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Influence of annealing atmosphere on ZnO thin films grown by MOCVD

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Abstract

ZnO films were deposited on *c*-plane sapphire substrates by metal-organic chemical vapor deposition (MOCVD). Annealing treatments for as-deposited samples were performed in different atmosphere under various pressures in the same chamber just after growth. The effect of annealing atmosphere on the electrical, structural, and optical properties of the deposited films has been investigated by means of X-ray diffraction (XRD), atomic force microscope (AFM), Hall effect, and optical absorption measurements. The results indicated that the electrical and structural properties of the films were highly influenced by annealing atmosphere, which was more pronounced for the films annealed in oxygen ambient. The most significant improvements for structural and electrical properties were obtained for the film annealed in oxygen under the pressure of 60 Pa. Under the optimum annealing condition, the lowest resistivity of 0.28 Ω cm and the highest mobility of 19.6 $cm^2 v^{-1} s^{-1}$ were obtained. Meanwhile, the absorbance spectra turned steeper and the optical band gap red shifted back to the single-crystal value.

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Keywords: XRD; Annealing atmosphere; Grain boundary; Oxygen

1. Introduction

ZnO has been of great interest recently because of its wide band gap (3.36 eV) and relatively high exciton binding energy (60 meV) at room temperature (RT) [1]. Besides, ZnO possesses many unique properties for optoelectronic applications such as solar cells [2], photodetectors [3], light emitting diodes (LEDs) [4], acoustic devices [5], and gases sensors, etc. [6]. After optical pumped UV lasing of ZnO films [7], ZnO had received more and more attention from researchers. The ZnO films have been prepared by several methods such as molecular beam epitaxy (MBE) [8–10], sputtering [11,12], ultrasonic spray pyrolysis (USP) [13], and metal-organic chemical vapor deposition (MOCVD) [14–16]. Among them, MOCVD possesses the advantage of growing high-quality films due to its versatility in controlling various thermodynamic interactions. However, certain pre-reaction occurs during the growth process, this may degrades the film's quality. For further applications, the realization of high-quality layers is indispensable.

It is generally accepted that annealing is an effective method to improve the qualities of thin film. Several groups have reported the effect of annealing treatments at different temperature on ZnO film grown by various methods [17–22]. However, the choice of annealing atmosphere and pressure remains controversial and the systematic investigation of the influence of annealing atmosphere on structural and electrical properties of ZnO films grown by MOCVD technique were still limited. In this paper, ZnO films grown by MOCVD were annealed in different atmosphere under different pressure, and the improvement of crystalline, surface morphologies, electrical and optical properties of ZnO layers in terms of the

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thermal annealing conditions were studied. The result confirmed that thermal annealing at 700 °C in O_2 atmosphere under 60 Pa was the most effective condition to achieve high quality ZnO films.

2. Experiment

ZnO thin films were deposited on *c*-plane Al_2O_3 substrates by plasma-assisted MOCVD with a rotating disk vertical reactor. The substrate surface was sequentially degreased in ultrasonic baths of methylbenzene, acetone and ethanol. The base vacuum pressure of our growth chamber was about 2×10^{-4} Pa. Diethylzinc (DEZn) and O_2 were chosen as source of Zn and O respectively. The precursors were introduced into the reactor through separate injectors, which could effectively avoid the vigorous pre-reaction of DEZn and O_2. Details about our MOCVD equipment can be found elsewhere [23].

The ZnO films were deposited at relatively lower temperature (400 °C), during the growing process, the O_2 flow and the chamber pressure were fixed at 200 sccm and 60 Pa, respectively. High-purity Ar was used as carrier gas. The growth time was 30 min for all the samples. In order to investigate the effects of annealing atmosphere, annealing treatments were performed in-situ in vacuum, oxygen under the pressure of 60 Pa, oxygen atmosphere (1 atm), nitrogen under the pressure of 60 Pa, and nitrogen atmosphere (1 atm) at the same temperature (700 °C) for 30 min, respectively.

The surface morphologies of the samples were investigated by AFM with BENYUAN CSPM-2000. The structural properties of ZnO films were determined by XRD with a CuKα radiation (0.15418 nm). The electrical properties were measured by Bio-Rad HL5500 system using Van de Pauw method at RT. The optical absorption spectra were recorded at RT using a Shimadzu UV160 spectrometer.

3. Results and discussions

Fig. 1 shows the AFM surface images of as-deposited sample (a) and that annealed at 700 °C in vacuum for 30 min (b). The scan area is 1 μm × 1 μm. The film surface for as-deposited sample is very coarse with the root mean square (rms) of 30 nm, while the film surface of sample annealed in vacuum at 700 °C is much smoother with the rms of 7 nm. It indicates that the surface morphologies of the film had been greatly improved after annealing. This can be elucidated as follows: high temperature could enhance the migration of the surface atom, which could help the Zn and O atom incorporate on the lattice sites, therefore, the roughness of surface decreased. The same behaviors were observed for the films annealed in other atmosphere.

In order to investigate the effect of thermal annealing on the crystalline of ZnO thin film, an XRD analysis was performed. The results were shown in Fig. 2. Fig. 2 reveals the formation of ZnO polycrystalline with a hexagonal wurtzite structure. No peak from other compounds is detected besides those from ZnO. Before annealing, the spectra show a very strong diffraction peak of ZnO (0 0 2) and a weaker diffraction peak of ZnO (1 0 1), as shown in Fig. 2(a). After annealing, it is obvious that the intensity of ZnO (0 0 2) diffraction peak increased after annealing, as shown in Fig. 2(b)–(d). Meanwhile, the intensity of ZnO (1 0 1) diffraction peak decreased, which indicated that the annealing treatments had improved the crystalline of the films. It is very interesting that considerable changes were observed in the films annealed in oxygen ambient (60 Pa). The reason will be discussed later.

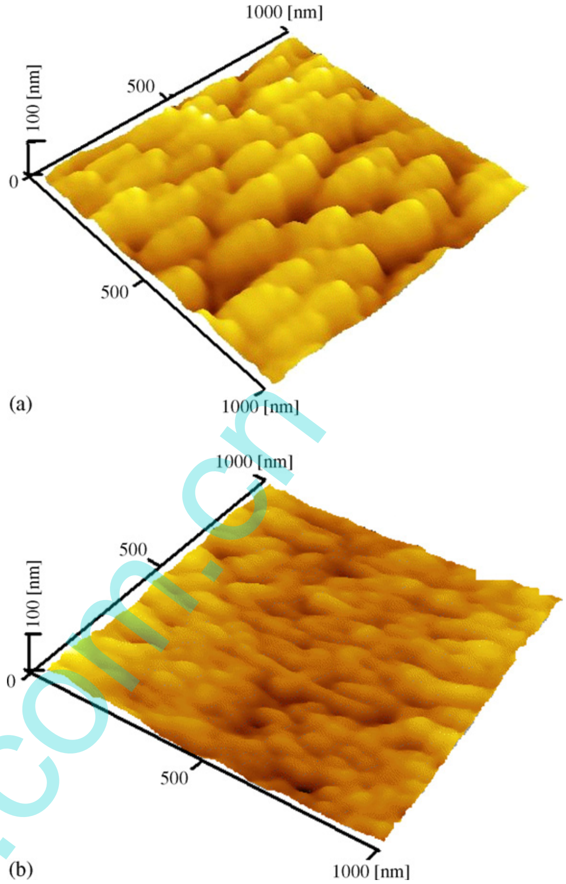

Fig. 1. AFM images of ZnO films. (a) As-deposited. (b) Annealed in vacuum at 700 °C.

Fig. 3 shows the full-width at half-maximum (FWHM) of the (002) diffraction peak according to the annealing condition. For evaluating the mean grain size (D) of the films based on the XRD results, we applied the Scherrer formula [24], $D = 0.94\,\lambda/B\cos\theta$. Where λ, B, θ were X-ray wavelength (0.15418 nm), the FWHM of ZnO (0 0 2) diffraction peak, and the Bragg diffraction angle, respectively.

After annealing, the FWHM of the (0 0 2) peak became smaller than that of un-annealed ones, which indicated that the film crystalline has been improved and the grain size became larger. The grain size increased with the increasing of oxygen pressure up to 60 Pa, but the grain size decreased when the annealing pressure increased further to 1 atm. We must underline that the highest values of grain size occur for films annealed in oxygen under the pressure of 60 Pa. In addition, it is found that after annealing the intensity of the (1 0 1) peak has

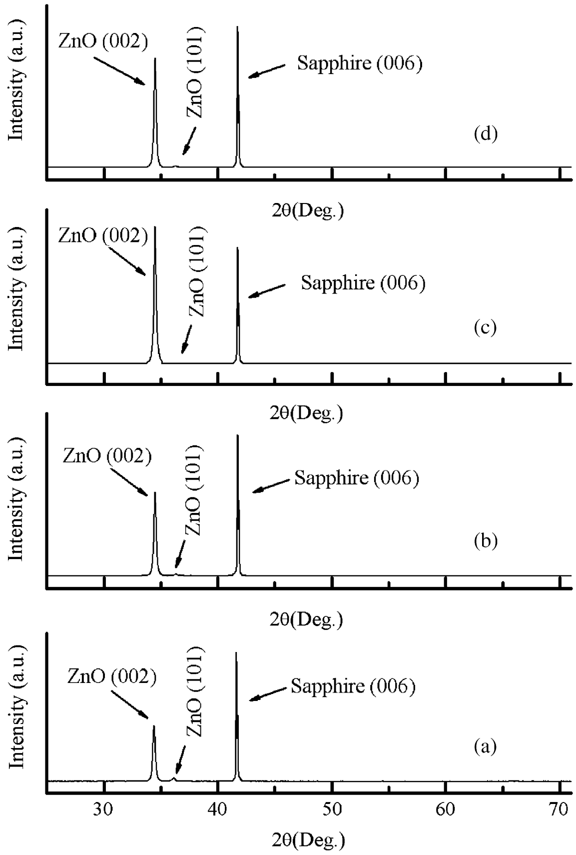

Fig. 2. XRD spectra of ZnO films. (a) As-deposited. (b) Annealed in vacuum at 700 °C. (c) Annealed in oxygen under 60 Pa at 700 °C. (d) Annealed in oxygen atmosphere (1atm) at 700 °C.

greatly decreased, especially for film annealed in oxygen ambient (60 Pa). This also indicated that the crystalline has been improved after annealing. However, the FWHM of the (0 0 2) diffraction peak of ZnO annealed in nitrogen under the pressure of 60 Pa and in nitrogen atmosphere (1atm) were 0.1817° and 0.1819°, respectively, which have changed a little than that of annealed in vacuum, not shown here. From above all, we can conclude that oxygen could affect the crystalline in our annealing treatments.

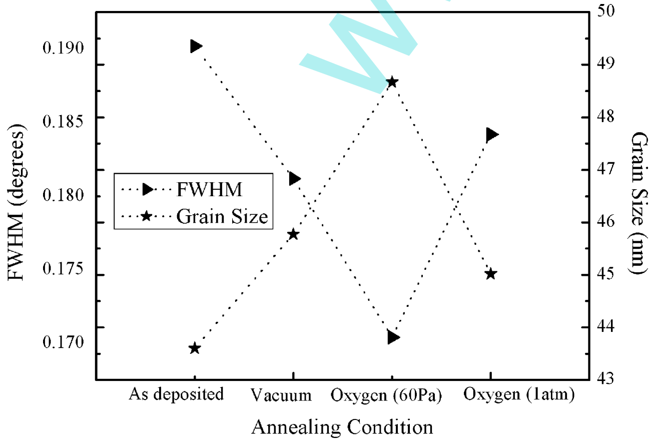

Fig. 3. FWHM and grain size of as-deposited and annealed films (all the samples were annealed at 700 °C).

The electrical parameters of ZnO films were investigated by Hall effect measurement, as listed in Table 1. With the increasing of oxygen pressure, the resistivity decreased, at the same time the Hall mobility increased, they were reached the extremes when the pressure up to 60 Pa. However, the carrier concentration didn’t changed obviously within this range. As the oxygen pressure increased further, the Hall mobility reduced and the resistivity increased. Meanwhile, the carrier concentration sharply decreased. It is well known that the major factor, which influences the mobility, is the scattering effects, including defects scattering, grain boundary scattering, etc. Minami studied the electron conduction mechanisms in ZnO thin films [25]. For undoped film with low carrier concentrations, he observed that the mobility was limited by scattering at grain boundaries. Noticeably, the carrier concentration changed slightly when the annealing pressure varying from base pressure to 60 Pa. It suggested that the major factor, which influences the Hall mobility in this range, is not the defects scattering occurring in the grain, but the boundary defects scattering. The increase of the Hall mobility after annealing in vacuum may attribute to the grain size’s becoming larger, and the decreasing of interfaces between the micro-crystallites, all these are consistent with the XRD results in Fig. 3. Much grain boundary defects were annihilated and the grain size increased because amount of oxygen could be supplied to the film, when the films were annealed in oxygen under the pressure of 60 Pa. However, the mobility and the carrier concentration decreased when the film were annealed in oxygen under higher pressure (1 atm). Sabioni et al reported the grain-boundary might provide a fast path for oxygen diffusion in ZnO [26]. 1 atm is much larger than 60 Pa, under so high oxygen pressure, too much oxygen could diffuse into ZnO film through grain-boundaries, and oxygen at the grain boundaries could act as acceptor states, which act as traps for electrons [27], so the carrier concentration decreased. Further more, excessive oxygen may introduce some new defects and prevent the grain’s incorporating, so the grain boundary scattering will be enhanced. B.X. Lin et al have found that excess oxygen could form new defects associate with oxygen and deteriorate the qualities of the ZnO film [28]. This is consistent with our results. All these factors enhance the scattering, consequently, the Hall mobility remarkably decreased. We also investigated the optical properties of the film (details about the optical properties will be reported later). The photoluminescence (PL) spectra show that, the intensity of deep level emission of ZnO films annealed in oxygen atmosphere (1 atm) dramatically increases than that of the as-deposited sample.

This also suggests that too much oxygen could form new defects in the film. The properties of the films annealed in nitrogen under various pressures were almost the same like that of the films annealed in vacuum. This also indicates that the oxygen play an important role in the annealing treatments process.

The distinct absorption edge existed in both as-prepared and annealed films. After annealing, the shoulder in the absorbance spectra turns steeper. To determine the energy gap, most authors use the model for direct interband transitions: $\alpha h\nu = A\,(h\nu\text{-}E_g)^{1/2}$. Where A is a constant, hν is photon energy, E_g is the optical band

Table 1
Electrical parameters for the ZnO samples obtained from Hall measurements

Sample	Resistivity (Ω cm)	Mobility ($cm^2\ v^{-1}\ s^{-1}$)	Carrier concentration (cm^{-3})
As-deposited	6.26	0.54	1.86×10^{18}
Annealed in vacuum (700 °C)	0.31	14.60	1.36×10^{18}
Annealed in oxygen under 60 Pa (700 °C)	0.28	19.60	1.12×10^{18}
Annealed in oxygen atmosphere (700 °C)	101.70	0. 25	2.40×10^{17}
Annealed in nitrogen under 60 Pa (700 °C)	0.31	14.20	1.40×10^{18}
Annealed in nitrogen atmosphere (700 °C)	0.33	13.90	1.35×10^{18}

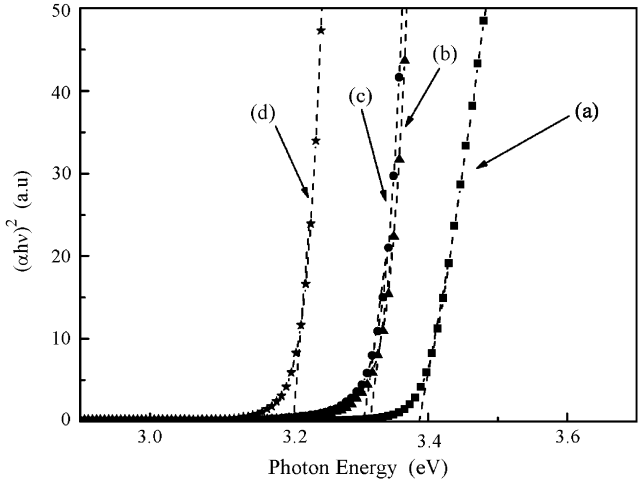

Fig. 4. Plot of $(\alpha h\nu)^2$ vs photon energy ($h\nu$) for ZnO films annealed under various annealing condition: (a) As-deposited. (b) Annealed in vacuum at 700 °C. (c) Annealed in oxygen under 60 Pa at 700 °C. (d) Annealed in oxygen atmosphere (1atm) at 700 °C.

gap, and α is the absorption coefficient. In this approximation, $(\alpha h\nu)^2$ is a linear function of $h\nu$. The E_g value can be obtained by extrapolating the linear portion to the photon energy ($h\nu$) axis in the Fig. 4. The optical band-gap values obtained are summarized in Table 2.

As is shown in Table 2, the band gap energy of the as-deposited film 3.38 eV, which is larger than that of band gap of single crystals ZnO (3.30 eV) [29], the blue shift of the band gap may due to poor crystalline of ZnO thin films grown at relatively lower temperature [30]. It can be easily observed from the AFM pictures that there are some nanostructure grains in the as-deposited film. Furthermore, the grain sizes were without uniformity. After anneal in the oxygen under 60 Pa, the crystalline has been improved (the grains distribute uniformly in the film, and the grain size become larger). Meanwhile, the adsorption edge becomes steeper and the optical band gap returns to 3.30 eV. However, annealing in oxygen atmosphere has narrowed the band gap to 3.21 eV, because too much oxygen could diffuse into the film and result in new defects.

Table 2
Estimated optical band gap of ZnO film

Sample	Estimated optical band gap (eV)
As-deposited	3.38
Annealed in vacuum at 700 °C	3.31
Annealed in oxygen under 60 Pa at 700 °C	3.30
Annealed in oxygen (1 atm) at 700 °C	3.21

4. Conclusion

In summary, ZnO polycrystalline thin films were deposited on sapphire substrates using the MOCVD technique. The influence of annealing process on the quality of film was investigated by annealing treatments in different gases under different pressures. The AFM images indicated that annealing is an effective method to improve the surface morphologies. It was found that nitrogen has little influence on the film annealing; however, oxygen plays an important role on the structural, electrical and optical properties of film. The most significant improvements for structural, electrical, and optical properties were obtained for the film annealed in oxygen under the pressure of 60 Pa. This may be explained by the defects associated with oxygen in the film, proper oxygen could greatly decrease the defects and improve the structural qualities and the grain size become larger, consequently the mobility increased.

Acknowledgements

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