

Effect of high-temperature annealing on the structural and optical properties of ZnO films

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Abstract

The annealing effect on the optical properties of ZnO epilayers was reported. The ZnO thin films were grown using metal organic chemical vapor deposition method, and annealed in atmosphere at 850 °C for different time periods. Double-crystal X-ray diffraction showed that, after annealing, the density of the edge-dislocations decreased dramatically upon annealing, however, the screw-dislocations were not affected significantly. Strong green photoluminescence was observed in the annealed ZnO films while the as-grown films showed only near band edge emission. The deterioration of the optical properties in the annealed film, however, only occurred near the film surface in a very thin layer.

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1. Introduction

ZnO is well-known as ceramic and phosphor material for decades. The discovery of room temperature ultra-violet (UV) lasing action in 1998 [1,2] triggered worldwide interests in research of ZnO as a promising UV semiconductor laser material to compete with GaN. ZnO has a large exciton binding energy (60 meV) [3], in addition, its band gap energy can be extended to 4.0 eV by adding Mg and narrowed to 2.8 eV by alloying with CdO [4], implying its high potential for use in many applications especially for light emitting devices. Using molecular beam epitaxy, metalorganic chemical vapor deposition (MOCVD), pulse laser deposition and other methods, high quality ZnO layers have been grown and their structural and optical properties have been extensively studied [5–7].

Thermal annealing is a widely used method to improve crystal quality and to study structural defects in materials. For semiconductors, thermal annealing is also used to activate dopants and to alloy ohmic contacts. During an annealing process, dislocations and other structural defects will move in the material and adsorption/decomposition will occur on the surface, thus the structure and the stoichiometric ratio of the material will change. The structural and optical properties are vital for semiconductor devices especially for light emitting devices. It is necessary to study how these properties are affected by thermal annealing. For ZnO films, several researches on thermal annealing have been reported [8–10]. In those researches, X-ray diffraction (XRD) symmetric (002) ω -scan or ω -2 θ scan and photoluminescence (PL) spectroscopy were used to characterize the structural and optical properties of the ZnO samples. It is well known that (002) rocking curves cannot completely reflect the structural quality of ZnO films because it is insensitive to edge dislocations [11]. On the other hand, PL measurement can only provide information from a thin surface layer rather than the whole film due to the large

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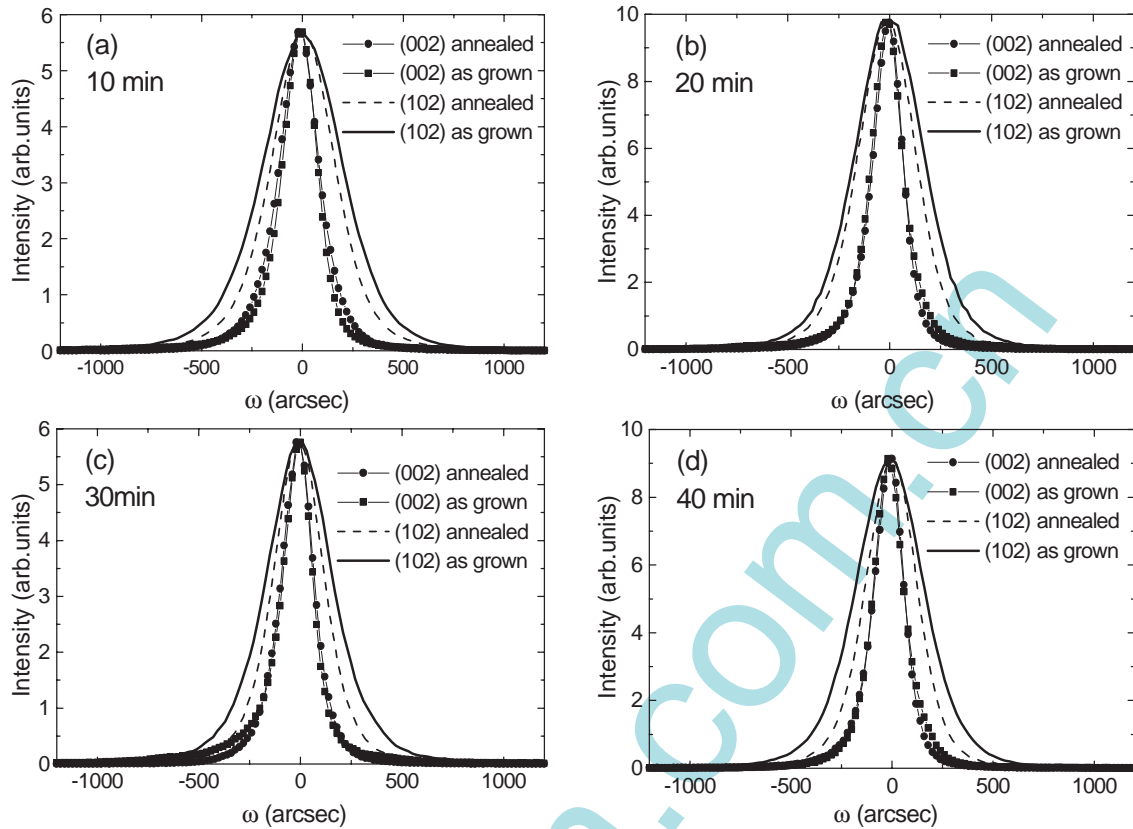


Fig. 1. (002) and (102) rocking curves of the ZnO samples measured before and after annealing. (a) 850 °C annealing for 10 min. (b) 850 °C annealing for 20 min. (c) 850 °C annealing for 30 min. (d) 850 °C annealing for 40 min. All the curves were normalized for plotting purpose.

absorption coefficient of the material for the excitation laser. To understand the effect of thermal annealing on the film properties more precisely, XRD asymmetric scan in skew geometry and etching process are needed. In the present paper we made an attempt to deal with these problems.

2. Experimental details

ZnO films were grown using a homemade vertical atmospheric pressure MOCVD system. Al₂O₃ (001) wafers were used as the substrates. Diethyl zinc and H₂O were used as the Zn and O precursors. The film thickness was about 3.0 μm. Four pieces from a 2-inch ZnO wafer were annealed at temperature 850 °C in atmosphere using a quartz-tube furnace for 10, 20, 30, and 40 min, respectively. Rocking

curves of all as-grown as well as the annealed samples were measured using a double-crystal X-ray diffractometer (QC200, BEDE Instruments, UK). Cu Kα₁ line was used as the source and Ge (004) was used as the reference crystal. The full width at half maximum (FWHM) values of the rocking curves were obtained by Pseudo-Voigt fitting. Room temperature photoluminescence spectra of the samples were measured before and after annealing using 325 nm line of a He–Cd laser (10 mW) as the excitation source (WDP500-D, Beijing Rayleigh Analytical Instrument Corp.). After annealing, the four samples were etched for 5 min by an induction-coupled plasma (ICP) etching system (2B, Beijing Chuangweina Tech. Co., Ltd.) and then room temperature PL spectra of the films were measured again. The plasma source used for etching was mixture of freon and argon. To measure the etching depth, a reference sample

Table 1
(002) and (102) FWHM values of ZnO samples measured before and after 850 °C annealing for various time

| Diffraction plane | Treatment | FWHM (arc sec) | | | |
|-------------------|-----------|----------------------|----------------------|----------------------|----------------------|
| | | 10-min-anneal sample | 20-min-anneal sample | 30-min-anneal sample | 40-min-anneal sample |
| (002) | As grown | 202 | 181 | 171 | 179 |
| (002) | Annealed | 229 | 176 | 196 | 175 |
| (102) | As grown | 447 | 400 | 387 | 399 |
| (102) | Annealed | 376 | 337 | 291 | 300 |

(also from the same ZnO wafer) was etched under the same conditions for 15 min. The reference sample was selectively pre-masked by rectangular photoresist film, and many trenches formed between the photoresist masks after etching. After removing the photoresist, depth of the trenches was measured using a scanning probe microscope (CSPM-3100, Benyuan Nano Tech.).

3. Results and discussion

It is well known that heteroepitaxial layers grown on largely lattice-mismatched substrates usually exhibit high density of dislocations, characterized by broad XRD rocking curves. There exist two types of dislocations: edge dislocation and screw dislocation, which leads to twist and tilt of lattice planes, respectively. In a wurtzite crystal, such as ZnO and GaN, the screw dislocations with a Burgers vector $b = [001]$ result in a tilt of lattice planes, which in turn reflects itself in the FWHM of symmetric XRD ω -scan. The edge dislocations with a Burgers vector $b = 1/3[110]$ twist the lattice planes by an azimuthal angle. It is difficult, however, to directly measure the twist angle by XRD, since these dislocations are only accessible either by χ -scan of a reflection plane perpendicular to (001) in transmission geometry, or by a Φ -scan of one of these planes in grazing incidence [12]. These techniques require a specifically designed diffractometer and high intensity X-ray source. Practically, a component of the twist can be extracted from ω -scan of asymmetrical reflections measured in skew geometry, such as the (102) rocking curve [11]. In our experiments, FWHM of (002) and (102) ω -rocking curves were used as the indicators of screw and edge dislocations, respectively.

Fig. 1 shows the ω -rocking curves of the four samples measured before and after annealing. The FWHM values of the rocking curves are listed in Table 1. Before annealing, the FWHM values of both (002) and (102) planes were similar with each other from sample to sample, showing the good uniformity of the films. From Table 1, we can see that the

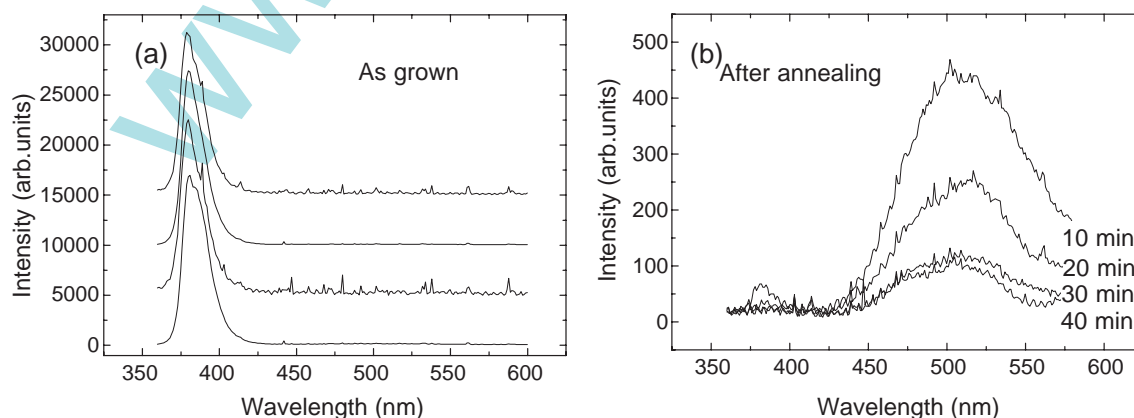


Fig. 2. PL spectra of the ZnO samples measured (a) as grown and (b) after annealed at 850 °C for various time.

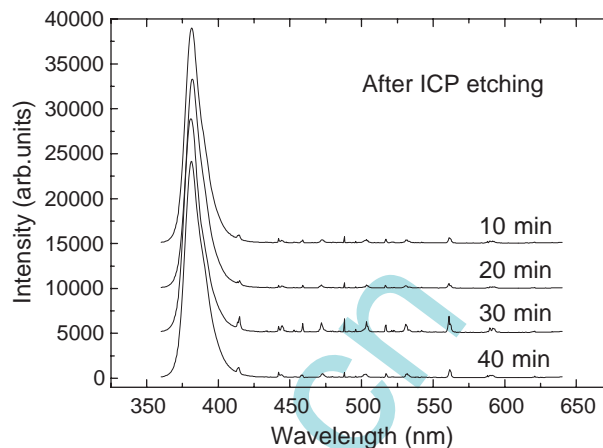


Fig. 3. PL spectra of the ZnO samples which were etched by ICP for 5 min after annealing.

(002) FWHM changed very little after annealing. Even for the 40 min annealed sample, the (002) FWHM decreased only 4 arc sec. In contrast, the FWHM value of the (102) rocking curves changed significantly upon annealing. The (102) FWHM of the 40-min annealed sample had decreased by 99 arc sec, which was about 25% of its original value. These results indicate that the screw dislocation density remained constant after annealing but the edge dislocation density was reduced significantly. But one cannot conclude that thermal annealing has no effect on screw dislocation in ZnO films because several papers [8–11] including our previous work [13] have confirmed that (002) FWHM of ZnO films can also be reduced by thermal annealing. The samples used in those research work had much broader (002) rocking curves than the ones used in the present work. Our hypothesis is that the different behavior of the two types of dislocations is due to their different densities in the present films and those of previous work. The screw dislocation density in the films reported in this work is too low to be reduced by annealing under these conditions. Comparing the results of the four samples, it can be found that the decrease of the (102) FWHM of the four samples upon annealing increases slightly with the increase of the annealing time.

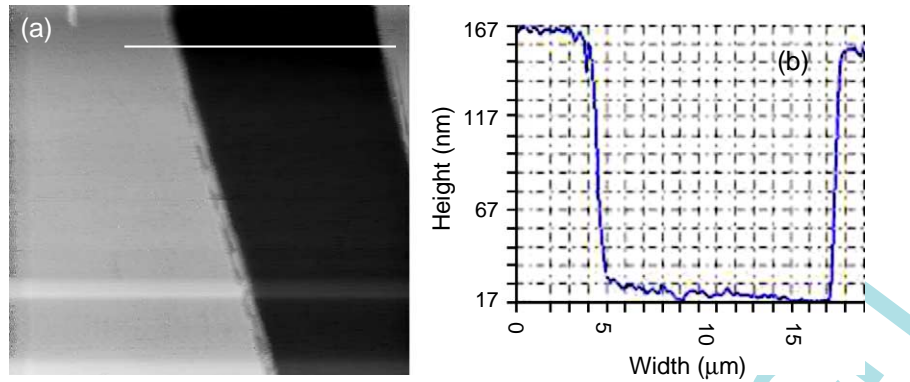


Fig. 4. (a) SPM image of the etching groove. (b) Lateral profile of the etching trench along the white line in (a).

Fig. 2 shows the PL spectra of the as-grown and annealed samples. As shown in Fig. 2 (a), only a strong UV emission is seen in the as-grown sample. This UV emission band has been previously attributed to the emission from free exciton in the literature [14]. The defect-related broad green emission is not seen in the as-grown sample. After annealing, the PL spectra of all the samples were greatly deteriorated, the UV peak was diminished and the green emission band appeared in the 10-min annealed sample, as shown in Fig. 2 (b). In the 20-, 30-, and 40-min-anneal samples, the UV emission band is completely disappeared, meanwhile the green peak also weakened. The origin of the green luminescence is still in dispute, but it is usually attributed to emission related to oxygen vacancy (V_O) [15]. The simultaneous weakening of the UV peak and the green peak is possibly caused by the increasing of the nonradiative recombination centers with the increment of annealing time.

Apparently, the degradation of PL is in contrast with the XRD results, which have shown improvement of crystal quality of the films. Keep in mind that in a PL measurement, the UV laser can only penetrate into a shallow depth, which is usually less than one micrometer, due to the large absorption coefficient. In contrast, in a XRD measurement, the X-ray can penetrate into a depth more than 10 μm . That means the signals collected in these two techniques are from different depth of the films, i.e. the PL from a thin layer near sample surface, while the XRD from the whole film. The absorption coefficient of ZnO is larger than 10^5 cm^{-1} [1]. Using the equation $I/I_0 = e^{-\alpha d}$, the penetrating depth is estimated to be $d = 0.2 \mu\text{m}$. In Fig. 3, we show the PL spectra of the ZnO films measured after 5 min ICP etching. The green luminescence disappeared completely in all the four samples. These results strongly suggest that the deterioration of the optical properties only occurred in a thin layer near the sample surface even for the 40-min annealed sample. Fig. 4 (a) is a $30 \times 30 \mu\text{m}$ SPM image of the reference sample after 15 min etching. Fig. 4 (b) is the lateral profile of the etching trench along the white line in Fig. 4 (a). The figure shows that the depth of the trench is 140 nm. Assuming a constant etching rate, the thickness of the removed layer of the samples etched for 5 min will be 47

nm. So the damaged layer where the green emission came from must be thinner than 47 nm. In addition, the FWHM of the UV peak shown in Fig. 3 is remarkably smaller than that of the as grown films (15 versus 19 nm for the 40-min annealed sample), indicating that the inhomogeneous strain in the films was greatly reduced.

4. Conclusions

ZnO films grown by MOCVD were annealed in atmosphere at 850 $^\circ\text{C}$ for different time periods. XRD results showed that high temperature annealing can significantly reduce the dislocation density and thus improve the crystal quality of ZnO films. Edge dislocation is more sensitive to annealing process than screw dislocation, probably due to its higher density in the films. Results of PL and ICP etching experiments show that high temperature annealing will damage the optical properties in a thin layer near the sample surface, however, the optical properties of the “bulk” part can be improved obviously upon annealing.

Acknowledgements

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