Effect of Surface-Covered Annealing on the Optical Properties of ZnO Films Grown by MOCVD

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Abstract: ZnO films grown by metal organic chemical vapor deposition at atmospheric pressure are annealed at 850 ℃, with the film surfaces exposed to air or covered by a sapphire wafer. The optical properties of the as-grown and the annealed samples are studied by photoluminescence (PL) spectroscopy. It is found that the air-exposure annealing effectively removes the hydrogen impurities from the ZnO films but greatly increases the deep-level emission. In the surface-covered annealed sample, an elimination of the hydrogen impurities is also observed, and the deep-level emission disappears completely. The free exciton emission is significantly enhanced in the ZnO film after surface-covered annealing.

Key words: zinc oxide; annealing; optical properties; exciton
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1 Introduction

ZnO has attracted considerable attention from the semiconductor community in recent years as a promising material for short wavelength light emitting devices. Recent investigations of ZnO have resulted in many remarkable developments, e. g. high crystal quality[1,2], laser emission[3], and homo-pn-junction LEDs[4].

In spite of these developments, high quality p-ZnO films with reproducible properties remain a contested goal. The problem is due in part to residual electron concentration, the origin of which has not yet been determined but is possibly related to hydrogen impurities[5]. Look *et al*.[6] have reported that the hydrogen atoms in ZnO films can be completely removed by annealing at temperatures higher than 750 ℃. Therefore, thermal annealing provides a simple way to reduce the background electron concentration in ZnO films. However, in the research of Look *et al*. and other groups[7,8], high temperature annealing was found to deteriorate the optical properties of ZnO films. The free exciton emission is annihilated, and the green luminescence is greatly enhanced after high temperature annealing. The deterioration of optical properties and the increase of green luminescence were attributed to the increase of the deep level concentration, possibly related to the decomposition of oxygen or zinc atoms from the film surface[7]. Thus a method for removing hydrogen impurities from ZnO films that can prevent the decomposition of surface atoms is desirable. In the present paper, we report a surface-covered annealing method that can effectively remove the hydrogen impurities from ZnO films and can prevent the generation of deep levels.

2 Experiment

The ZnO films in this study were grown on Al_2O_3 (001) substrate by metal organic chemical vapor deposition (MOCVD) at atmospheric pressure. Diethyl zinc (DEZn) and H_2O were used as the Zn and O precursors, respectively. The film thickness was about 3.0μm. Three segments from a 50mm ZnO wafer were labeled as sample A, sample B, and sample C, respectively. Sample A was untreated. Sample B was annealed at 850 ℃ for 20min with the surface exposed to air. Sample C was annealed at 850 ℃ for 20min with the surface covered by a sapphire wafer. Photoluminescence

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(PL) spectra of the three samples were taken at 10 ,50 ,80 K,and room temperature. The 325nm line of a He-Cd laser (10mW) was used as the excitation source for the PL measurements (WDP500-D , Beijing Rayleigh Analytical Instrument Corp.).

3 Results and discussion

Figure 1 shows the temperature-dependent PL spectra of the sample A. At 10 K,the dominant emission peaks are located at 3. 365 and 3. 360eV in the bound exciton range. These two peaks are attributed to I_4 and I_8[6,9] ,respectively ,and the small shifts of energy positions are due to the residual strain in the film. A peak at 3. 375eV can be clearly observed on higher energy side of the dominant peaks ,and it can be attributed to the free exciton A (FE_A) because its energy position is very close to that of the A exciton observed in reflectance spectra of bulk ZnO[10]. As the temperature increased to 50 K,the intensity of the free exciton peak increased ,while the bound exciton peak intensities decreased. At 80 K,the free exciton peak became dominant in the spectrum and the bound exciton peaks became very weak. This is a result of the decomposition of bound excitons to free excitons due to the increased thermal energy.

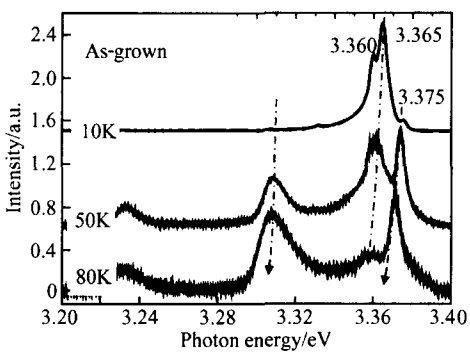

Fig. 1 Temperature-dependent PL spectra of the as-grown sample at temperatures from 10 to 80 K The dashed lines are guides to the eye for the position evolution of the exciton lines.

In Fig. 2 ,the annealing dependence of the exciton lines is presented. We note that all the spectra were normalized to I_8. For the as-grown sample , the relative intensities of I_4 and FE_A are 1. 4 and 0. 15 ,respectively. As annealed with the surface exposed to air ,sample B shows a band edge PL spectrum with significant differences. The intensity of I_8 in this sample is much less than in sample A. But

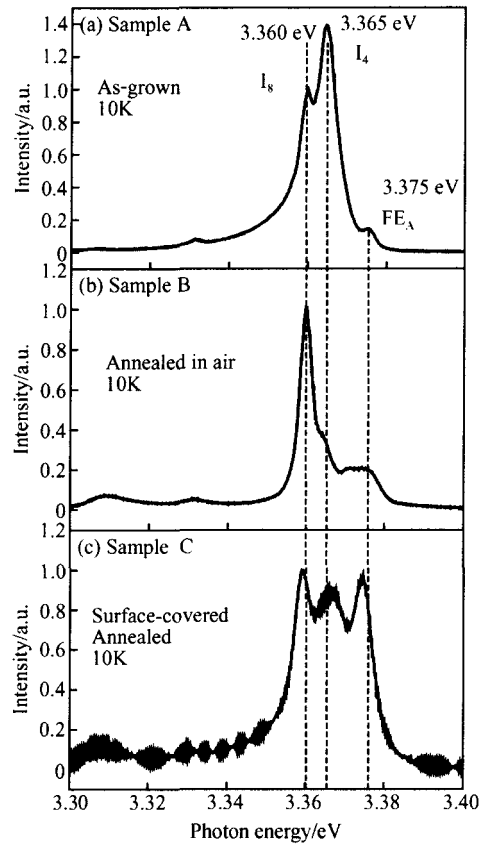

Fig. 2 PL spectra at 10 K (a) As-grown ZnO film; (b) ZnO film annealed with the surface exposed to air; (c) ZnO film annealed with the surface covered by a sapphire wafer

FE_A only increased lightly. The relative intensities of I_4 and FE_A of the sample B are 0. 38 and 0. 20 , respectively. In Ref. [6] ,Look *et al*. have reported that I_4 can be annihilated by annealing the films in air at temperatures higher than 750 ℃. They have identified I_4 as a donor bound exciton related to hydrogen impurities. Therefore ,the weakening of I_4 in sample B is due to the out-diffusion of hydrogen atoms from the film during annealing. As mentioned above ,the free exciton emission in sample B was not enhanced markedly with the decrease of the concentration of hydrogen. This means new trap centers were created along with the decrease of hydrogen impurities during annealing. Chen *et al*.[7] has attributed the trap centers to some kind of deep levels because they found that the high-temperature-annealed films showed strong green luminescence with the reappearance of the bound exciton line. The origin of the green luminescence in ZnO is still in dispute but is usually attributed to non-stoi-

chiometric defects such as oxygen vacancy and zinc vacancy[11]. It is obvious that these non-stoichiometric defects were created by the decomposition of the surface atoms.

Figure 2(c) shows the band edge PL spectrum of sample C. It can be seen clearly that the I_4 line is diminished markedly compared to sample A, indicating the effective removal of hydrogen from the film. More interestingly, the intensity of FE_A in this sample is dramatically enhanced and nearly equals the intensity of I_8 in this sample, as seen in Fig. 2(c). The relative intensities of I_4 and FE_A are 0.87 and 0.97, respectively. The enhancement of free exciton emission can be explained as follows. Because hydrogen atoms are very small and can diffuse easily in crystal lattices, the sapphire wafer will not block the out-diffusion of hydrogen from ZnO. However, the sapphire coating wafer can prevent the out-diffusion of oxygen and zinc atoms from the ZnO film surface because they are too large to move in the sapphire lattice. On the other hand, the Al—O bonds in sapphire are very robust and do not decompose easily during annealing at 850 ℃. This excludes the risk of contaminating of the ZnO films by Al atoms. Figure 3 shows the temperature dependence of the PL spectra of sample C. As the temperature increased from 10 to 50 K, the free exciton emission increases greatly and becomes solely dominant. At 80 K, the bound excitons disappear completely and only the free exciton with its longitudinal optical phonon replicas exists.

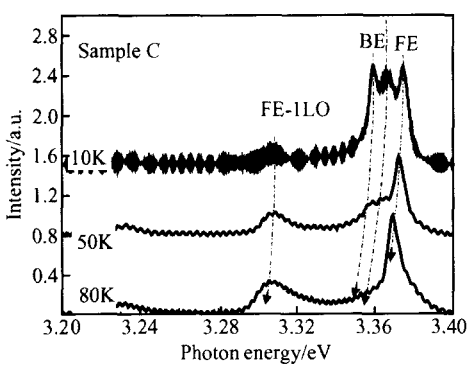

Fig. 3　Temperature-dependent band edge PL spectra of sample C in a range from 10 to 80 K. The dashed lines are guides to the eye for the position evolution of the exciton lines.

To investigate the deep-level concentrations, PL spectra in the visible light range have been measured at room temperature for all three samples, which are shown in Fig. 4. Sample A shows a strong near-band-edge emission peak in the UV range and a weak deep-level peak in the green range. For sample B, the green emission is greatly increased while the near-band-edge emission becomes very weak. In sample C, however, the green emission disappeared completely, indicating the absence of deep-levels in this sample. These results strongly confirm the above discussion about the exciton emissions.

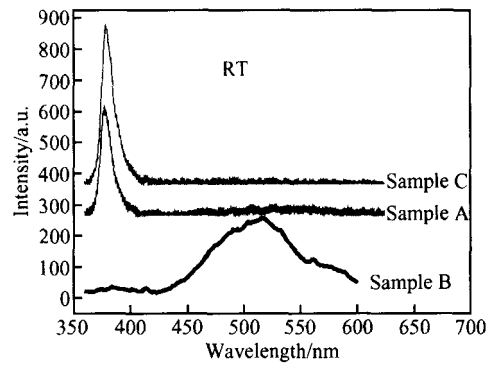

Fig. 4　Room temperature PL spectra in visible light range of the as-grown and annealed ZnO samples

4　Conclusion

We demonstrated that the hydrogen impurities in ZnO films can be effectively removed and the free exciton emission can be significantly enhanced by surface-covered annealing at 850 ℃. The effect of surface-covered annealing on ZnO films was explained by ability of the sapphire coating wafer to prevent the decomposition of the ZnO film surface and thus prevent the creation of deep levels, which can trap free excitons. But the coating wafer does not block the out diffusion of hydrogen atoms because of their small size.

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表面覆盖退火对 ZnO 薄膜光学性质的影响

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摘要: 研究了暴露在空气中退火和表面覆盖蓝宝石基板退火对 MOCVD 生长的 ZnO 薄膜光学性质的影响. 研究发现,暴露在空气中退火虽可以去除薄膜中的氢杂质,并在低温光致发光(PL)谱中观察到与氢相关的束缚激子峰消失,但是退火后样品室温 PL 谱中可观察到很强的可见光发射,表明样品中引入了大量的深能级,样品的自由激子发光没有增强. 而表面覆盖蓝宝石基板退火的样品,有效去除了氢杂质,但没有观察到可见光发射,说明表面覆盖蓝宝石基板退火可以有效地保护 ZnO 表面不分解,不生成深能级中心. 由于激子束缚中心的减少,表面覆盖退火样品的自由激子发射大大增强.

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