	443	35	4:5	4
D	503	35	4:5	4

GFRR, the gas flow rate ratio of $Zn(C_2H_5)_2$ to CO_2.

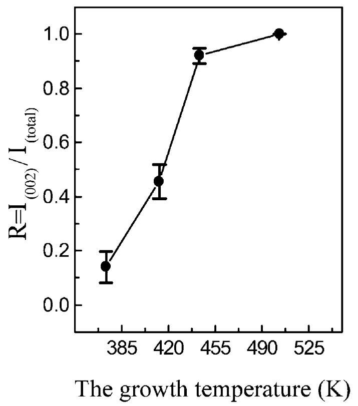

Fig. 3. The dependence of the diffraction intensity ratio of the ZnO (0 0 2) peak to all the peaks on the substrate temperature, $R = I_{(002)}/I_{total}$ (see text).

several diffraction peaks due to ZnO crystal grains occur with different orientations, as shown in Fig. 2a. The intensity of the diffraction peak of (0 0 2) ZnO increases, and the diffraction peak of (1 1 0) ZnO disappears as the substrate temperature is increased. When the growth temperature reaches 443 K, the diffraction peak of (0 0 2) ZnO increases. A preferred orientation of (0 0 2) is obtained when the growth temperature reaches 503 K, as shown in Fig. 2d. The relative number of crystal oriented in a certain direction could be related to the area under the XRD peak, representing that reflection. Thus, the ratio of the diffraction intensity of the (0 0 2) ZnO peak to all the peaks was defined (Fig. 3):

$$R = I_{(002)}/I_{total},$$

where the $I_{(002)}$ and I_{total} are the diffraction intensity of (0 0 2) peak and the total of all the peak, respectively; which were plotted as function of the growth temperature is shown in Fig. 3. It is noted that the growth temperature under which to realize a c-axis oriented ZnO thin film is much lower by using PECVD than other reports. It was due to mobility of atoms on the surface was increased. It was well known that a lot of high energy particles in plasma, they would collide with the species that were adsorbed in the surface and exchange the momentum each other. Thus, the mobility of the atoms was enhanced by using PECVD. Moreover, the full width at half maximum (FWHM) of (0 0 2) ZnO at 34.42° decreases significantly with increasing substrate temperature. The FWHMs of samples A, B, C and D are 0.41°, 0.44°, 0.29° and 0.26°, respectively. The mean grain size d is obtained by the Scherrer formula [15]:

$$d = 0.94\lambda/(B\cos\theta), \tag{1}$$

where λ, B and θ are the X-ray wavelength (1.54 Å), the Bragg diffraction angle, and the line width at half maximum of the peak approximately 34.42°, respectively. Correspondingly, the mean sizes of the samples A, B, C and D are approximately 25, 23, 35 and 39 nm, respectively. The lattice constants of ZnO thin films are changed with increasing the growth temperature; which of samples A, B, C and D are $a = 3.244$ Å, $c = 5.218$ Å; $a = 3.242$ Å, $c = 5.212$ Å; $a = 3.238$ Å, $c = 5.198$ Å; $c = 5.198$ Å, respectively (the lattice constants of bulk ZnO are $a = 3.249$ Å and $c = 5.205$ Å). The deviation of lattice constant a and c change in the range of -1.5–3.4×10^{-3} and -1.3–2.5×10^{-3}, respectively, indicating the lattice constants of ZnO thin films are nearly equal to that of the bulk ZnO.

In order to understand the dependence of thin film quality on the substrate temperature, the thin film process must be discussed. The plasma-enhancement technique employs a glow discharge to generate active species such as atoms, ions, molecules or free radicals. The active species decomposed particles are deposited onto the surface of the substrate. And then the species will gain thermal energy from the substrate and diffuse into lattice positions. Additionally, ZnC_2H_5 will decompose due to the thermal reaction:

$$ZnC_2H_5 \xrightarrow{\Delta E} Zn + {}^{\bullet}C_2H_5, \tag{2}$$

where the ΔE is the thermal active energy supplied by the substrate. The ${}^{\bullet}C_2H_5$ ion will be released from the substrate. When the substrate temperature is too low, the Zn and O species with low surface mobilities will be localized at different positions within the substrate. Moreover, Eq. (2) becomes ineffective due to a lack of thermal energy. Thus, ZnC_2H_5 is embedded in the film and adversely affects the film quality. Additionally, at low temperatures, the ambient gases are also adsorbed in the films, limiting the mobility of the reactants and preventing further growth of grains. Thus, the initial crystal nucleus tends to grow in the direction of available

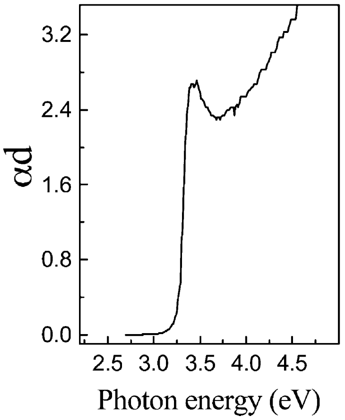

Fig. 4. The optical absorption spectra of ZnO thin film prepared at a temperature of 503 K with the gas flow ratio of $Zn(C_2H_5)_2$ to CO_2 of 4:5.

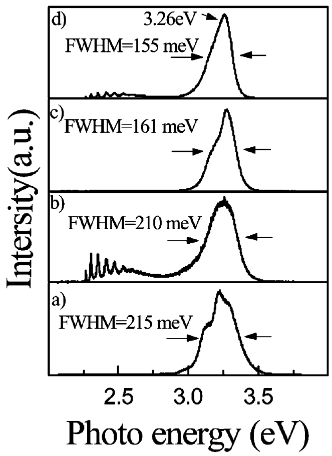

Fig. 5. The PL spectra of ZnO thin films prepared at different growth temperature: (a) 373 K; (b) 413 K; (c) 443 K; (d) 503 K.

reactant flux [16], leading to different orientations of crystal grains and the formation of polycrystalline films. As the substrate temperature is increased the mobility of reactants is increased and gas products will be released from the substrate. The grain size can then increase and the film quality is improved with increasing the substrate temperature.

Fig. 4 shows the optical absorption spectrum of ZnO prepared at 230 °C with a fixed gas flow rate ratio of $Zn(C_2H_5)_2$ to CO_2 of 4:5. Because of the large binding energy of exciton, the exciton effect can be observed at room temperature in ZnO [17]. A pronounced absorption peak of the free exciton, which is located at 3.4 eV, is clearly visible near the absorption edge, as shown in Fig. 4. In general, the exciton effect is closely correlated with film quality. From Fig. 4, we can deduce that high quality ZnO films have been prepared. In terms of exciton absorption peak, we can estimate that the band gap of ZnO is approximately 3.46 eV by using the formula: [18]

$$E_g = P_1 + E_b, \tag{3}$$

where the P_1 and the E_b are the absorption peak of free exciton and the exciton binding energy of 60 meV.

Fig. 5a–d shows the PL spectra of the ZnO thin films prepared by PECVD at different temperatures with a fixed gas flow rate ratio of $Zn(C_2H_5)_2$ to CO_2 of 4:5. The main emission properties are closely dependent on the substrate temperature. One feature of the spectra is the weak-level deep emission correlation to native defects. Another is the strong UV band emission with a low energy tail extending from the near band emission. The UV band consists of the free exciton recombination [17,19,20]. In our experiment, a typical exciton absorption line was observed from the transmission spectrum. The properties of the UV band are closely related to the growth temperature. The FWHMs of the PL spectra become narrow with an increase in growth temperature, as shown in Fig. 4. The FWHMs of the PL spectra decreases from 215 to 155 meV, as the temperature increases from 373 to 503 K. Because the initial crystal nucleus tends to grow in the direction of available reactant flux at low temperature, the distribution of the grain size is larger, and a wider PL spectrum is observed. At high temperatures the grain size becomes larger and more homogeneous, thus the FWHMs of the PL spectra become narrower. It is remarkable that the deep-level emission band at approximately 2.5 eV is weak, although these deep defects are obviously not related to the growth temperature. The most important PL property of ZnO thin films grown by PECVD is the strong UV band emissions at approximately 3.26 eV without the deep-level emission at approximately 2.5 eV at room temperature, indicating a stoichiometric ZnO thin film. The intensity ratio of the free exciton emission to the deep-level emission of the sample B and D is 7 and 17 at room temperature, respectively. However, ZnO thin films which are grown by metal-organic chemical vapor deposition achieve at best a ratio below 1 at room temperature [21]. The deep-level emission is related to oxygen vacancies and interstitial zinc ions [22–24], which are produced due to an insufficient supply of active oxygen during the film growth. The binding energy of an oxygen molecule is 5.16 eV, and it is difficult to break O_2 into active oxygen atoms by using a conventional method at low temperature. In our experiment, the ZnO thin films are formed on the substrate by plasma impact. The reactive zinc species react directly with active oxygen species obtained from CO_2 that is decomposed by the plasma. Thus, it is much easier to obtain stoichiometric films. Another advantage is that the thin films can be prepared at lower temperature. This can reduce native defects. The line shape of the PL spectra shows an asymmetric structure on the low energy side, perhaps caused by defects [25,26]. These defects are reduced with the increase of growth temperature. As a result, the narrow FWHM of the PL spectrum can be obtained.

In order to investigate the origins of UV band, the temperature dependent PL spectra of sample D are measured in the temperature range of 81–583 K. It is remarkable that there is only one UV PL band without any luminescence related to deep-level defects, even at high temperature. The P1 at high energy side and P2 at low energy side are assigned to be the free exciton recombination and the binding exciton recombination, respectively, as shown in Fig. 6a. Thus, a low energy tail is mainly from binding exciton correlated to the defects, as shown in Fig. 5. For clarity, the temperature dependence of the energy peak of P1 is plotted, as shown in Fig. 6b. It follows the free exciton temperature dependence in bulk ZnO [27]. The transition energy position of P1 is simulated by Varshni's empirical

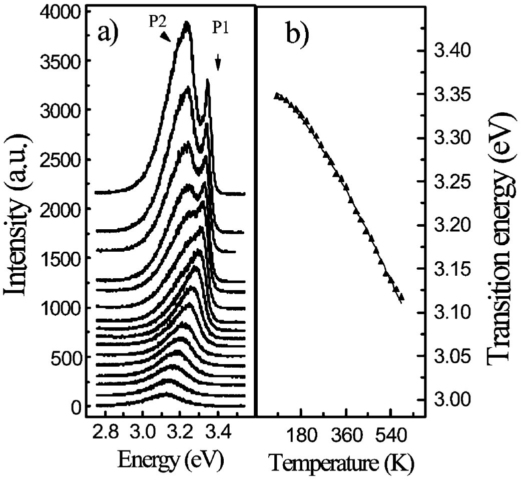

Fig. 6. *Left:* Temperature dependent PL spectra of sample D for temperature 81–581 K (a). *Right:* the dependence of the peak energy (down triangle) on temperature for the free exciton emission (b). The solid line denotes the theoretical simulation by Varshni's empirical function.

function as follow [18]:

$$E_g(T) = E_g(0) - \alpha T^2/(T+\beta), \tag{4}$$

where $E_g(0)$, α and β are fitting parameters. The obtained α, β and $E_g(0)$ are 8.1×10^{-4} eV/K, 512 K and 3.361 eV, respectively.

4. Conclusions

ZnO thin films on Si (1 0 0) substrate are prepared by PECVD using a gas mixture of $Zn(C_2H_5)_2 + CO_2$ at low temperatures. The dependence of the film quality on temperature is studied. ZnO thin films with a *c*-axis-orientated wurtize structure are obtained at a growth temperature of 230 °C. The strong UV band emission with a weak deep defect emission indicates the ZnO thin films are stoichiometric. The origin of the UV band is from free exciton recombination testified by the temperature dependent PL spectra.

Acknowledgments

This work was supported by the Program of CAS Hundred Talents, the National Fundamental and Applied Research Project, the Key Project of the National Natural Science Foundation of China No. 69896260, the National Natural Science Foundation of China, the innovation foundation of CIOFP, Excellent Young Teacher Foundation of Ministry of Education of China and Jilin Distinguished Young Scholar Program.

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