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Influence of the annealing temperature on violet emission of ZnO films obtained by oxidation of Zn film on quartz glass

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The photoluminescence (PL) emission properties of ZnO films obtained on quartz glass substrate by the oxidation of Zn films with the oxygen pressure of 50Pa at temperature of 773 K~973 K were studied. The strong single violet emission centering on 424 nm (or 2.90 eV) without any accompanying deep-level emission and UV emission was observed in the PL spectra of the ZnO films at room temperature. The intensity of violet emission increased with increasing annealing temperature in the range of 773 K~873 K and decreased with increasing annealing temperature in the range of 873 K~973 K. These violet emission bands are attributed to the electron transition from interstitial zinc (Zn_i) level (2.91 eV) to the valence band.

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1. Introduction

One important advantage of ZnO is that it is a II–VI semiconductor of wurtzite structure with a wide direct-band-gap of 3.3 eV [1] at room temperature. The most unique property of ZnO is its large exciton binding energy of 60 meV, which is much larger than those of GaN (24 meV), ZnSe (19 meV) and ZnS (39 meV) [2]. Because of this large binding energy, the exciton is stable at room temperature even in bulk crystals. Owing to these properties, ZnO is considered as a promising material for light-emitting devices and semiconductor lasers with low thresholds in the UV region. Generally, the corresponding photoluminescence (PL) spectra obtained from ZnO thin films shows defect-related deep-level emission [3–6] (yellow-green emission around 510 nm and red emission around 650 nm) as well as ultraviolet (UV) near-band-edge emission around 380 nm, which strongly depends upon the preparation methods and growth conditions. Recently, many methods were being used to obtain ZnO thin films, including metal-organic chemical vapor deposition (MOCVD) [7], molecular beam epitaxy (MBE) [8], rf magnetron sputtering[9], pulse laser deposition (PLD) [10] and the oxidation of the metallic Zn [11]. In these reports the main investigation concentrated on the ultraviolet (UV) emission and yellow-green emission, only a few researchers reported that there was accompanied violet light emission [12–14] and there was no report on single violet emission from ZnO films.

In this paper, we report a simple method for achieving polycrystalline ZnO thin films with single violet luminescent properties by the oxidation of metallic Zn films above melting temperature (692 K). The influence of oxidation temperature on the strength of violet emission peak was studied and the reason of the violet emission was explained.

2. Experimental

The metallic Zn films were deposited on quartz glass substrates by pulse laser deposition. The substrates were rinsed three times in acetone with ultrasonic vibration, each rinse for fifteen minutes; and then rinsed in ethanol

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for fifteen minutes before they were put into the deposition chamber. The base pressure of the deposition chamber was kept at 5×10^{-4} Pa, and the deposition time of 15 min was maintained. The applied laser energy density was measured to be about 7.6 J/cm^2. Zn (99.99% purity) targets were ablated by a Nd-YAG laser (wavelength of 1064 nm, with pulse duration of 100 ns, frenquency of 10Hz). The Zn film thickness measured by the cross section image of SEM was about 1.0 μm. In the present experiment, the heater block temperature is considered as the substrate temperature, which was kept at 573 K.

After deposition, the oxidation of Zn films was carried out in an oxidation furnace with oxygen pressure of 50Pa and at different annealing temperature (773 K ∼973 K) for one hour. Crystal structure of the ZnO films was investigated by X-ray diffraction (XRD, Rigaku Dymax) with a Cu target and a monochronmator at 50 kV and 300 mA. Atomic force microscopy (Q350) was used to characterize the surface morphology of the ZnO thin films. The optical properties of the ZnO thin films were characterized by photoluminescence with an Ar ion laser as a light source using an excitation wavelength of 325 nm. All spectra were measured at room temperature.

3. Results and discussion

3.1. The structure of ZnO film

Fig. 1 shows the XRD (I-2θ) of Zn film on quartz glass substrate obtained by PLD with the argon pressure of 11 Pa at substrate temperature of 573 K. It can be seen that isotropy Zn thin film is obtained. Fig. 2 shows the XRD traces (I-2θ) of the ZnO thin films on quartz glass substrate obtained by the oxidation of Zn film with the oxygen pressure of 50 Pa at different temperatures of 773 K∼973 K. The XRD patterns indicate that they possess a random polycrystalline hexagonal wurtzite crystal structure ($a = 3.249$, $c = 5.206$) with no preferred orientation.

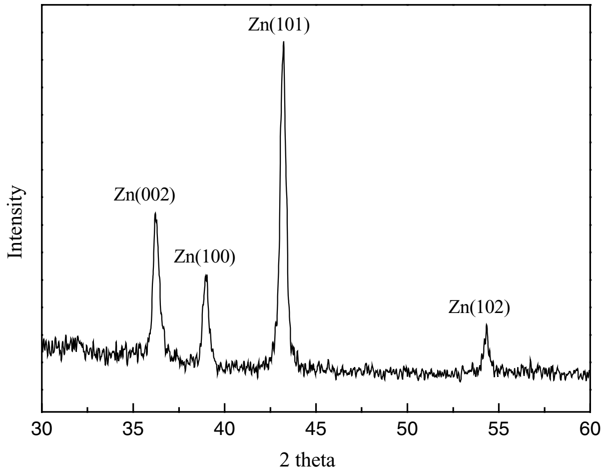

Figure 1 XRD spectra obtained from Zn films obtained by PLD on quartz glass at the substrate temperature of 573K with the Argon pressure of 11Pa

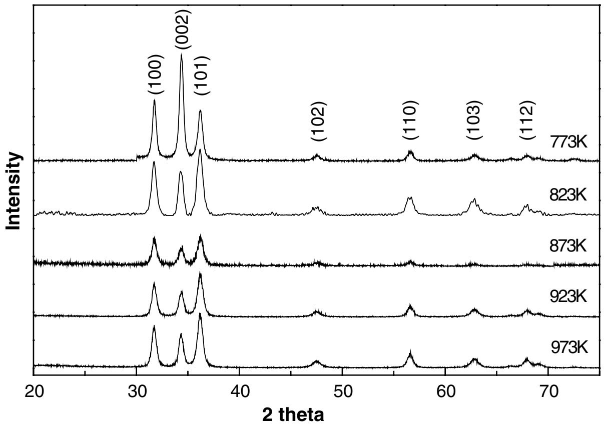

Figure 2 XRD patterns of ZnO thin films on quartz glass obtained by oxidation of metal Zn films at various annealing temperatures

Fig. 3 shows three typical AFM micrographs of the ZnO thin films obtained at the annealing temperature of 773 K, 873 K and 973 K, respectively. It is seen that the ZnO film is composed of inhomogeneous and random orientation grains, and they intersect each other so that the grain boundaries cannot be distinguished clearly. It is clearly seen that the roughness of surface of ZnO films increase with the increase of oxidation temperature. This may be attributed to the fast oxidation velocity of melted Zn films under the higher annealing temperature conditions, which results in random growth of ZnO grains.

3.2. Photoluminescence characteristics of film

Fig. 4 shows the room temperature photoluminescence (PL) spectra of the ZnO thin films on quartz glass substrate obtained by the oxidation of metal Zn film with the oxygen pressure of 50Pa at the annealing temperatures of 773 K∼973 K. It can be seen that all samples show a strong single violet emission centering about 424 nm (or 2.91 eV) without any accompanying deep-level emission and UV emission. Intensity of violet emission peaks increase with the increase of annealing temperature up to 873 K and rapidly decrease again with the increase of annealing temperature from 873 K to 973 K. The FWHM of violet emission peaks at 873 K is 38.1 nm, which is slightly narrower than those at other temperature. This indicates that the annealing temperature of 873 K is an optimum condition for the formation of ZnO film with a single violet luminescence emission.

Generally, the UV emission comes from the ZnO films with a few crystal defects [15] or from (002) oriented ZnO films [16]. Different defects in ZnO films contribute to different emissions of the PL spectra. Sun had calculated the energy levels of various intrinsic defects in ZnO by applying the full-potential linear muffin-tin orbital method [17], which is shown in Fig. 5. According to Sun's calculation results, the calculated energy interval from interstitial zinc (Zn$_i$) level to the valence band is 2.9 eV, which is well consistent with the violet emission

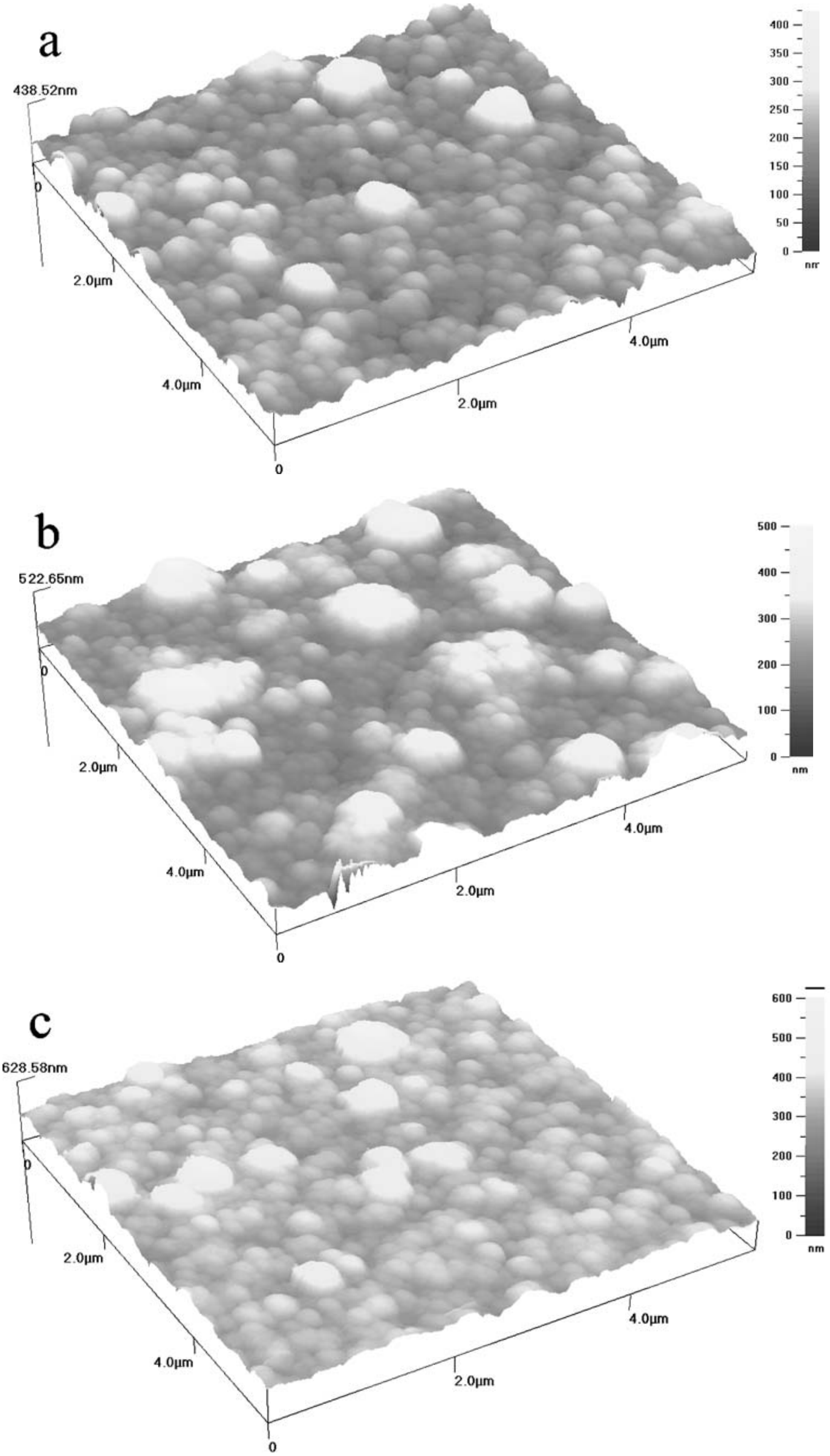

Figure 3 AFM of ZnO thin films on quartz glass obtained by oxidation of metal Zn films at different annealing temperature, 773 K a), 873K b) and 973K c)

peaks centered around 424 nm (or 2.91 eV) of ZnO film obtained by oxidation at temperature of 773 K ~973 K. Therefore, it can be deduced that the violet emission of PL spectra of the ZnO thin films is attributed to the energy transition of electrons from the interstitial zinc (Zn_i) level to the valence band.

The concentration of the interstitial zinc (Zn_i) defects in the ZnO films should depend on the annealing temperature and the oxygen pressure. In the present experiment, the very low oxygen pressure (50 Pa) is crucial for the formation of interstitial zinc (Zn_i) defects, as low oxygen pressure implies the lack of oxygen during oxidation. The lack of oxygen redounds to the formation of interstitial zinc defects. The annealing temperature (for example, 873 K) higher than the melting temperature (692 K) of metal Zn is also important. Wang *et al.* [18] reported that the ZnO film obtained by oxidation of Zn film at 683 K are more stoichiometric and less defective, however, the increase of oxidation temperature to above melting temperature (692 K) resulted in evident increase of defects. It is well known that melted metal (Zn) is in short-range order, which could be considered as micro uneven distribution of Zn or possessing high concentration of interstitial zinc (Zn_i) defects in some regions. The oxidation rate at relative high temperature is rapid. If the supply of oxygen on the surface of film is assumed to be even, some of interstitial zinc (Zn_i) defects in melted Zn film may be reserved in the ZnO film. However, the evaporation of Zn atoms from ZnO thin films is promoted at too high temperature (for example, 973 K) [19], which decreases the concentration of interstitial zinc (Zn_i) defects in ZnO films, and a decrease in the violet emission is shown in the PL spectra at 973 K (see Fig. 4). As a result, in the present experiment, 873 K or so may be the optimal annealing temperature for the violet luminescence emission from ZnO thin films obtained by oxidation of metallic Zn film.

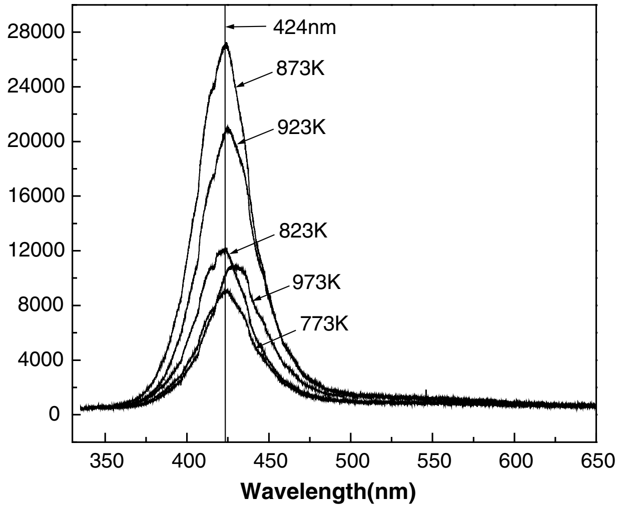

Figure 4 Room temperature (298 K) PL spectra of ZnO thin films on quartz glass obtained by oxidation of metal Zn films at various annealing temperatures.

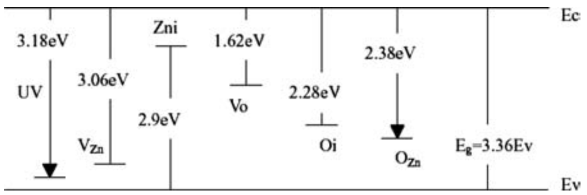

Figure 5 The draft of calculated defect's levels in ZnO film (ref. [17]).

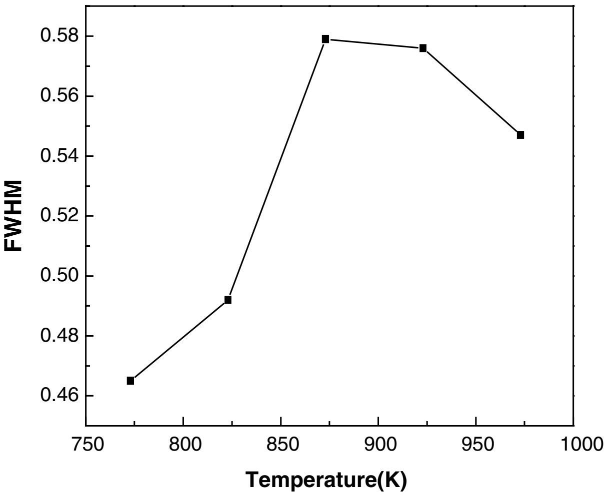

Figure 6 The FWHM of XRD spectra of ZnO thin films on quartz glass obtained by oxidation of metal Zn films varying with annealing temperatures.

The defects concentration in ZnO film can be qualitatively estimated by the FWHM of XRD spectra of ZnO films, which is shown in Fig. 6. It can be seen that the FWHM of XRD spectra of the ZnO film annealed at temperature of 873 K is relatively wider, which suggests that there are more crystal defects in the ZnO thin films. This result is in agreement with the strong violet emission caused by interstitial zinc defect, which is observed from the ZnO film oxidated at 873 K.

4. Conclusion

ZnO film on quartz glass was obtained by the oxidation of Zn films in oxygen pressure of 50 Pa. The influences of the annealing temperature on optical properties of ZnO film were studied.

1. The ZnO films prepared with oxygen pressure of 50Pa at the annealing temperature of 773K ~973K show a typical single violet luminescence behavior. The intensity of violet emission depends on the annealing temperature.
2. The electron transitions from the interstitial Zn (Zn_i) defect levels to the valence band should mainly contribute to the violet emission of PL spectra of the ZnO films.

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References

1. L. I. BERGER, Semiconductor Materials (CRC Press, New York, 1997).
2. A. S. YAMAMOTO, K. S. MIYAJIMA and T. GOTO, *J. Appl. Phys.* **90** (2001) 4973.
3. S. BETHKE, H. PAN and B. W. WESSEIS, *Appl. Phys. Lett.* **52** (1988) 138.
4. Y. CHEN, D. M. BAGNALL, H. J. KOH, K. T. PARK, K. HIRAGA, Z. ZHU and T. YAO, *J. Appl. Phys.* **84** (1998) 3912.
5. R. DINGLE, *Phys. Rev. Lett.* **23** (1969) 579.
6. B. S. PIERCE and R. L. HENGEHOLD, *J. Appl. Phys.* **47** (1976) 644.
7. W. I. PARK and G. C. YI, *J. Electron. Mater.* **30** (2001) L32.
8. H. J. KO, Y. F. CHEN, Z. ZHU, T. YAO, I. KOBAYASHI and H. UCHIKI, *Appl. Phys. Lett.* **76** (2000) 1905.
9. K. K. KIM, J. H. SONG, H. J. JUNG, W. K. CHOI, S. J. PARK and J. H. SONG, *J. Appl. Phys.* **87** (2000) 3573.
10. J. A.SANS, A. SEGURA , M. MOLLAR and B. MAR. *Thin Solid Films* **453-454** (2004) 251.
11. S. CHO, J. MA, Y. KIM, Y. SUN, G. K. L. WONG and J. B. KETTERSON, *Appl. Phys. Lett.* **75** (1999) 2761.
12. S. H. JEONG, B. S. KIM and B. T. LEE, *ibid.* **82** (2003) 2625.
13. Q. P. WANG, D. H. ZANG, Z. Y. XUE and X. T. HAO, *Appl. Surf. Sci.* **201** (2002) 123.
14. B. J. JIN, S. IM and S. Y. LEE, *Thin Solid Films* **366** (2000) 107.
15. B. J. JIN, H. S. WOO, S. IM, S. H. BAE and S. Y. LEE, *Appl. Surf. Sci.* **169-170** (2001) 521.
16. X. M. FAN, J. S. LIAN, Z. X. GUO and H. J. LU, *ibid.* **239** (2005) 176.
17. Y. M. SUN, Ph.D. thesis, University of Science and Technology of China, July, 2000.
18. Y. G. WANG, S. P. LAU, H. W. LEE and S. F. YU, *J. Appl. Phys.* **94** (2003) 354.
19. J. D. YE, S. L. GU, S. M. ZHU, T. CHEN and W. L. LIU, *J. Vac. Sci. Technol. A,* **21** (2003) 979.

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