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A novel simple preparation technique of ZnO thin film with good structural and optical properties

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ZnO thin films were prepared by two-step thermal oxidation of thermal evaporation Zn films on glass substrates. The oxidation was carried out in air by a two-step, first at 250°C for 2 hours, then at 400°C,450°C 500°C, and 600°C for 1 hour, respectively. The structural and optical properties of ZnO films were investigated by X-ray diffraction (XRD), Scanning electron microscopy (SEM) and optical transmittance. X-ray diffraction (XRD) and scanning electron microscopy (SEM) studies indicated that the ZnO film obtained at 500°C oxidation temperature for 1h has the highest crystallinity quality. The photoluminescence (PL) measurements performed at RT show that the film oxidized at 500°C exhibits the highest intensity and the narrowest full-width at half-maximum (FWHM) of ultraviolet (UV) emission at 370nm . The optical transmittance measurements show that ZnO films are highly transparent in the visible region and the absorption edge blue shifts with increasing oxidation temperature from 5000 – 600 ^{o}C. The optical bandgap at 500 °C were calculated to be 3.27 eV. In conclusion, by optimizing the preparation parameters in this simple technique, high crystallinity quality ZnO thin films with good optical properties can be successfully achieved.

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Keywords: ZnO thin film, Evaporating deposition, PL spectra, Optical properties

1. Introduction

Zinc oxide (ZnO) present many exceptional characteristics due to their direct gap of 3.37 eV at room temperature, good optical properties, strong free-exciton binding energy of about 60 meV, and excellent piezoelectric properties. Therefore, they have many potential applications in various technological domains, such as transparent conducting films/electrodes in display devices and solar energy cells, gas sensors , short wavelength light-emitting devices, surface acoustic wave devices (SAW) and acoustic-optical devices [1–5]. Another advantage of ZnO relative to other materials is its low price, placing it as a highly potential candidate for industrial applications [6]. In recent years, more and more researchers have been attracted to study the fabrication techniques and properties of ZnO films. Many techniques are being employed to prepare ZnO thin films on various substrates, such as sol–gel deposition, metal-organic chemical vapor deposition (MO-CVD), magnetron sputtering, ion beam-assisted reactive deposition, spray pyrolysis, pulsed laser deposition (PLD) [7] , thermal oxidation [8-14], etc. Among the various deposition techniques, direct thermal oxidation of metal Zn thin film is a simpler, and cheaper method than the others and gives the possibility of obtaining the ZnO thin films with suitable electrical and optical properties for large area solar cell applications. But there are still much open problems on the structural, electrical and optical properties of the ZnO films prepared by metal Zn oxidation.

The aim of this work is to prepare ZnO thin films on glass substrate by using a resistive thermal evaporation technique followed by a two-step thermal oxidation and to investigate the possible influences of change in oxidation temperature on the films' microstructures and optical properties.

2. Experimental

The substrates selected in this experiment were glass slides. The glass slides are ultrasonically cleaned in acetone and alcohol for 15 min, respectively. Then, they are rinsed in distilled water and dried in flowing hot air. Zn metal films were deposited on the substrates by thermal evaporation. A diffusion-pumped vacuum system with a base pressure of 2×10^{-3} Pa was used for the deposition. The substrates were mounted directly over the tungsten

boat with about 18 cm separation. Metallic Zn powder (99.999 % pure) was evaporated from resistively heated tungsten boats. The glass slide surface temperature was measured by a thermocouple and was below 40°C during the deposition process. The thickness of the deposited Zn thin films was about 600 nm. After deposition, the Zn films were successively transferred into a thermal tube furnace for oxidation. Moreover, to avoid out diffusion of Zn at high temperature, all the Zn films were oxidized at 250 °C for 2 h at first, then the oxidization temperature rise quickly to 400 °C, 450 °C, 500 °C and 600 °C and was kept at the temperature for 1 hour, respectively. After oxidation, the sample was cooled down to the room temperature in the furnace.

X-ray diffraction (XRD) (Rigaku D/Max-IIIC) analysis was performed to investigate the crystallographic properties The wavelength of the x-ray beam used in diffraction is 0.1542 nm. All samples were scanned from 25° to 65° of 2θ angle continuously. The surface morphology of the films was characterized by scanning electron microscopy (SEM) (Hitachi S4800). Photoluminescence spectra were measured in the wavelength range of 350–600 nm at RT using a He–Cd laser (325 nm) with a power of 50mW as the excitation source to investigate the optical properties of these films. Optical transmission spectra were measured with a double beam spectrometer (UV-3000). A clean glass slide was used as reference sample.

3. Results and discussion

The crystalline quality and orientation of ZnO thin films were investigated by the x-ray diffraction (XRD). Fig. 1 shows the XRD spectra of the films prepared at 400 °C 450 °C, 500 °C, 550 °C and 600 °C oxidation temperatures. In order to discuss both the main peak and small peaks in detail, we plot the XRD spectra in log-scale.

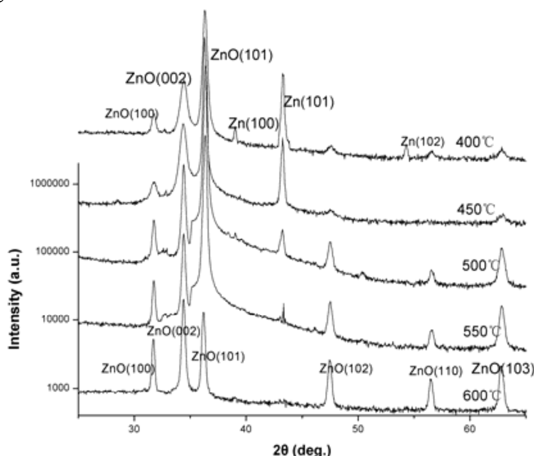


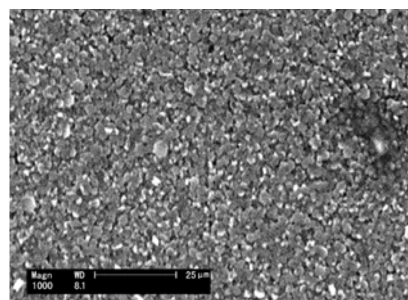
Fig.1. XRD spectra of the samples prepared under the various oxidation temperatures.

It can be seen that besides the peaks from hexagonal close packed lattice metallic zinc diffraction, there are some peaks appearing on this spectrum of the films oxidized at 400 °C, which can be attributed to hexagonal structure ZnO diffractions, indicating formation of a two-phase structure. This formation of a two-phase structure reveals that partial metallic Zn has transformed to ZnO at 400 °C. As the oxidation temperature increases from 450 °C to 550 °C. All of the films show a main peak at 2θ=36.7°, which correspond to (101) diffraction of the hexagonal wurtzite ZnO structure, the intensity of (101) peak increases and reaches a maximum at 500 °C, then decreases. Meanwhile, some weak peaks at 2θ= 31.9, 34.6°, 47.6° and 63.2° also appear on some of the films, which can be attributed to (100), (002), (102),and (103) diffractions of the hexagonal wurtzite ZnO structure, respectively. The intensities of these peaks increase monotonically with the increase of oxidation temperature. On the other hand, the Zn (100),(101)and(102)peaks at 39.2°, 43.3° and 54.4° decreases monotonically with the increase of oxidation temperature. All of the peaks attributed to metallic Zn disappear When the oxidation temperature reach 600 °C, which indicates that metallic Zn was transformed to ZnO completely at this temperature. The XRD spectra of ZnO films reveals that ZnO thin films prepared on glass substrates by oxidation of metallic Zn possess a polycrystalline hexagonal wurtzite structure. The intensity and full width at half maximum (FWHM) of ZnO (101) peak from the film oxidized at 500°C is the highest and narrowest, respectively. Using Scherrer formula

$$\mathrm{GS} = \frac{0.9\lambda}{\mathrm{B}\cos\theta}, \tag{1}$$

we can evaluate the mean grain sizes (GS) of the films, where λ, θ, and B are the X-ray wavelength (0.154 nm), Bragg diffraction angle and line-width at half-maximum of (101) peak around 36.7°, respectively. The calculated grain sizes of the samples are 23.7, 45.3, 37.4 and 31.3 nm for the samples oxidized at 45 0°C, 500 °C, 550 °C and 600 °C, respectively. This indicates that the particle size increases with increasing oxidizing temperature below 500 °C and decreases with a further increase of temperature.

By taking into account that the melting point of metallic Zn is 419.5 °C, when the oxidizing temperature is higher than the melting point too much, the Zn thin film under the top ZnO layer will be melt, resulting in the supply of oxygen to the Zn layer and the continuing growth of the oxide particles to be limited. Therefore, in order to obtain high quality ZnO thin film we should raise the oxidation temperature and lengthen the oxidation duration in the first- step to make more Zn particles oxidized below the melting point of metallic Zn.



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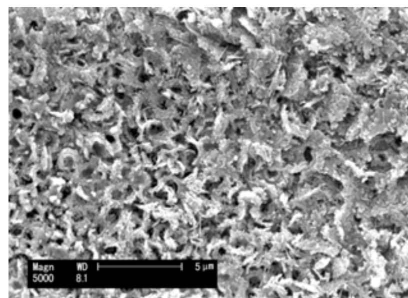

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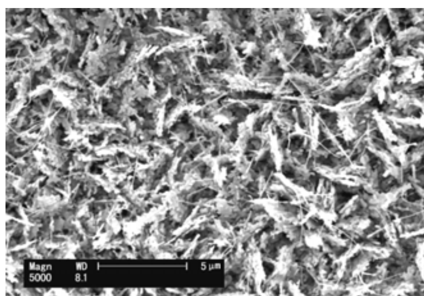

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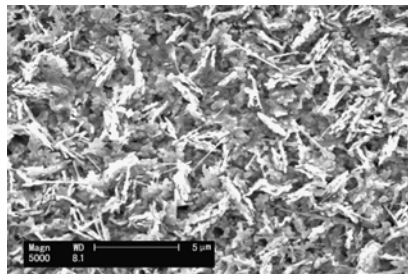

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Fig. 2. The typical surface SEM image of the as-deposited sample (a) and the samples prepared under different oxidation temperature of 400 ℃ (b), 500 ℃ (c) and 600 ℃ (d).

Shown in Fig. 2 are the typical SEM images of the surface morphology of the as deposited zinc film and the oxidized films at various oxidation temperatures. The Zn film is composed of uniform particles with micron size. After oxidation, the surface morphology of the film changes significantly. With the increase of the oxidization temperature from400 °C to 500 °C, the sizes of the grains become bigger and the surface of the films become loose more and more, the grain curved first and formed dendritic-like structure then and they intersect each other. When the sample oxidized at 600 °C, the sizes of the grains become smaller than at 500 °C. The dendritic grain formed on the top of the film and the bottom layer become compact again. The change of gain size agrees with the results of XRD analysis.

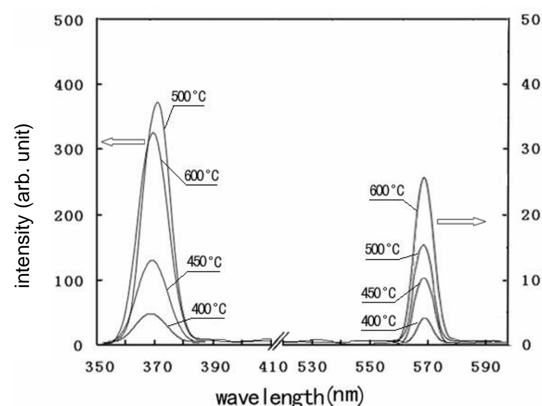

Fig. 3. The PL spectra of the samples prepared at various oxidation temperatures of 400, 450, 500 and 600 ℃.

Fig. 3 presents the PL spectra of the samples prepared at various oxidation temperatures of 400, 450, 500 and 600 °C. The PL spectra for all the samples have similar main features, and can be divided into two luminescence bands of UV emission at 350–380 nm and yellow emission around 560–580 nm . The UV emission is attributed to free excitonic transition of the near-band-edge and yellow emission attributed to the deep-level transition. This does not agree with the results in others' reports on ZnO films synthesized by oxidation of metallic Zn. In their work, the typically emission peaks are around 378 nm (UV emission) and 510 nm (green emission) [15,16]. We think that the results are probably associated with the grain size of ZnO films prepared by by the two-step thermal oxidation. As the annealing temperature increases, the UV peak position is basically unchanged, but the intensity increases, and reaches a maximum at 500 °C, then the UV emission intensity decrease. The FWHM of UV peaks reaches the narrowest value (110 meV) at 500 °C. On the other hand, the deep-level emission intensity increases monotonously with annealing temperature. The PL intensity ratio of the near-band-edge UV emission to the deep-level green emission is often used to evaluate the concentration of structural defects in ZnO. In the present experiment, the ratio reaches a maximum 32 at 500 °C, and then decreases with the increase of the oxidation temperature. When the Zn films are oxidized at high temperatures in air, in addition to oxygen other impurities such as nitrogen, carbon dioxide, and so on also introduced into the films, and the corresponding defects and impurity levels are formed in the band gap. So the films become more non-stoichiometric and the emission intensity from these deep-levels increases.

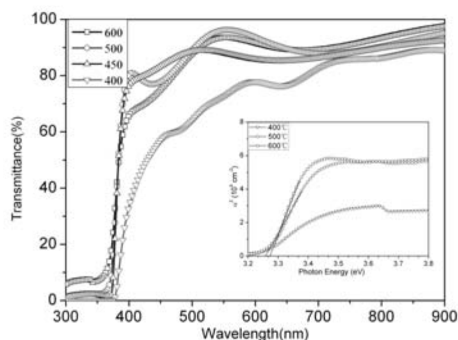

Fig. 4. Transmission spectra of the films oxidized at different temperatures.

The optical properties of the films oxidized at different temperatures were characterized by transmission spectra measured. Fig. 4 shows the transmission spectra of the films oxidized at different temperatures. It can be seen that the fundamental absorption edges of the films oxidized at 450-600 ^{o}C locate at around 380 nm. The films are highly transparent in the visible region and the average transmittance is over 80%. The optical bandgaps can be determined from a conventional method [17]. It is found that oxidation temperature has evident influences on the optical bandgaps of the films. The optical bandgap shifts towards blue with increasing the oxidation temperatures from 500 – 600 ^{o}C as shown in the inset of Fig.4. For the films oxidized at 500 ^{o}C, the optical bandgap reaches 3.27 eV in agreement with the results from [18] (3.27 eV). The blue shift of the optical bandgap can be attributed to the continuous decrease of Zn in the films as confirmed by XRD, which makes the films be more stoichiometric. For the films oxidized at 400 ^{o}C, too much metallic Zn in the films, so the fundamental absorption edges shifts towards the red.

4. Conclusions

Polycrystalline ZnO thin films with the hexagonal wurtzite structure have been successfully prepared on glass substrates by oxidation of metallic Zn in two-step. XRD reveal that the film oxidized at 500°C exhibits the best crystalline quality. The PL spectra at room temperature contain a UV near-band-edge emission peak around 3.35 eV and a defect-related deep-level emission peak around 2.18 eV. The PL spectrum for the film oxidized at 500°C displays the highest intensity ratio (32) of UV emission to deep-level emission and the narrowest FWHM (110 meV) in the oxidation temperature range investigated. With the increase of oxidation temperature the intensity of the deep-level emission increases more and more. This might be due to the non-stoichiometry effect in the ZnO films. The films are highly transparent in the visible region and the average transmittance is over 80 %. For the films oxidized at 550 ^{o}C, the optical bandgap reaches 3.27 eV.

Acknowledgments

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