

Photoluminescence in ZnO film prepared by electrostatic-enhanced ultrasonic spray pyrolysis

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ZnO have been fabricated using electrostatic-enhanced ultrasonic spray pyrolysis. The luminescent films had a polycrystalline hexagonal wurtzite type structure. The influence of precursor concentration on ZnO films morphology was explored by SEM, dense and smooth films were prepared using lower concentration precursor. The influence of preparation conditions on photoluminescence were discussed, photoluminescence and Raman spectra of ZnO show that blue and green luminescence observed in ZnO films can be attributed to Zn_i and V_{Zn} .

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1. Introduction

Zinc oxide, a representative II–VI group compound semiconductor with a direct wide bandgap of 3.37 eV at room temperature and large exciton binding energy of 60 meV, is an important photoelectric material and draws much attention. ZnO is of interest for low-voltage and short wavelength light emitting devices such as light-emitting diodes, diode lasers, and ultraviolet photo-detectors [1, 2]. Various physical techniques have been explored to fabricate ZnO thin films, for instance, RF-magnetron sputtering, pulsed laser deposition and molecular beam epitaxy [3-5]. Among these techniques, ultrasonic spray pyrolysis (USP) is a convenient, fast and relatively low-cost method for preparing ZnO film [6], however, the deposition efficiency of USP is relatively low because of most of the aerosol precursor was loss to the surroundings. To improve the deposition efficiency, a modified method, which is called Electrostatic-enhanced Ultrasonic Spray Pyrolysis (EUSP), was developed to fabricate ZnO thin film.

In this paper, ZnO thin films were fabricated by EUSP technique. The influence of processing parameters on morphology and optical properties of ZnO thin films was investigated. Meanwhile, luminescent mechanism and the defects of ZnO thin film were studied by Photoluminescence (PL) and Raman spectra.

2. Experiments

A schematic diagram of the EUSP system is illustrated in Fig. 1. The liquid precursor was prepared by dissolving

$Zn(NO_3)_2$ in distilled water, the solution was atomized at a frequency of 1.7 MHz by an ultrasonic nebulizer. The aerosol precursor was transported by carrier gas through nozzle with a discharge needle, on which high negative voltage (15 kV) was applied, and the strong electrostatic field was established between nozzle and grounded substrate holder. Droplets in aerosol precursor captured charge from the discharge needle, and then these droplets were deposited efficiently on heated substrate by Coulomb force. ZnO films were grown on quartz glasses, the deposition time for the film was about 10 min, and high-purity N_2 was used as carrier gas at flow rate of 200 sccm.

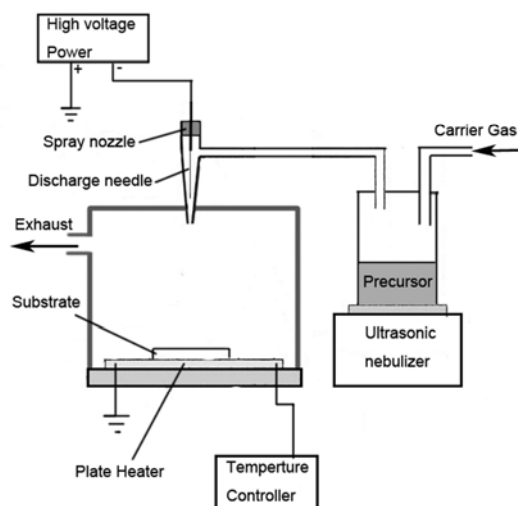


Fig. 1. Schematic set-up for EUSP.

A PHILIPS PW1710 X-ray diffraction spectrometer (CuK α radiation) was employed to study the phase and crystallinity of the films. A scanning electron microscope (SEM PHILIPS XL-30) was used to examine the morphology of the samples. Optical property was analyzed by room temperature photoluminescence spectrum (9700CRT). Raman scattering measurement was carried out using a LABHR-UV micro-Raman system at room temperature, and the 514 nm line of an Ar⁺ laser was used as an excitation source.

3. Results and discussion

3.1. Structural properties

Structural identification of the ZnO films was investigated using XRD in the range of 2θ between 30° – 60° . Fig. 2 shows typical XRD of the ZnO grown under different precursor concentration: (a) 0.1M, (b) 0.01M, and (c) 0.005M. The diffraction peaks of the ZnO at around 31.70° , 34.38° , 36.18° , 47.46° , and 56.46° correspond to the (100), (002), (101), (102), and (110) planes, respectively, based on JCPDS card 79-0207, it is evident from Fig. 2 that ZnO polycrystalline in wurtzite type structure. The ZnO film grown with precursor concentration of 0.1M has a powder like pattern with no preferred orientation. As precursor concentration decreased, the films exhibit predominantly one peak showing orientation along the c -axis perpendicular to the substrate. The inset table shows crystallite size of the ZnO films, which is calculated from the Scherrer's formula, it indicate the ZnO film deposited with precursor concentration of 0.1 M has the smallest crystallite size in all sample.

On higher precursor concentration, the deposition is performed at high rate, which is typically non-equilibrium process, so that it difficult for the atoms move to the preferred (002) plane, consequently, ZnO film exhibit no preferred orientation; meanwhile non-equilibrium growth process led the formation of a large number of nuclei, as a result the small size grain was achieved.

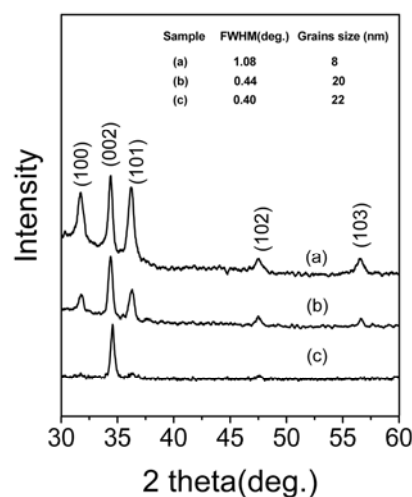


Fig. 2 XRD patterns of the ZnO films deposited with different precursor concentration: (a) 0.1 M, (b) 0.01 M, and (c) 0.005 M.

Under low precursor concentration, the deposition rate is prolonged, so ZnO film illustrates c -axis orientation and its crystallite size become large.

3.2. The influence of precursor concentration on ZnO films morphology

Fig. 3 illustrates the influence of precursor concentration on ZnO films morphology. Fig.3 (a), (b), and (c) show the films deposited with different precursor concentration of 0.1 M, 0.01 M and 0.005 M respectively. The film shown in Fig. 3(a) is porous with rough surface; the film of Fig. 3(b) was not very smooth, and some small exfoliated parts were observed; as shown from Fig. 3(c), the film was dense and smooth. Fig. 3(d) shows the SEM image of ZnO thin film deposited with precursor concentration of 0.1 M at 400°C for only 15 sec. It can be observed from Fig. 3(d) that there were many circular marks in the substrate; this indicated that the droplets pyrolysis had taken place in the hot substrate instead of above the hot substrate. It was reported an ideal deposition condition to fabricate dense ZnO film is when the droplet approaches the substrate just as the solvent is completely removed, and if the droplets directly landed on the substrate, the film tended to be porous and rough [7], but our experiments show that dense and smooth films can be also prepared using lower concentration precursor, even though the droplets directly deposited on the substrate.

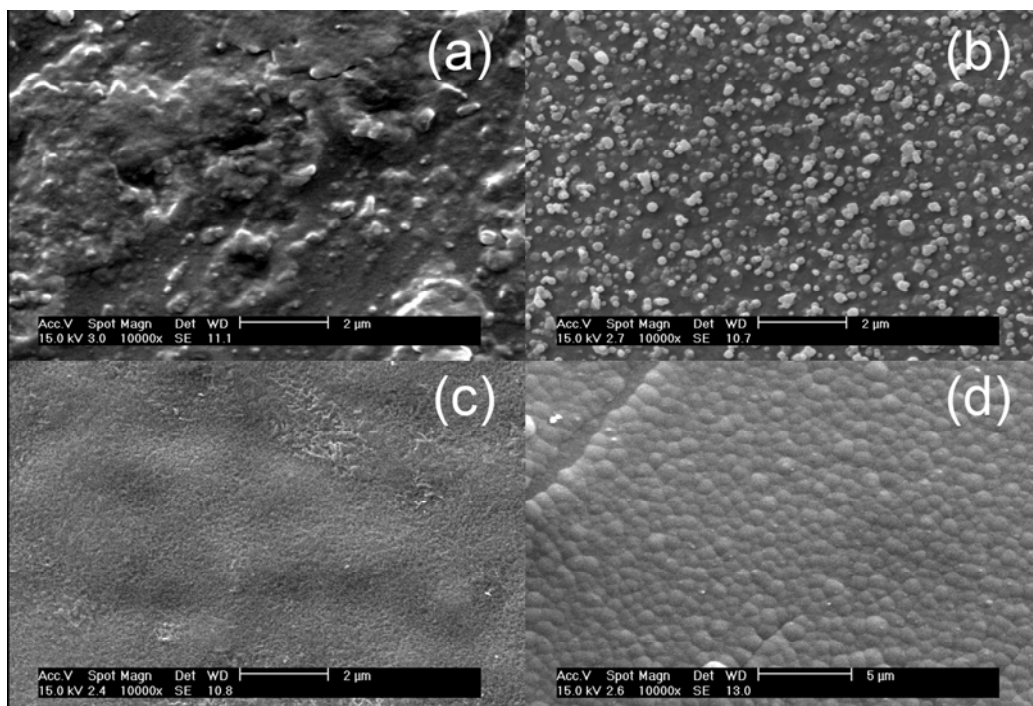


Fig. 3 SEM micrographs of the films deposited with different precursor concentration and time: (a) 0.1 M, 10 min, (b) 0.01 M, 10 min, (c) 0.005 M, 10 min, and (d) 0.1 M, 15 sec.

For the droplets with high concentration landed on hot substrate, droplets were quickly vaporized and decomposed, so large amounts of crystal nuclei come into being, and this led to the rough surface of ZnO film. While the lower concentration droplets splashed onto the substrate, the removal of the solvent need a relatively longer time, in the meantime, other droplets would deposit on substrate where precursor had not fully decomposed, the growth behavior of film might be more like a heterogeneous liquid epitaxy, so dense and smooth ZnO film was achieved [8].

3.3 The influence of preparation conditions on photoluminescence

Fig. 4 shows the room temperature PL spectra of the ZnO thin films prepared with precursor concentration of (a) 0.1 M, (b) 0.01 M, and (c) 0.005M for 10 min. Two prominent PL emission bands at 422 nm, 468 nm are observed from Fig. 4(a); three PL bands have peaks at 390, 417 and 466 nm are shown from Fig. 4(b); it can be found from Fig. 4(c) that there is a strong UV emission band peaked at 390 nm. Three PL bands had peaks around 390, 417-422 nm and 466-468 nm assigned to UV emission, blue emission and green emission, respectively.

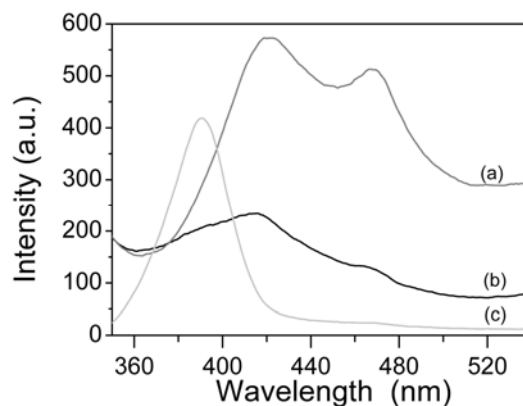


Fig. 4. Photoluminescence with different precursor concentration of: (a) 0.1 M, (b) 0.01 M, and (c) 0.005 M at room temperature.

The strong UV emission peak around 390 nm originates from the recombination of free or bound excitons. Lin et al. calculated the energy levels of the intrinsic defects in un-doped ZnO [9], and their result indicates that the energy interval from the level of Zn_i to the valence band is exactly consistent with the energy (2.9 eV) of the blue emission. So the blue emission, which

observed in our experiment, is caused by Zn_i . Kohan et al. [10] calculated formation energies and electronic structure of native point defects in ZnO, their research indicated that the transition level between the -1 and -2 charge states of V_{Zn} occurs at ~ 0.8 eV above the valence band. It could be expected transitions from the conduction band or a shallow donor to V_{Zn} acceptor at around 2.6 eV in ZnO, so the green luminescence observed in the ZnO films can be attributed to V_{Zn} .

For the ZnO film prepared with precursor concentration of 0.1 M, the stronger emission of Zn_i and V_{Zn} are prominent, and UV emission can not be found. Owing to droplets on hot substrate were quickly vaporized and decomposed, zinc ions had no sufficient time to transfer corresponding position in ZnO lattices, which brought about large amounts of Zn_i and V_{Zn} defects in ZnO film. As to the film prepared with precursor concentration of 0.01 M, V_{Zn} emission become weak, and UV emission appeared at 390 nm, this indicates Zn_i and V_{Zn} defects reduce with the lower of concentration. While ZnO prepared with precursor concentration of 0.005 M, zinc ions had enough time to locate their position in lattices as solvent evaporation time prolonged, which led to decrease of Zn_i and V_{Zn} defects and enhance the quality of ZnO film, hence only UV emission was found in the film prepared precursor concentration of 0.005 M.

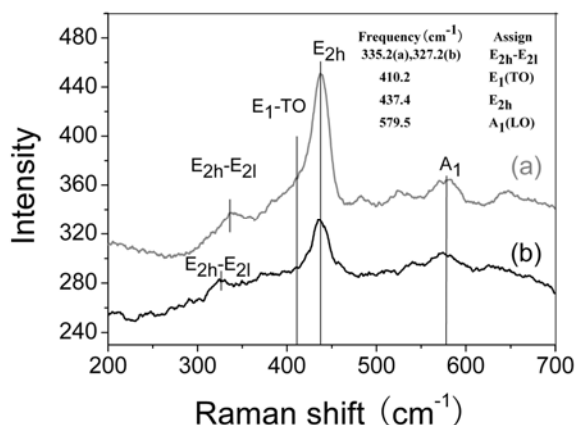


Fig. 5. Raman spectra with precursor concentration of: (a) 0.005 M, (b) 0.1 M.

To provide additional information on the optical properties of defects in the ZnO thin films, Raman scattering investigations were carried out on these ZnO samples. The space group of the hexagonal wurtzite ZnO belongs to C_{6v}^4 , with two formula units per primitive cell. According to the group theory, at the Γ point of the Brillouin zone, there is an existence of following optic modes: $\Gamma = A_1 + 2B_1 + E_1 + 2E_2$, classified as $A_1 + E_1 + 2E_2$ modes (Raman active), $2B_1$ modes (Raman silent), and $A_1 + E_1$ modes (infrared active). Moreover, the A_1 and E_1

modes split into longitudinal optical (LO) components and transverse optical (TO) components [11]. For the lattice vibrations with A_1 and E_1 symmetries, the atoms move parallel and perpendicular to the c -axis, respectively. The low-frequency E_2 (E_{2l}) mode is associated with the vibration of the heavy Zn sublattice, while the high-frequency E_2 (E_{2h}) mode involves only the oxygen atoms.

Fig. 5 shows the Raman scattering spectrum of the ZnO thin film synthesized with precursor concentration of (a) 0.005 M and (b) 0.1 M. In the Raman spectrum of the both samples, three Raman lines due to E_{2h} , A_1 longitudinal optical modes and E_1 transverse-optical (E_1 -TO) at 437.4, 579.5, and 410.2 cm⁻¹, respectively, are observed as expected from the Raman selection rules in wurtzite crystal structure. The E_{2h} - E_{2l} mode frequencies of sample (a) and (b) were observed at 335.2 and 327.2 cm⁻¹. The significant difference for E_{2h} - E_{2l} mode frequencies was caused by the shift of E_{2l} , the shift is associated with variation of Zn sublattice. It could be presumed that the E_{2l} shift is related to the phonon localization by V_{Zn} .

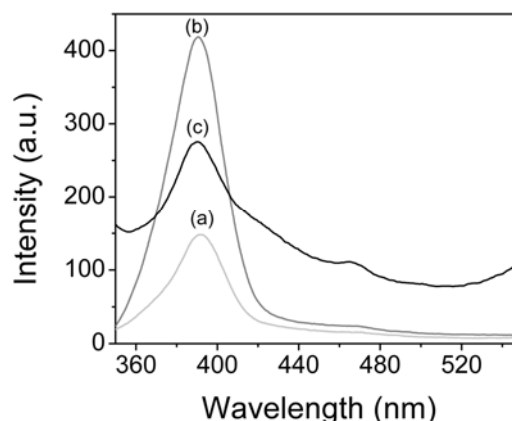


Fig. 6. PL spectra at different substrate temperatures of: (a) 350°C, (b) 400°C and (c) 500°C.

Fig. 6 shows PL spectra for a set of ZnO films deposited at different substrate temperatures of (a) 350 °C, (b) 400 °C, and (c) 500 °C for 10 min with 0.005 M precursor. The UV emission band can be found in all samples, the luminescence intensity depends strongly on the deposition temperature. The film prepared at 400°C shows stronger UV emission intensity than other film; the film obtained at 500°C show a moderate UV emission intensity and a weak emission of V_{Zn} . For the film deposited at 350°C, the weak UV emission may be attributed to the poor crystallization, which relate with deposition temperature for the pyrolysis of zinc nitrate [12]. However, at temperature of 500 °C, rapid rate of crystallization led to the increase of defects, hence the UV emission intensity decrease and a weak emission of V_{Zn}

appeared.

4. Conclusions

ZnO films were grown by EUSP technique. The influence of precursor concentration on ZnO films morphology was explored by SEM, dense and smooth films were prepared using lower concentration precursor. The influence of preparation conditions on photoluminescence were discussed, PL and Raman spectra of ZnO show that blue and green luminescence observed in ZnO films can be attributed to Zn_i and V_{Zn} . The relationship between substrate temperatures and photoluminescence was researched. It is shown that the films deposited at the temperature of 400°C revealed good structural quality without obvious defect emission.

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