

## Influence of preparation methods on photoluminescence properties of ZnO films on quartz glass

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**Abstract:** The influence of preparation methods on the photoluminescence properties of ZnO film was studied. Two methods were applied to fabricate ZnO films in a conventional pulsed laser deposition apparatus. One is high temperature (500–700 °C) oxidation of the metallic zinc film that is obtained by pulsed laser deposition. The other is pulse laser ablation of Zn target in oxygen atmosphere at low temperature (100–250 °C). The photoluminescence property was detected by PL spectrum. The room temperature PL spectra of the ZnO films obtained by oxidation method show single violet luminescence emission centered at 424 nm (or 2.90 eV) without any accompanied deep-level emission and UV emission. The violet emission is attributed to interstitial zinc in the films. Nanostructure ZnO film with *c*-axis (002) orientation is obtained by pulsed laser deposition. The ZnO film deposited at 200 °C shows single strong ultraviolet emission. The excellent UV emission is attributed to the good crystalline quality of the film and low intrinsic defects at such low temperature.

**Key words:** nanostructure; ZnO film; pulsed laser deposition; photoluminescence

### 1 Introduction

Zinc oxide(ZnO), a compound semiconductor of the II–VI family, which has a direct band gap (3.37 eV at RT) in the ultraviolet(UV) range[1], is a promising material that possesses various applications, such as transparent electrodes and ultraviolet-emitting devices [2–3]. Recently, luminescence attracts much attention among the potential applications[4–5]. ZnO film exhibits two kinds of emissions: one is an ultraviolet UV emission centered at approximately 380 nm; and the other is a visible deep-level emission with a peak in the range of 450–730 nm[6]. The UV emission is considered the near-band-edge emission which depends on the crystal quality of the film, while the visible emissions are related to various intrinsic defects in ZnO crystal. But both of them depend greatly on the preparation methods and conditions. Many methods were used to grow ZnO thin films on various substrates, such as metal-organic chemical vapor deposition(MOCVD)[7], molecular beam epitaxy(MBE)[8], sol-gel deposition[9], rf magnetron

sputtering[10], spray pyrolysis[11], oxidation of metallic zinc[12], and pulse laser deposition (PLD)[3,13–15]. In this work, in order to study the influences of the preparation method on the photoluminescence properties, two representative methods were applied to deposit ZnO films on quartz glass substrate. One was the oxidation of metallic zinc film at high temperature and the other was the pulse laser ablation of Zn target in oxygen atmosphere at low temperature. The microstructure and optical properties of the ZnO films obtained by different methods were investigated. The influence of structure and intrinsic defects on the photoluminescence was emphasized.

In our previous work, it has been shown that high-quality ZnO film could be formed on Si(111) substrate by pulse laser ablation of Zn target in a controlled oxygen atmosphere[14]. Based on the technological advantages and potential application, high-quality ZnO films grown on amorphous substrate such as quartz glass and glass substrate have attracted more attention[16]. So quartz glass substrate was used throughout in this work.

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## 2 Experimental

A conventional pulsed laser deposition apparatus was applied to deposit ZnO film on quartz glass. This system based on a turbo-molecular pump yielding a base pressure of  $5 \times 10^{-4}$  Pa. An Nd-YAG laser (wavelength of 1 064 nm, with pulse duration of 100 ns, frequency of 10 Hz) was used as the ablation laser. Zn (99.99% purity) target was used as zinc source for the direct deposition or oxidation-deposition of Zn film and ZnO film, respectively.

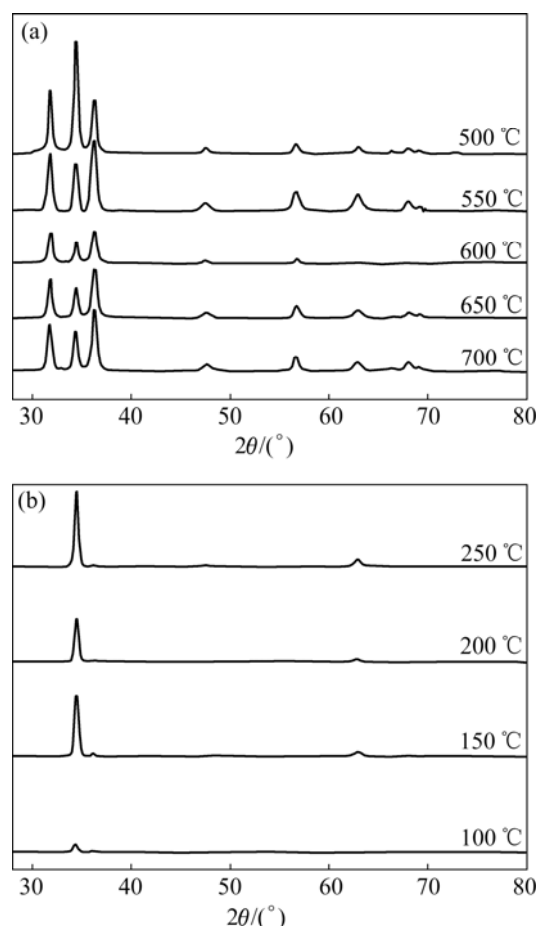
The metallic Zn films were deposited on quartz glass substrates in argon atmosphere (11 Pa) and the substrate temperature was kept at 300 °C. The applied laser energy density was measured to be about 7.6 J/cm<sup>2</sup>. The deposition time of 15 min was maintained. After deposition, the oxidation of Zn films was carried out in an oxidation atmosphere with oxygen pressure of 50 Pa. The annealing temperature of 500–700 °C was used. The deposition of ZnO film was performed at oxygen pressure of 11 Pa. Low energy fluency was set at 7 J/cm<sup>2</sup> for all samples in order to avoid molten droplet[15]. The deposition time was 10 min. In order to get nanostructured ZnO thin films, deposition was realized at relatively low substrate temperatures of 100–250 °C.

The crystal structures of all the ZnO films were investigated by X-ray diffractometry (XRD, Rigaku D/max) with a Cu target and a monochromator at 50 kV and 300 mA. FESEM (JSM-6700F) was used to characterize the surface morphology of the 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 Structure of films

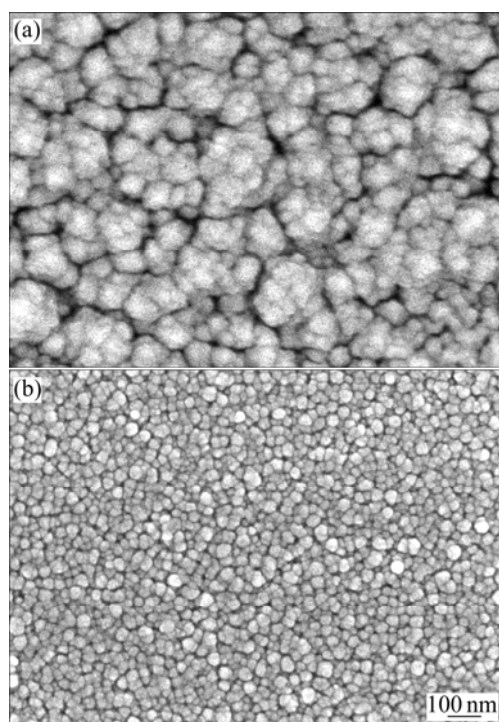
Fig.1 shows the XRD patterns of ZnO films obtained by the oxidation of metallic Zn film and the as-deposited ZnO film. For the ZnO films obtained by oxidation of Zn film, as shown in Fig.1(a), the diffraction peaks show the hexagonal wurtzite ZnO structure without evident growth orientation. In Fig.1(b), the as-deposited ZnO films show strong *c*-axis (002) orientation growth. The average grain size of the as-deposited ZnO films was estimated by the full width at half maximum (FWHM) value of (002) diffraction peaks through the Scherrer formula. The calculated average grain sizes for the ZnO films deposited at substrate temperature of 100, 150, 200, and 250 °C are 28, 31, 34, and 35 nm, respectively.



**Fig.1** XRD patterns of ZnO thin films on quartz glass substrate: (a) Obtained by oxidation of metal Zn films at high annealing temperatures; (b) Obtained by pulsed laser deposition at low substrate temperatures

Fig.2 shows two typical surface morphologies of the ZnO films fabricated by different methods. It is seen that the morphologies of ZnO films obtained by different methods are different completely. The ZnO film with average grain size of 120 nm obtained by oxidation of Zn film shows large surface roughness, while the as-deposited ZnO film with average grain size of about 45 nm shows column morphology.

ZnO film with nanostructure was successfully obtained by direct pulsed laser deposition at relative low substrate temperature. The average grain sizes of the as-deposited ZnO films deposited at different substrate temperatures are measured to be 34, 34, 45 and 44 nm, respectively. It is seen that the grain sizes estimated by the FWHM of XRD diffraction peak are somehow lower than those estimated by the direct FESEM observation. It is believed that the broadening of the peaks occurs for two reasons: 1) limitations in the spatial extent of the coherent scattering volume (in our case the grain size), and 2) the presence of inhomogeneous strain (for example



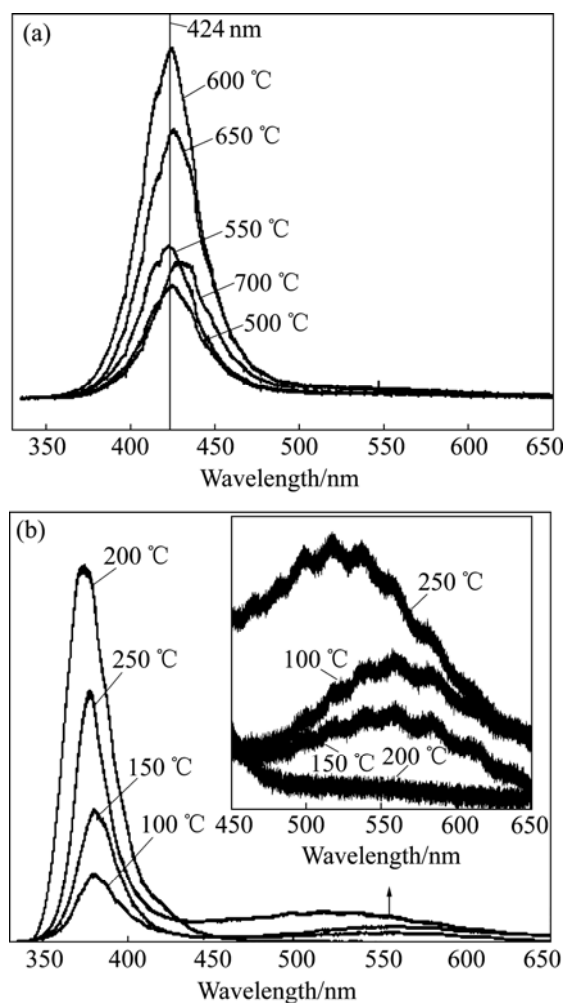
**Fig.2** FESEM images of ZnO thin film grown on quartz glass substrate fabricated by different methods: (a) Oxidation of Zn film at 600 °C; (b) Pulsed laser deposition at 200 °C

dislocations)[17]. Therefore, the difference implies that there should be other growth defects, for example, lattice or intrinsic GB dislocations, which are often included in nanocrystalline structures.

### 3.2 Photoluminescence properties of films

Fig.3 shows the room temperature photoluminescence(PL) spectra of ZnO films on quartz glass substrate obtained by different methods. Obviously, two entirely distinct PL spectra are got. The films obtained by oxidation of Zn film show single visible emission, while the films obtained by pulsed laser deposition show UV emission with slight visible emission and even single UV emission.

It is seen in Fig.3(a) that after high temperature annealing all samples show a strong single violet emission centered at about 424 nm (or 2.91 eV) without any accompanying deep-level emission or UV emission. To our knowledge, single visible light emission has seldom been reported. In recent study[18], single green emission was obtained from the ZnO film fabricated on quartz glass by rf sputtered. The influence of oxygen pressure on the intensity and peak position of violet emission from ZnO film was studied previously[12]. In the present work, the influence of annealing temperature on the intensity of violet emission peaks was investigated. It is seen that the intensity increases with the increase of



**Fig.3** PL spectra of ZnO thin films on quartz glass substrate: (a) Obtained by oxidation of metal Zn films at high annealing temperatures; (b) Obtained by pulsed laser deposition at low substrate temperatures

annealing temperature up to 600 °C and decreases with the further increase of annealing temperature from 600 °C to 700 °C. At deposition temperature of 600 °C, the maximum intensity with narrowest full-width at half-maximum(FWHM) of violet emission peak was obtained. This indicates that the annealing temperature of 600 °C is an optimum condition for the formation of ZnO film with a single violet luminescence emission.

The photoluminescence (PL) spectra obtained from as-deposited ZnO film (Fig.3(b)) show strong UV emission (around 378 nm) accompanied with deep level emission. It can be seen that the intensity of UV emission peaks increases with the increase of substrate temperature in the range of 100–200 °C. The intensity of the UV emission peak decreases slightly when the substrate temperature increases to 250 °C. Inset in Fig.3(b) shows the intensities of the deep level emissions. The deep level emission centers of the ZnO films deposited at 100, 150 and 250 °C are 558 nm (2.25 eV),

558 nm (2.25 eV) and 518 nm (2.39 eV), respectively. It is interesting to note that the ZnO film deposited at substrate temperature of 200 °C shows only strong ultraviolet emission with a narrow full-width at half-maximum(FWHM) of 20 nm (or 0.16 eV).

Generally, it is believed that the UV emission comes from the ZnO films with less crystal defects[19] or from (002) oriented ZnO films[14], and the deep level emission of ZnO relates to the intrinsic defects in ZnO film[20]. It was reported[20–21] that there are five intrinsic defects in ZnO film, such as zinc vacancy  $V_{Zn}$ , oxygen vacancy  $V_O$ , interstitial zinc  $Zn_i$ , interstitial oxygen  $O_i$ , and antisite oxygen  $O_{Zn}$ . SUN calculated the energy levels of various intrinsic defects in ZnO by applying the full-potential linear muffin-tin orbital method[20], which is shown in Fig.4. According to SUN's calculation results, the calculated energy interval from the upside of the valence band to interstitial zinc ( $Zn_i$ ) level is 2.9 eV, which is well consistent with the violet emission peaks centered at around 424 nm (or 2.91 eV) of ZnO film obtained by oxidation. Therefore, the violet emission of PL spectra of the ZnO thin films would be attributed to the energy transition of electrons from the upside of the valence band to the interstitial zinc ( $Zn_i$ ) level. Main origins of interstitial zinc ( $Zn_i$ ) defects in ZnO films should come from two aspects. One is the influence of oxygen pressure. In 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 second aspect is the annealing temperature. The annealing temperature (for example, 600 °C) is higher than the melting temperature (419 °C) of metal Zn. In this case, oxidation is carried out at an unstable liquid state. It can be considered that the concentration of interstitial zinc ( $Zn_i$ ) defects in liquid Zn increases with increasing annealing temperature. However, after Zn oxidation to form ZnO, because the annealing temperature compared with the melting temperature (1 973 °C) of ZnO became very low, the diffusion velocity of Zn atoms in ZnO should be slower. Therefore, the interstitial zinc defects previously existed in liquid Zn may be greatly reserved in ZnO film. As a result, a great number of interstitial zinc defects cause strong violet emission in PL spectra as observed at 600 °C (see Fig.3(a)). However, too high temperature (for example, 700 °C) promotes the evaporation of Zn atoms from ZnO thin films[22], 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 700 °C (see Fig.3(a)). Therefore, in the

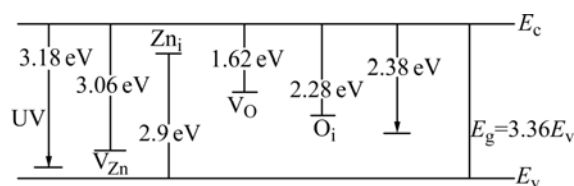


Fig.4 Draft of calculated defect's levels in ZnO film[20]

present experiment, 600°C may be the optimal annealing temperature for the formation of ZnO thin film with violet luminescence emission ZnO thin films.

For the as-deposited ZnO film, a fixed partial-oxygen pressure of 11 Pa is kept, the reactive velocity should be decided by the competition between the substrate temperature and oxygen pressure. When the deposited temperature is lower (for example 100–150 °C), the oxidation reactive velocity maintains a lower level and the number of oxygen atoms at the fixed oxygen pressure of 11 Pa are sufficient to combine with Zn ions to form ZnO, and there are still residual O atoms which may exist as  $O_i$  defects in ZnO films. When the substrate temperature increases to about 200 °C, the balance between the substrate temperature and oxygen pressure, i.e. the reactive velocity assort with the supply of oxygen under this oxygen pressure, leads to the formation of ZnO film with the lowest concentration of intrinsic defects. As a result, highest UV emission with no deep level emission is observed. When the temperature increases further to 250 °C, compared with the reactive velocity at this temperature, oxygen atoms are inadequate, which leads to the formation of  $V_{Zn}$  and  $O_{Zn}$  defects. As a result, deep level emission is expected (see the inset chart of Fig.3(b)).

From SUN's calculated result the energy interval for electronics transition from the upside of the valence band to the interstitial oxygen  $O_i$  level is 2.28 eV, while the energy interval from the bottom of the conduction band to the antisite oxygen  $O_{Zn}$  level is 2.38 eV[20]. In our experiments the deep level emission centered at about 2.25 eV and at 2.39 eV are observed from the films deposited at 100, 150 and 250 °C, respectively. These agreements between the present experiments and the theoretical consideration confirm the above explanation about the deep level emission.

The above experiments reveal that ZnO films with different structures or defects will show different photoluminescence properties, for example, the ZnO films with large number of interstitial zinc ( $Zn_i$ ) defects show single violet emission, while the ZnO films with less intrinsic defects show classical UV emission. Therefore, it is possible to obtain ZnO films with different photoluminescence properties by varying its structure or intrinsic defect structure through different

preparation methods.

## 4 Conclusions

1) The ZnO films prepared with oxygen pressure of 50 Pa at the annealing temperature of 500–700 °C show a typical single violet luminescence behavior. The intensity of violet emission depends on the annealing temperature.

2) The as-deposited ZnO films obtained at low substrate temperatures under oxidation pressure show nanocrystalline structure with grain size in the range of 34–45 nm. This as-deposited films show typical ultraviolet emission with accompanied deep-level emission in PL spectra. However, it is possible to adjust the substrate temperature (at 200 °C) to obtain the ZnO film with lowest concentration of intrinsic defects, which exhibits strong UV emission with no deep-level emission.

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