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Effects of thermal annealing on ZnO films grown by plasma enhanced chemical vapour deposition from $Zn(C_2H_5)_2$ and CO_2 gas mixtures

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Abstract
To improve ZnO thin film quality, the ZnO thin films grown on silicon (100) by plasma enhanced chemical vapour deposition from $Zn(C_2H_5)_2$ and CO_2 gas mixtures at a low temperature of 120˚C are annealed in an oxygen ambient at temperature ranging from 600˚C to 1000˚C. X-ray diffraction spectra indicate that ZnO films possess a polycrystalline hexagonal wurtzite structure. Atomic force microscopy results show an increase of ZnO grain size with the increase of annealing temperature. The photoluminescence is closely related to the annealing temperature. The free exciton binding energy deduced from the temperature-dependent PL spectra is about 59 meV for the ZnO film annealed at 900˚C, suggesting that the film quality can be improved by annealing process.

1. Introduction

ZnO is a wide direct band gap ($E_g = 3.4$ eV) semiconductor with a large excition binding energy of 60 meV at room temperature. This is of great interest in short-wavelength opto-electronic device application, such as UV laser, optical wave-guide, and exciton-related devices [1–3]. To produce these devices, many techniques have been used to prepare high quality ZnO films, such as molecular beam epitaxy (MBE) [4, 5], metal organic chemical vapour deposition (MOVCD) [6], magnetron controlled sputtering [7], pulsed laser deposition (PLD) [8] and plasma enhanced chemical vapour deposition (PECVD) [9].

PECVD is a promising technology for depositing ZnO thin films from $Zn(C_2H_5)_2$ and CO_2 gas mixtures. Because the chemical bond energy of oxygen is as high as 5.16 eV, in general, it is difficult for some techniques to break the oxygen–oxygen bond, which will lead to oxygen deficiency during growing procedure. However, it is easy to break the oxygen–oxygen bonds by using the PECVD technique at low temperature. Although the deposition at low temperature is favourable to prevent impurity redistribution induced at high temperature, there is a side effect for low temperature PECVD technique. During the growing process, $Zn(C_2H_5)_2$ is decomposed to ZnC_2H_5 and C_2H_5, then ZnC_2H_5 is further decomposed to Zn and C_2H_5 by the thermal energy. For low temperature, ZnC_2H_5 is not decomposed completely and is easily embedded into the film, in turn, affecting the film quality. Moreover, some zinc and oxygen ions have the low surface mobility due to the low substrate temperature, which is unfavourable to form high quality ZnO films. Post-annealing process just makes up for this drawback. When the film is annealed at high temperature, ZnO bonds undergo a relaxation

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process to cause network reconstruction. So the film quality can be improved through the post-annealing process. High quality ZnO thin film grown by PECVD has been reported [9]. The effect of growth conditions on the film quality has been studied, including substrate temperature and gas flow rate. However, the influences of thermal annealing on the properties of ZnO thin film grown by PECVD have barely been investigated.

In this paper, to elucidate the relation between annealing temperature (T_a) and ZnO thin film properties, a systematic study is presented. The dependence of thin film quality on T_a is studied by x-ray diffusion (XRD) spectra, atomic force microscopy (AFM) and photoluminescence (PL) spectra.

2. Experiment

The ZnO thin films are grown by PECVD from $Zn(C_2H_5)_2$ and CO_2 gas mixtures. The PECVD system and the prepared parameters have been reported in the previous article [9], here, the silicon (001) is selected as substrate, which is kept at 120°C. Prior to growth, the substrate is cleaned by RCA process. The as-deposited sample is cleaved into several pieces, followed by different annealing processes from 600°C to 1000°C in oxygen ambient for 1 h.

The crystalline quality of the ZnO thin films is investigated by the x-ray diffraction (XRD), using a rotating anode x-ray diffractometer with $CuK_{\alpha 1}$ radiation of 1.542 Å. Surface morphology is observed by AFM made by PARK scientific instrument company in America. The room temperature photoluminescence spectra (RT-PL) of the ZnO thin films are measured by using the UV Labran Infinity Spectrophotometer made by JY company in France. The 325 nm line of a He–Cd laser with a power of 50 mW is used as the excitation light.

3. Results and discussion

Figure 1 shows the θ–2θ XRD patterns of the as-deposited ZnO thin film and these films annealed at different temperatures. It is indicated that the films possess a hexagonal wurtzite crystal structure with different orientations of (100), (002), (101), (102), (110) and (103). When the T_a is less than or equal to 700°C, no significant changes are observed in crystalline orientations. However, when the T_a gets to 900°C, the (002) peak almost disappears. Besides the orientational change, the intensities of all peaks increase with the increase of annealing temperature. When the T_a reaches 1000°C, the intensities of XRD peaks obviously decrease. Only the (101) peak exists and the other peaks almost disappear. To calculate the mean grain size of the sample, the Debye–Scherer formula [10],

$$D = \frac{0.9\lambda}{B\cos\theta_B},$$

is employed. Where λ is the x-ray wavelength of 1.542 Å, θ_B is the Bragg diffraction angle, and B is the full width at half maximum (FWHM). For as-deposited sample, the mean grain size is about 21 nm. The mean grain sizes of the samples annealed at 600°C, 700°C and 900°C are 22 nm, 23 nm and 38 nm, respectively. The grain size of ZnO increases with the increase of T_a, which can be understood by considering the ZnO particles merging process induced from thermal annealing. In general, the interface reactions can be easily realized due to the existence of a lot of interface defects for the nanoparticles, which leads to an increase in chemical potential to enhance interface reaction. For ZnO nanoparticles, there are many zinc or oxygen defects (dangling bonds) at the grain boundaries. These defects are favourable to the merging process, as a result of this, to form large ZnO grains. So it can be observed that the intensities of the diffraction peaks increase with the increase of annealing temperature. For the sample annealed at 900°C, the crystal lattices a and c calculated from x-ray patterns are 3.250 Å and 5.250 Å, respectively, which are similar to those of standard ZnO film. However, as the T_a increases to 1000°C, the defects related with oxygen vacancies are formed resulting in an increase of voids, so the mean grain size decreases to 25 nm. These defects cause a decrease in UV-band edge emission and an increase in visible emission related with oxygen vacancies, which will be discussed later.

To testify the dependence of the mean grain size on the T_a, the surface morphology of ZnO thin films annealed at different temperatures are measured. Although we could not clearly distinguish individual nano-particles, the varying trend of the mean grain size with the increase of T_a can be observed, as given in figure 2. For the as-deposited sample, the surface of the thin film is smooth. However, the surface roughness increases and the mean grain size becomes large with the increase of T_a due to the interface reaction. When the T_a gets to 900°C, the mean grain size reaches the maximum, then the grain size decreases as the T_a increases to 1000°C. The AFM results agree well with the results of the XRD.

To evaluate the effect of the annealing temperature on film quality, the PL spectra of ZnO thin films annealed at different temperatures are measured, as shown in figure 3. The PL spectra can be divided into two regions. One is located at UV region from exciton emission [11, 12]. The other is located at visible region (green band) from deep level (DL) defect emission associated with oxygen vacancies or zinc interstitial in ZnO lattices [13, 14]. As the annealing temperature increases from 600°C to 900°C, the PL integrated

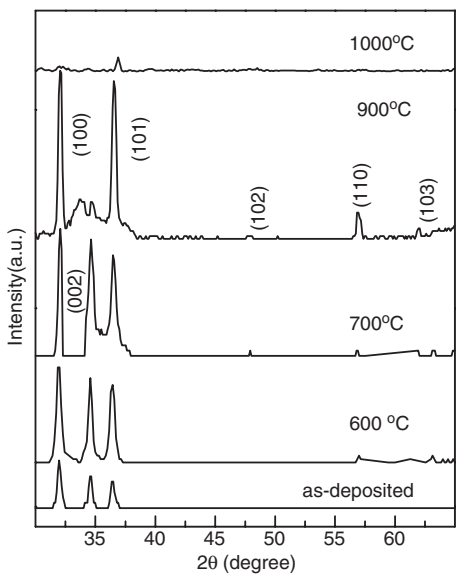

Figure 1. XRD spectra of the ZnO thin films annealed at different temperatures.

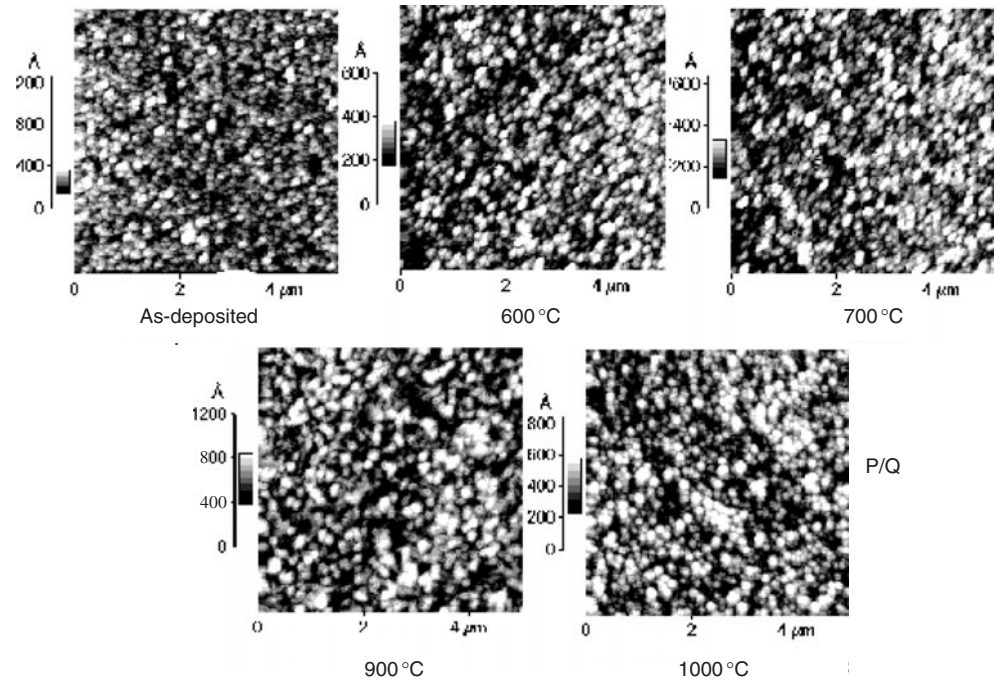

Figure 2. AFM images ($5 \times 5\,\mu m^2$) of ZnO thin films annealed at different temperatures.

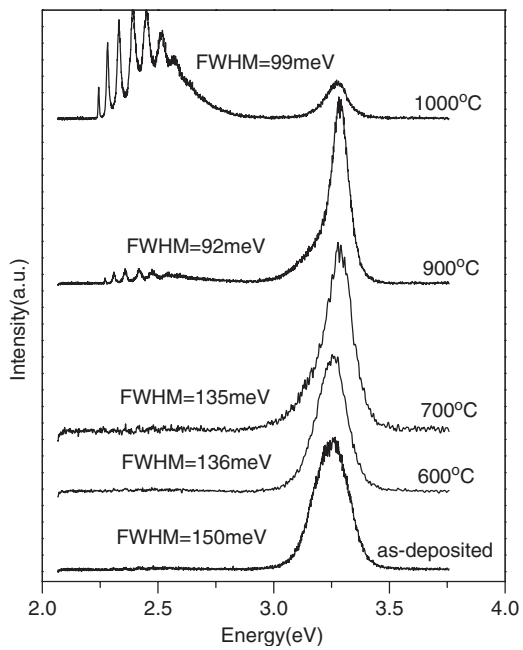

Figure 3. The PL spectra of ZnO thin films at room-temperature versus annealing temperatures.

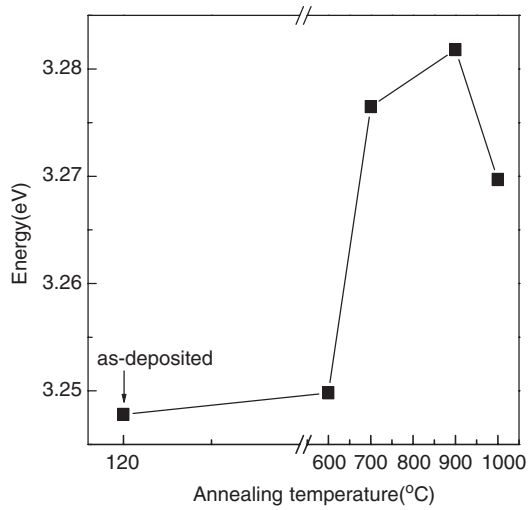

Figure 4. The PL peak positions of the ZnO thin films versus annealing temperatures.

intensity of the exciton emission increases remarkably and the FWHM decreases gradually with the increase of annealing temperature. For the sample annealed at 900˚C, the strongest UV exciton emission with the FWHM of 92 meV is observed around 3.28 eV. However, the DL emission is weak, the ratio of the exciton emission intensity to the DL emission intensity is 20, indicating that the high quality thin film has been obtained. From figure 3, it can be observed that the FWHM decreases with the increase of T_a from 600˚C to 900˚C. The PL spectrum in the UV region consists of the free exciton and the bound exciton emission correlated with defect concentration. The bound exciton emission overlaps with the free exciton emission. As the T_a increases from 600˚C to 900˚C, the interface reaction enhances and the nanoparticle merging process expedites with the increase of annealing temperature, which results in the decrease of defect concentration with a slight increase of grain size. So the bound exciton emission decreases and free exciton emission increases, as a result, the FWHM becomes narrow. Simultaneously, the PL peak at UV-region has a slight shift to high-energy side, as shown in figure 4. For the sample annealed at 1000˚C, the UV emission obviously decreases and the DL emission increases observably. At high temperature, a lot of DL defects are induced from high

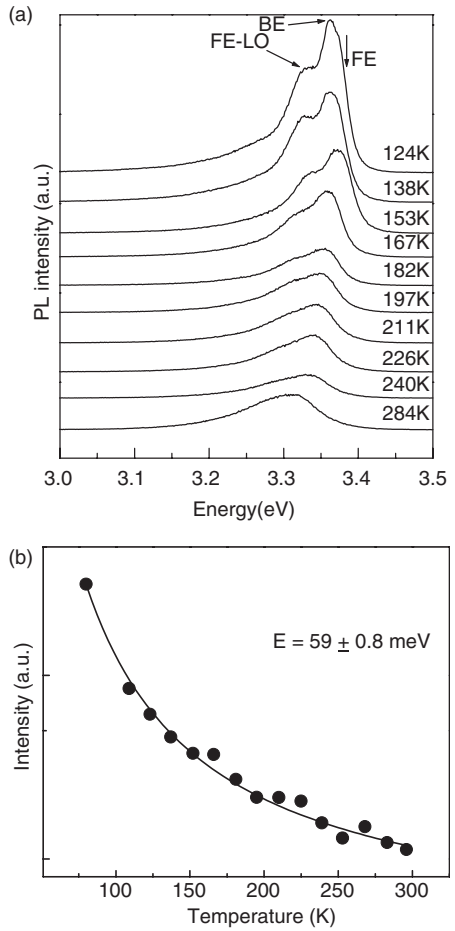

Figure 5. (*a*) The UV PL spectra as a function of temperature from 80 to 300 K; (*b*) the integrated PL intensity dependence on temperature. The circles are experimental data, and the solid curve is the fit line.

thermal fluctuation energy, as confirmed by XRD results. So the strong green band emission and the bound exciton emission increase obviously. As a result of this, the position of PL peak at UV-region has a red shift and the FHWM of PL at UV-region has a significant increase.

To identify the ZnO film annealed at 900˚C with high quality, the UV PL spectra as a function of temperature from 80 to 300 K were measured, as given in figure 5(*a*). As temperature increases, the PL peak moves to lower energy from 3.36 to 3.28 eV and the FWHM increases obviously. The PL integrated intensity decreases with temperature as displayed in figure 5(*b*). The integrated intensity data are fit to the form [15, 16]:

$$I(T) = I_0 \left[1 + D \exp\left(-\frac{E}{k_B T} \right) \right]^{-1},$$

where E is the exciton binding energy and D contains rations of optical-collection efficiencies and is effective between the unbound and bound states. The calculated temperature dependence is shown by the solid curve. A fine fit to the data get $E = 59 \pm 0.8$ meV, which is close to the reported free exciton binding energy of ZnO crystal, suggesting that the high quality ZnO film can be obtained by annealing process.

4. Conclusions

The film quality of ZnO grown on silicon (100) by PECVD at a low temperature of 120˚C can be improved by using post-annealing method. As the T_a increases from 600˚C to 900˚C, the merging process of ZnO particles enhances with a slight increase of grain size and the DL defect concentration decreases. When the T_a reaches 900˚C, the strongest UV exciton emission with a small FWHM of 92 meV is observed around 3.28 eV. The free exciton binding energy is about 59 meV, suggesting that the high quality film can be obtained. When the T_a is over 900˚C, a lot of DL defects are formed induced from high thermal fluctuation energy, which causes a decrease in UV-band edge emission and an increase in visible emission.

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