

Photocatalytic activity of ZnO thin films prepared by two-step thermal oxidation of Zn films

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ZnO thin films were prepared by two-step thermal oxidation of dc-magnetron sputtered Zn films on glass substrates. The structural and optical properties of ZnO films were investigated by X-ray diffraction (XRD), Scanning electron microscopy (SEM) and optical transmittance. XRD reveals that Zn films completely convert to ZnO films after annealing in oxygen at 550 °C for 2 h. SEM shows that floccule-like ZnO nano-wires form on the surface of the films when annealing temperatures exceed 500 °C. The average diameter of the nano-wire is about 20 nm. The optical transmittance measurements show that ZnO films are highly transparent in the visible region and the absorption edge blueshifts with increasing oxidation temperature from 450 – 550 °C. The optical bandgap at 550 °C were calculated to be 3.27 eV. Photocatalytic decomposition results show that the decomposition rate of phenol aqueous solution on ZnO films increases with increasing oxidation temperature. Maximum photodecomposition of 72.6% is obtained with 10 mg/l phenol concentration for 6 hours.

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1. Introduction

Zinc oxide (ZnO) presents many exceptional characteristics due to its direct gap of 3.37eV 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 [1-4]. Another advantage of ZnO relative to other materials is its low price, placing it as a highly potential candidate for industrial applications. Recently, ZnO micro and nanowires have been grown [5] as well as Mn doped nanobelts [6]. Zinc oxide photocatalysis gives the advantages of degrading pollutants using only oxygen as an oxidant, low costs and resulting in safe and environmentally friendly products [7-10]. In recent years, more and more researchers have been attracted to study the fabrication techniques and properties of ZnO films [11-16]. Many techniques have been 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), thermal oxidation [11-20], etc. Among the various deposition techniques, direct thermal oxidation of metal Zn thin films is a rather simple and cheap method and gives the possibility of obtaining ZnO thin films with suitable electrical and optical properties for photocatalysis. Despite of its obvious economic and simplicity, there are still much open problems on the structural, electrical and optical properties of the ZnO films prepared by thermal

oxidation of metal Zn films [21,22].

In this work, ZnO thin films on glass substrate were prepared by two-step thermal oxidation of dc-magnetron sputtered Zn films. The effects of oxidation temperature on the structural, optical properties and photocatalytic activity of ZnO films were investigated.

2. Experimental

The substrates selected in this experiment were glass slides with a size of 2.5 × 2.5 cm². The glass slides are ultrasonically cleaned in acetone and alcohol for 15min, respectively. Then, they are rinsed in distilled water and dried in flowing hot air. The metallic zinc with 99.95% purity was used as target with a diameter of 60 mm and a thickness of 4 mm. The sputtering chamber was evacuated below 2.5 × 10⁻⁴ Pa with a combination of turbo molecular pump and rotary pump. Ar used as sputtering gas, was introduced into the sputtering chamber through a mass flow controller, and the flow rate was regulated to 15 sccm. The working pressure was kept at 1.5 Pa. The target-substrate distance was maintained at 60 mm. The substrates were maintained at 150 °C. A variable dc power supply of 30 - 200 W was used as a power source. Before deposition, the zinc target was pre-sputtered in argon atmosphere for about 15 min in order to remove the surface oxide layer of the target. The sputtering time was 30 min and the dc power was kept at 50 W. The thicknesses of the films measured by cross section SEM micrograph were about 500 nm.

After deposition, the as-deposited Zn films were transferred into a tube furnace filled with high purity O₂ for oxidation. To avoid the evaporation of Zn at high temperatures, all the Zn films were oxidized at 300°C for

2 h at first. Then, the oxidation temperature was quickly elevated to 400°C, 450°C, 500°C, 550°C and kept at these temperatures for 2 hours, respectively. After oxidation, all the samples were cooled down to the ambient temperature in the furnace.

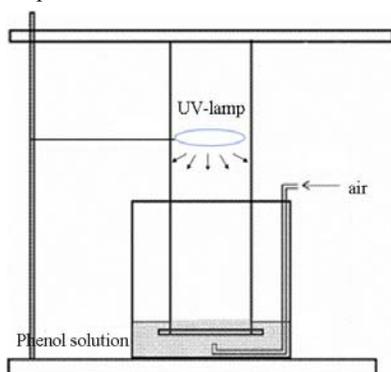


Fig.1 Schematic representation of photo-catalytic setup.

The photocatalytic ability of ZnO films were measured with our home-made setup with an ultraviolet lamp as the light source, and phenol as the degraded target as shown in Fig.1. The process of photocatalytic degradation was monitored by withdrawing definite quantity of aqueous solutions at regular intervals and measuring the absorbance in UV-Vis spectrophotometer (UV- 3 000) for decolourisation. The absorbance of phenol aqueous solutions with different concentrations was measured to exhibit a function relationship between absorbance and concentration.

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. The surface morphology and thickness of the films were characterized by scanning electron microscopy (SEM) (Hitachi S4800). Optical transmission spectra were measured with a double beam spectrometer. A clean glass slide was used as reference sample.

3. Results and discussion

The crystallinity and orientation of the ZnO thin films were investigated by XRD. Fig.2 shows the XRD patterns of Zn films at different oxidation temperatures. In order to discuss both the main peak and weak peaks in detail, we plot XRD patterns in log-scale. It can be seen that besides the diffraction peaks from hexagonal-close-packed metallic zinc lattice there are also some diffraction peaks from hexagonal ZnO after oxidizing Zn films at 400°C. This indicates that a two-phase structure forms at this stage and metallic Zn has partially converted to ZnO. It can be also seen from Fig.1 that all films show a strong peak at $2\theta = 36.7^\circ$, which corresponds to the (101) diffraction peak of hexagonal ZnO, as the oxidation temperature increases from 450 °C to 550 °C. The intensity of (101) peak increases with increasing oxidation temperature from 450 - 500 °C while decreases when the oxidation temperature exceeds 500 °C. In addition, some weak peaks at $2\theta = 31.9, 34.6, 47.6$ and 63.2° also appear

in the XRD patterns. These peaks can be attributed to (100), (002), (102), and (103) diffraction peaks of the hexagonal ZnO, respectively. The intensities of these peaks increase monotonically with increasing the oxidation temperatures. On the contrary, (100), (101) and (102) peaks from hexagonal-close-packed metallic zinc lattice decrease monotonically with increasing the oxidation temperatures. These peaks disappear when the oxidation temperature reaches 550 °C, which indicates that the metallic Zn has been completely transformed to ZnO at this stage. The XRD patterns of ZnO films show that the ZnO thin films on glass substrates prepared by oxidizing the metallic Zn thin films possess polycrystalline structure without any preferential growth orientation.

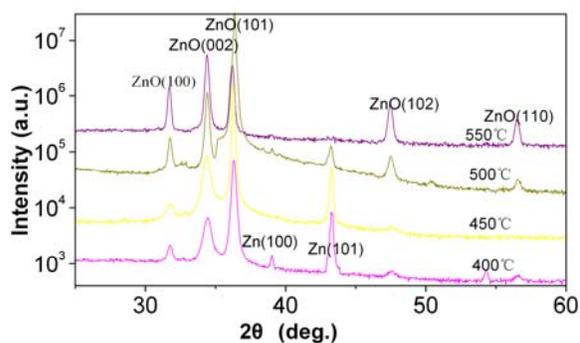


Fig.2. XRD patterns of Zn films at different oxidation temperatures.

Because the melting point of metallic Zn is 419.5 °C, it will melt and be evaporated when the oxidizing temperature exceeds the melting point. Therefore, the supply of oxygen to the Zn layer and the continuing growth of the oxide particles will be hindered. In order to obtain loose ZnO thin films, we elevate the oxidation temperature to a lower point (300 °C) below the melting point of metallic Zn and keep at this stage for 2 h to make most of Zn be oxidized.

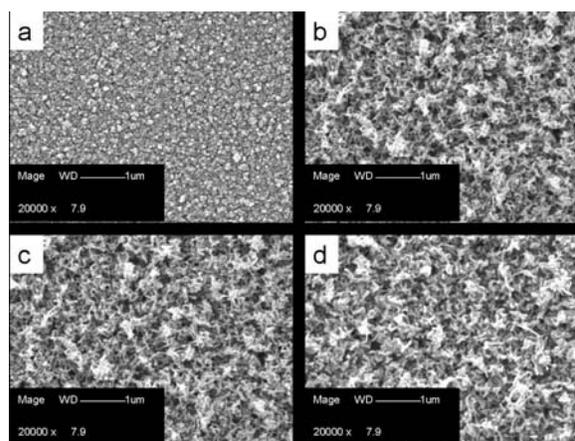


Fig. 3. SEM images of Zn films oxidized at different temperatures. (a: as-deposited Zn films; b: oxidized at 450 °C; c: oxidized at 500 °C; d: oxidized at 550 °C.).

Fig. 3 shows the typical SEM images of Zn films oxidized at different temperatures. It can be seen that the as-deposited Zn film is composed of uniform particles with micron size. After oxidation, the surface morphology of the films changes significantly and many floccule-like ZnO nano-wires form on the surface of the films. The average diameter of ZnO nano-wires is estimated to be about 20nm. It is noted that with increasing the oxidation temperatures ZnO nano-wires become thicker and the surface of the films become looser. We note that the photocatalytic ability of the ZnO thin films may be affected by porosity of the films and surface state of grains. The rough and highly porous surface would favor the electron-hole separation and enhances the photocatalytic ability.

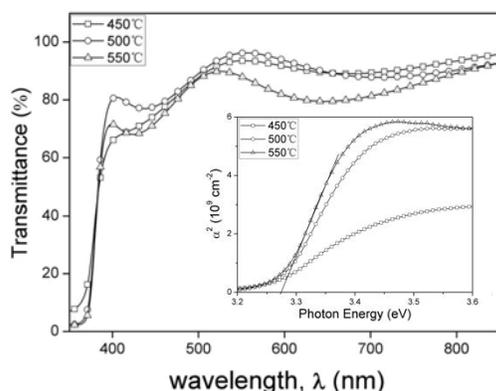


Fig.4. Transmission spectra of the films oxidized at different temperatures.

The optical properties of the films oxidized at different temperatures are characterized by transmission spectra measured in the wavelength range of 250 - 900 nm. Fig.4 shows the transmission spectra of the films oxidized at different temperatures. It can be seen that the fundamental absorption edge locates 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 [23]. It is found that oxidation temperature has evident influences on the optical bandgaps of the films. The optical bandgap blueshifts with increasing the oxidation temperatures from 450 – 550 °C as shown in the inset of Fig.4. For the films oxidized at 550 °C, the optical bandgap reaches 3.27eV. 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.

The photocatalytic ability of the ZnO thin films were investigated with the home-made setup as shown in Fig.1. In this study, the 500mL phenol solution (10mg/L) was illuminated by a 6W Xenon UV-lamp working at the wavelength of 365 nm. The heterogeneous photocatalysis has been found to be pH dependent [9, 19]. In this experiment, the pH value of the primal phenol solution was set at about 6.7. To eliminate high frequency UV light radiation, irradiation from the Xenon UV-lamp lamp was filtered through a 320 nm UV cut-off filter. The incident

intensity was set to be 5 mW·cm⁻². Photocatalytic decomposition of the phenol solutions was characterized by a UV-Vis spectrometer. The wavelength that is prevalingly absorbed by phenol is 510 nm. The air flow can supply O₂ and stir the phenol solutions.

It is known that conduction band electrons (e⁻) and valence band holes (h⁺) are generated on the surface of ZnO particles when ZnO thin film is illuminated by light with energy greater than the band gap energy, as demonstrated in R1. Holes can react with water adhering to the surface of ZnO particles to form highly reactive hydroxyl radicals (OH•), as shown in R2. Oxygen acts as an electron acceptor by forming a super-oxide radical anion (O₂•⁻), as shown in R3. The suspension of super-oxide radical anions may act as oxidizing agents or as an additional source of hydroxyl radicals via the subsequent formation of hydrogen peroxide as shown in R4–R6. The powerful oxidants associated with hydroxyl radicals react with the phenol, and make the solution colorless, as shown in R7. Since decomposition reaction of the phenol is composed of several steps.

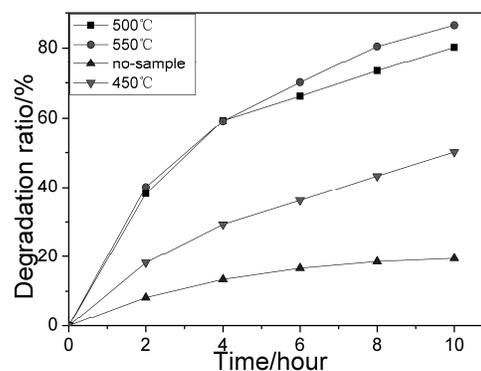
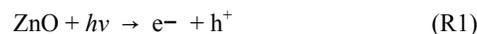


Fig.5. The degradation of phenol under the UV irradiation ($\lambda = 365 \text{ nm}$) as a function of time for ZnO films oxidized at different temperatures.

Degradation of the phenol solutions under the UV light radiation as a function of time for various ZnO films oxidized at different temperature is illustrated in Fig. 5. It can be seen that the decomposition rates for all samples are high within the first 4 hours. As phenol concentration decreases, probability of phenol molecules reacting with ZnO particles decreases and consequently decomposition rate decreases. The overall decomposition rates associated with individual specimens decrease in the order: 450-ZnO < 500-ZnO < 550-ZnO. The overall decomposition rate of 550-ZnO reached 85%. It was observed that the rate of degradation of phenol over ZnO increases with increasing the oxidation temperature. The photocatalytic activity of

the 550-ZnO is much higher as compared to those of 450-ZnO. It was concluded that separation of charge carriers (e^-/h^+), rough and high porous surface of ZnO are the major reasons for its enhanced photocatalytic activity in the present study.

4. Conclusions

Polycrystalline ZnO thin films with hexagonal wurtzite structure have been successfully prepared on glass substrates by two-step oxidation of metallic Zn in high purity O_2 ambience. The ZnO thin films prepared on glass substrates by oxidizing the metallic Zn thin films possess polycrystalline structure. When the oxidization temperature increased to 550°C, the films had better properties for photo-catalysis: the high interstitial rate of the films, high transmittance rate (above 85%). The ZnO thin films with high photocatalytic activity (overall decomposition rate of 85%) can be successfully achieved by optimizing the preparation parameters by this simple technique.

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