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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 $2 \times 10^{-4}$ 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.

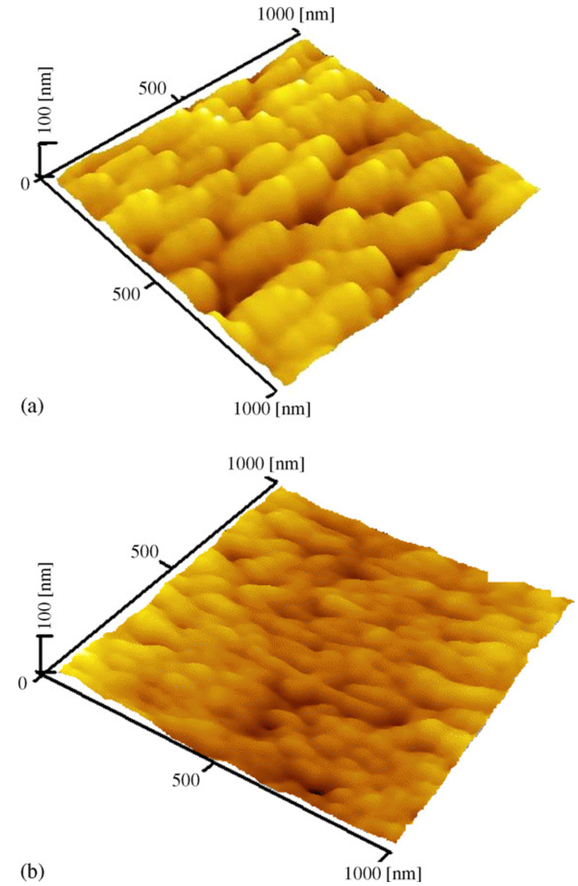


Fig. 1. AFM images of ZnO films. (a) As-deposited. (b) Annealed in vacuum at 700 °C.

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