The study of deep-level emission center in ZnO films grown on c-Al$_2$O$_3$ substrates

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Abstract

ZnO films were grown on c-Al$_2$O$_3$ substrates by metal-organic chemical vapor deposition (MOCVD). Thermal annealing was performed at 700 　 in growth conditions and in oxygen atmosphere for 30minutes. The X-ray diffraction (XRD) patterns of all samples showed sharp diffraction peaks for ZnO (002), which indicated that the films were highly c-axis oriented. The photoluminescence (PL) spectra at room temperature of as-grown and annealed ZnO films were measured, respectively. We could find the intensity of the ultraviolet (UV) emission peak increased much through annealing. The deep-level emission peak decreased after annealing in growth conditions. However, it increased markedly after annealing in oxygen. Upon further analysis, we suggested that the deep-level emission corresponded to zinc vacancy (Vz$_n$) and antisite defect (Oz$_n$) rather than oxygen vacancy (Vo), interstitial zinc (Zn$_i$) and interstitial oxygen (O$_i$).

Introduction

It is well known that ZnO is a direct wide band-gap semiconductor. ZnO has an exciton binding energy of 60meV. Besides, ZnO can be deposited at a lower temperature than GaN. Recently, ZnO is extensively studied because of its potential applications in various fields, such as gas sensor, solar cells [1], photodetectors [2], light emitting diodes (LEDs) [3] and laser systems etc.

Especially after optical pumped UV lasing of ZnO films was reported [4], ZnO has received more and more attention from researchers. ZnO films have been grown by many methods, such as sputtering [5], molecular beam epitaxy (MBE) [6-8] and metal organic chemical vapor deposition (MOCVD) [9-11] and so on.

Generally there are two emission peaks centering at UV and visible region in the PL spectra of ZnO. The UV emission can be an exciton transition. However, the visible emission (deep-level emission) is caused by different intrinsic defects in ZnO films [12-14]. In order to reduce the deep-level emission, it is necessary to study the intrinsic defects in ZnO films. In this paper, ZnO films were deposited on c-Al_2O_3 substrates by MOCVD. Thermal annealing was performed in growth conditions and in oxygen atmosphere. The PL spectra of the as-grown and annealed ZnO films were measured. The influence of annealing conditions on PL spectra of ZnO films was studied.

Experiment

ZnO films were grown on C-Al_2O_3 substrates by MOCVD with rotating disk vertical reactor. The best vacuum of our chamber was about 1×10^{-3} Pa.The source materials were the pure 99.999% diethiyzinc (DEZn) and O_2. The carrier gas was argon (Ar). The detailed growth conditions of the samples were as follows: The chamber pressure was about 1 Torr. The N_2 flow was 600 sccm and the O_2 flow was 80 sccm. Ar passed through the bubbler at 2 sccm. The growth temperature was 600   and the growth time was 20minutes. Thermal annealing was performed at 700   in growth conditions and in oxygen for 30minutes, respectively. The unannealed sample was named S1. The samples annealed in growth conditions and in oxygen were named S2 and S3, respectively.

We used SIEMENS D08 Discover X-ray Diffractometer to investigate crystal quality. PL spectrum was measured by 325 nm He-Cd laser. The PL signal from the sample was filtered by a monochromator and picked up by a computer.

Results and discussions

Fig.1 (a), (b) and (c) showed the XRD spectra of S1, S2 and S3, respectively. From Fig.1, we could see that each film has a high ZnO (002) diffraction peak, which indicated that each sample was strongly c-axis oriented. Comparing Fig.1 (b), (c) with Fig.1 (a), we could see not only the stronger ZnO (002) diffraction peak but also the decreasing of the value of full-width at half-maximum (FWHM) for (002) diffraction peak, which meant that the quality of ZnO film was improved after being annealed.

Fig.2, 3 and 4 showed the PL spectra at room temperature of S1, S2 and S3, respectively. The PL spectra of all samples had two emission peaks centering at 375nm (UV, E_g=3.30eV) and 495nm (deep-level, E_g=2.50eV). PL intensity ratio of the UV emission to the deep-level emission was 10.6 for S1. For S2, the intensity of the UV emission increased while the intensity of the deep-level emission decreased. The ratio of them was 67.5. For S3, the intensity of UV emission was a little larger than that of S1, but the intensity of the deep-level emission increased clearly. Their intensity ratio was 1.1. Besides, we noticed that the deep-level emission peak was composed of a high-energy peak and a low-energy peak (shoulder peak), centering at 492nm (E_g=2.52eV) and 520nm (E_g=2.38eV) in fig.4. In respect to the UV emission peak increasing after annealing, we believed that it was due to the crystal quality being improved after annealing. On the other hand, we also believed that the variation of the intensity of the deep-level emission was related to the variation of defects in ZnO films.

It was well known that the defects in ZnO film included oxygen vacancy (Vo), Zinc vacancy (Vz$_n$), interstitial zinc (Zn$_i$), interstitial oxygen (Oi) and antisite oxygen (Oz$_n$). Some researchers thought that the deep-level emission was caused by different intrinsic defects in ZnO film, such as Vo, Vz$_n$, Zn$_i$, etc [15-18]. Because the deep-level emission center (2.50eV) is smaller than the band gap energy of ZnO (3.37eV), the deep-level emission must be related to the defect level in band gap.

During annealing, the forming of the defects could be expressed as follows:

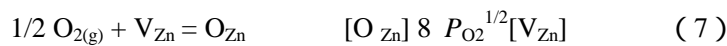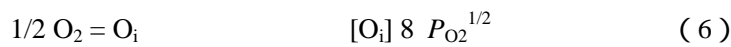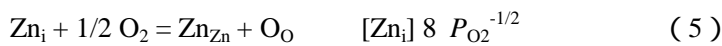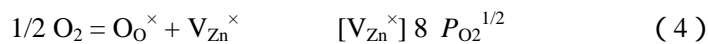$$ZnO \Leftrightarrow Zn_{Zn}(V_{Zn}{}^{\times})O_O(V_O{}^{\times})   \quad (1)$$
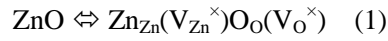
Under thermodynamic equilibrium, the concentration of the defects could be expressed as follows:

$$[V_{Zn}{}^{\times}] \Leftrightarrow [V_O{}^{\times}] \Leftrightarrow \exp\left(-\frac{\boldsymbol{e}_s}{2KT}\right) \quad (2)$$

Here, [Vo$^{\times}$] and [Vz$_n$$^{\times}$] were the concentrations of the nonionized vacancies of oxygen and zinc, respectively. $\boldsymbol{e}_s$ was the binding energy of a pair of oxygen vacancy and zinc vacancy. K was Boltzmann constant. T was thermodynamic temperature.

During annealing, the variations of these defects with the oxygen pressure (P_{O2}) could be expressed as follows[18]:

$$1/2\ O_2 + V_O{}^{\times} = O_O{}^{\times} \qquad [V_O{}^{\times}] 8\ P_{O2}{}^{-1/2} \qquad 3$$

$$1/2\ O_2 = O_O{}^{\times} + V_{Zn}{}^{\times} \qquad [V_{Zn}{}^{\times}] 8\ P_{O2}{}^{1/2} \qquad 4$$

$$Zn_i + 1/2\ O_2 = Zn_{Zn} + O_O \qquad [Zn_i] 8\ P_{O2}{}^{-1/2} \qquad 5$$

$$1/2\ O_2 = O_i \qquad [O_i] 8\ P_{O2}{}^{1/2} \qquad 6$$

$$1/2\ O_{2(g)} + V_{Zn} = O_{Zn} \qquad [O_{Zn}] 8\ P_{O2}{}^{1/2}[V_{Zn}] \qquad 7$$

Here, [Zn$_i$], [O$_i$] and [O$_{Zn}$] were the concentration of interstitial zinc, interstitial oxygen and

antisite oxygen, respectively. Equation (3) and (5) indicated that concentrations of the oxygen vacancy and the interstitial zinc decreased with the increase of oxygen pressure P_{O_2}, while Equations (4), (6) and (7) indicated that concentrations of the zinc vacancy, the interstitial oxygen and antisite oxygen increased with the increase of the oxygen pressure (P_{O_2}). We knew that P_{O_2} in oxygen atmosphere was much larger than P_{O_2} in growth conditions. The deep-level emission peaks of S_2 and S_3 decreased and increased, respectively, which indicated the intensity of the deep-level emission peak should increase with the increase of P_{O_2}, that is, the concentrations of the defects should increase with the increase of P_{O_2}. Therefore, the deep-level emission might be independent of Zni and Vo. Since the diameter of oxygen atom was larger than that of zinc atom, there was little probability of forming Oi. So we could conclude that V_{Z_n} and O_{Z_n} are related to the deep-level emission.

By full-potential linear muffin-tin orbital method, Sun [18] calculated the energy levels of the intrinsic defect in ZnO films. The result was showed in Fig.4. It could be seen from Fig.4 that the energy interval from the bottom of the conduction band to the O_{Z_n} level (2.38eV) was exactly consistent with the low-energy peak of the deep-level emission in our experiment. We suggested that the high-energy peak of the deep-level emission was caused by the energy interval between the Zni level and the V_{Z_n} level (2.60eV). The first reason was that this energy interval (2.60eV) approximately conformed to high-energy peak of the deep-level emission (2.52eV) in our experiment. The second reason was that the defect Zni was easily formed due to small diameter of zinc atom. The concentration of the defect Zni hardly varied with the increase of oxygen pressure P_{O_2}, while many defects V_{Z_n} were formed in ZnO film. Therefore, the intensity of the deep-level emission increased with the increase of the oxygen pressure P_{O_2} in oxygen atmosphere for S_3.

Besides, we believed that the deep-level emission of S_2 decreased because P_{O_2} in growth conditions was much smaller than P_{O_2} in oxygen atmosphere so that the concentrations of V_{Zn} and O_{Zn} were little after annealing in growth conditions.

Conclusion

ZnO films were grown on c-Al_2O_3 by MOCVD. Thermal annealing was performed on ZnO films in growth conditions and in oxygen atmosphere. We could only find the X-ray diffraction pattern of (002) ZnO film indicating strong c-oriented growth. The PL spectra of as-grown and annealed ZnO films were performed at room temperature, and the variations of deep-level emission of the all samples were studied by the PL spectra. By analyzing our experimental results, we suggested that the deep-level emission corresponds to the zinc vacancy (V_{Zn}) and antisite defect (O_{Zn}).

Reference

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Figure Captions

Figure.1 X-ray diffraction spectrum of as-grown and annealed ZnO films, (a) the as-grown

sample (b) the sample annealed in growth conditions (c) the sample annealed in oxygen.

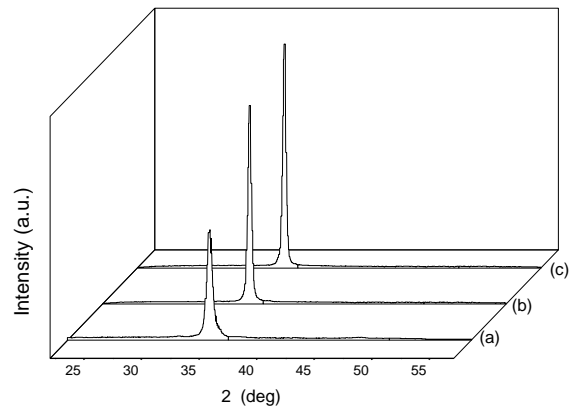Figure.2 The PL spectrum at room temperature of the as-grown sample.

Figure.3 The PL spectrum at room temperature of the sample annealed in growth conditions.

Figure.4 The PL spectrum at room temperature of the sample annealed in oxygen atmosphere.
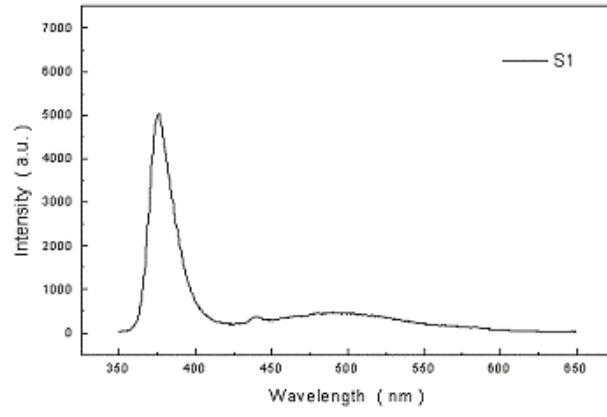
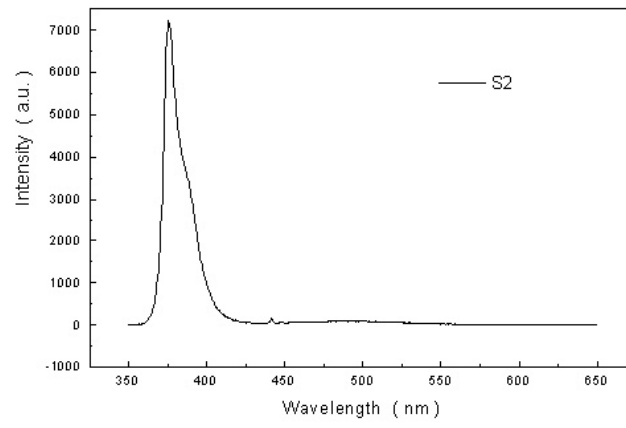Figure.5 The draft of the calculated defect's levels in ZnO film.
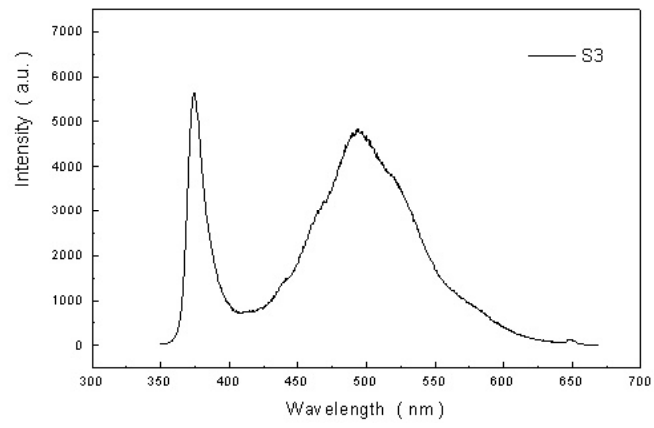
Zhang YT, et al, Fig.1

Zhang YT, et al, Fig.2

Zhang YT, et al, Fig.3

UV
3.18eV

3.06eV

Zn_i

1.62eV

V_O

2.28eV

2.38eV

$E_g = 3.36eV$

V_{Zn}

2.90eV

O_i

O_{Zn}