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A Novel Approach to Synthesizing Porous ZnO Films: Inorganic Chelating Sol-Gel Method*

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Abstract: Porous ZnO films are synthesized by inorganic chelating sol-gel method, which is a novel sol-gel technique using zinc nitrate as starting materials and citric acid as the chelating reagent. The crystal structure, surface morphology, porous and optical properties of the deposited films are investigated. X-ray diffraction pattern analysis shows that crystal structure of the ZnO films is hexagonal wurtzite. Scanning electron microscopy (SEM) shows that the ZnO film is porous. The curve of pore size distribution has two peak values at about 2.02nm and 4.97nm and BET surface area of the ZnO film is 27.57m^2/g. In addition, the transmittance spectrum gives a high transmittance of 85% in the visible region and optical bandgap of the ZnO film (fired at 500℃) is 3.25eV.

Key words: porous ZnO film; inorganic chelating sol-gel method; pore size distribution; properties
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1 Introduction

ZnO is an n-type semiconducting material with interesting properties such as transparency in the visible and high infrared reflectivity, acoustic characteristics, high electrochemical stability, and excellent electronic properties. It has been widely used in chemical sensor[1], surface acoustic wave device[2], and photoanode films of solar cell[3,4]. Reports are available in the preparation of ZnO films by a variety of techniques including sputtering[5~7], chemical vapor deposition (CVD)[8], thermal oxidation[9], spray pyrolysis[10], and sol-gel process[11~14]. These studies have shown that the properties of ZnO films depend greatly on the method and conditions of deposition.

The present paper reports on synthesis of ZnO films through a novel process involving chelate complex of sol-gel derived precursor films, which uses zinc nitrate as starting materials and citric acid as the chelating reagent. The crystal structure, surface morphology, porous and optical properties of ZnO films are reported.

2 Experimental procedure

2.1 Preparation

Zinc nitrate[$Zn(NO_3)\cdot 6H_2O$](AR) was first dissolved in absolute ethanol(AR) at room temperature. The solution was mixed thoroughly on a magnetic stirrer, once entirely dissolved, a suitable amount of citric acid (AR) was added as chelating agent. The molar ratio of citric acid to zinc nitrate was 1∶1 and the concentration of zinc nitrate was 0.5mol/L. After stirring the solution for 2h, a homogeneous and transparent sol (zinc chelates) was

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obtained. Quartz glass was degreased in an acetone ultrasonic bath and then used as a substrate. The solvent was evaporated at 60~ 70℃ in air and a dried gel formed.

Dip-coating method was used to coat sol on quartz glass substrates and the drawing rate is about 6cm/min . The film was dried at 110℃ in air for 10min. The process was repeated eight times so as to add the thickness of films, and then the wet film was dried at 110℃ in air for 30 min. Finally, the film was fired to the various temperatures. The dip conditions were the same for all samples.

2.2 Characterization

Phase compositions were determined using Philips X-ray diffractometer model D/Max-2500X with nickel filter CuKα. The FT-IR absorbance spectrum of dried gel was also achieved by using FTS3000 spectrometer in the wave number range 400~ 4000cm^{-1}. The microstructure and cross-section of films were observed in Philips XL-30 scanning electron microscope (SEM). Surface area and the pore size distribution (PSD) of 152.7mg samples scraped off the substrate were determined by a gas adsorption method using a BET adsorption-desorption isotherm (high purity N_2 as adsorbate, ASAP 2000, Micromeritics). The optical transmittance of the film was measured by DU-8B UV/VIS double-beam spectrophotometer.

3 Results and discussion

3.1 Structural analyses

To determine the formation of the metal chelates between Zn^{2+} and citric acid, Figure 1 gives the FT-IR absorbance spectra of citric acid and dried gel. The samples were dispersed in a KBr pellet. Curve *a* indicates the standard peaks of citric acid. The peaks at 1750cm^{-1} and 1716cm^{-1} indicate C = O which are diagnostic peaks of carboxylic acid. Curve *b* is the FT-IR absorbance spectra of dried gel. The diagnostic peaks of C= O disappear

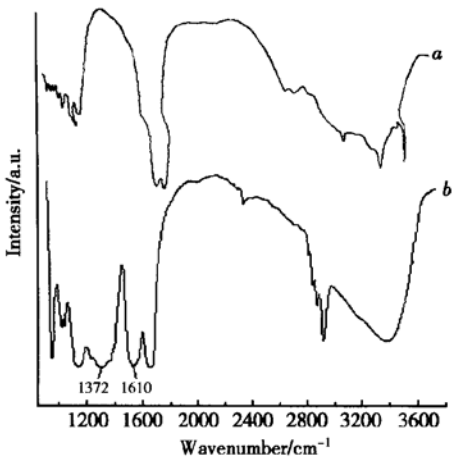
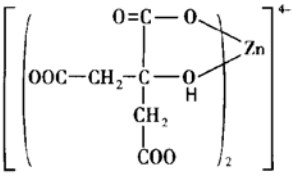
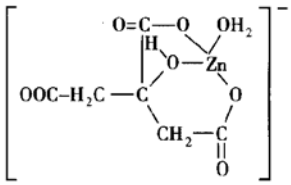


Fig. 1 Comparison of FT-IR absorbance spectra of citric acid (*a*) with dried gel (*b*)

and the peaks of carboxylate appear at 1610cm^{-1} and 1372cm^{-1}. It shows that stable chelated carboxylate has formed between citric acid and Zn^{2+}. Two chelated ways between citric acid and Zn^{2+} are exhibited as follows[15]:





Because absolute ethanol is used as solvent, the stronger peaks of esterified carboxylic acid exist in the range of 1050 ~ 1160cm^{-1}, 1160 ~ 1260cm^{-1}, and 1730cm^{-1}. The diagnostic peaks of citric acid disappear, which shows that no chelated carboxylic acid has been esterified.

X-ray diffraction (XRD) patterns (shown in Fig. 2) of ZnO thin films at different firing temperatures show that ZnO is polycrystalline and the crystal structure is hexangular wurtzite. At 400℃, (100), (002), (101), (110), and (103) diffraction peaks appear. With the increase of temperature, the intensity of (002) diffraction peak becomes

stronger and the intensity of other peaks gradually becomes weak or disappears. Therefore, the ZnO film exists a preferential orientation of *c*-axis.

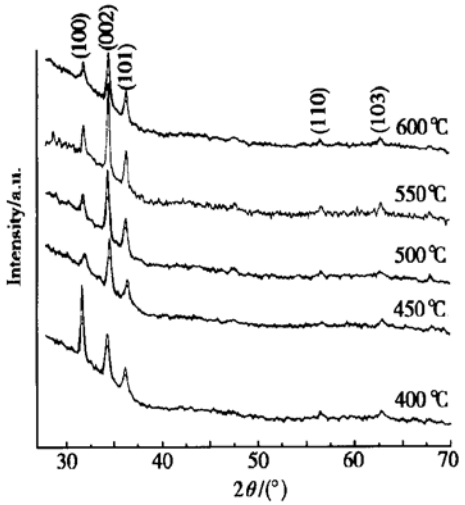


Fig. 2　XRD patterns of ZnO thin films at various firing temperatures

The crystallite size of the ZnO film fired at 500℃ is calculated from the full width at half the maximum (FWHM) of the (002) diffraction peak by the Sherrer equation: $D = 0.94\lambda/\beta\cos\theta$, where λ is X-ray wavelength ($\lambda = 0.15405$nm) and β is the FWHM (4.92×10^{-3}) in radians. So the average grain size is about 30.90nm.

3.2　Characteristics of properties

3.2.1　Porosity

The SEM photographs (Fig. 3) show the surface and cross-section of ZnO films prepared by the repeating dip-coating method. It is observed that the surfaces of ZnO films fired at 400℃ are smooth and the grain are unclear, indicating the microstructures of zinc citrate have not been completely decomposed. Nano-grains and a roughness surface of ZnO films appear at 500℃ and the grains size of ZnO films increase with annealing temperature up to 600℃. The grains of film fired at 600℃ grow large(about 40nm) but some aggregated and the surface appears a porous structure. The films thickness is about 157nm in the cross-section image(d) of the film fired at 500℃.

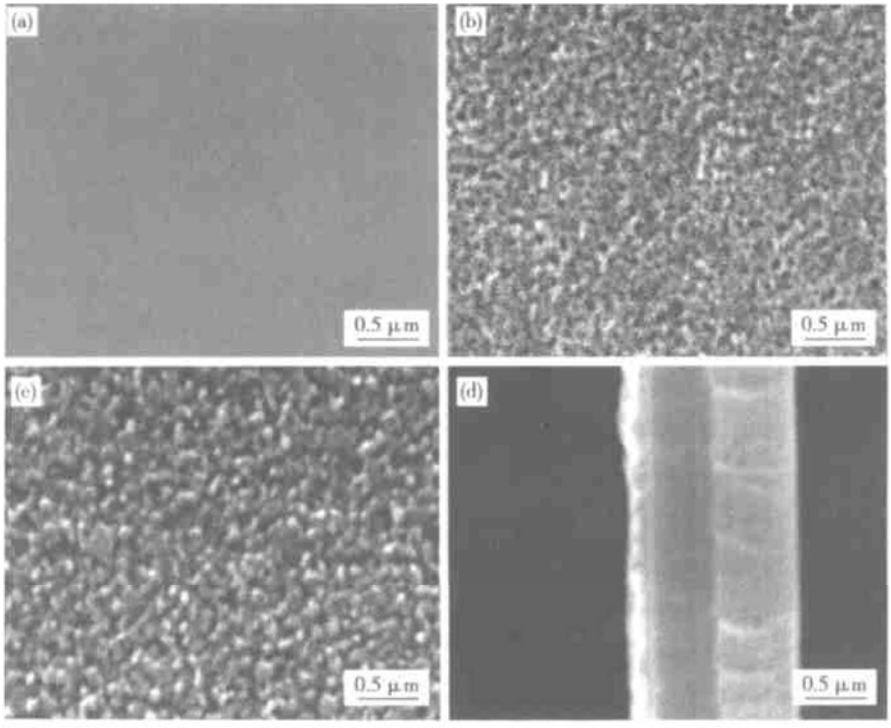


Fig. 3　SEM micrographs and cross-section of ZnO thin films annealed at (a) 400℃, 1h; (b) 500℃, 1h; (c) 600℃, 1h and (d) 500℃, 1h

Nitrogen adsorption is a standard procedure for the determination of the pore size distribution (PSD) of porous solids. The PSDs of the samples are calculated by employing the regularization method according to density functional theory (DFT) that is based on a molecular model for adsorption of nitrogen in porous solids[16]. As illustrated in Fig. 4, the ZnO film fired at 500℃ (Fig. 4 (a)) exhibits an adsorption-desorption isotherms

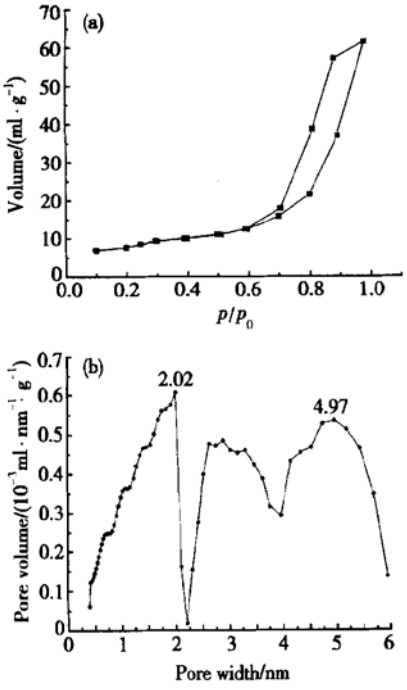


Fig. 4 (a) Nitrogen adsorption-desorption isotherms measured at 77K of ZnO films; (b) Pore size distribution of ZnO films obtained by DFT analysis.

of type Ⅴ according to IUPAC[16]. There exists a sharp adsorption at relative pressure $p/p_0 = 0.7$ and a largest adsorption at relative pressure $p/p_0 = 0.98$, showing that pore of ZnO film consists of micropores or mesopores. BET surface area is calculated to be 27.57m^2/g. The curve of pore size distribution of ZnO films obtained by DFT analysis has two peak values at about 2.02nm and 4.97nm showing the film mainly comprises mesopores of 2.02nm and 4.97nm. It can be concluded that the film possesses some micropores and a large amount of mesopores.

3.2.2 Optics property

Figure 5 shows optical transmittance of ZnO films at different firing temperatures in the wavelength (λ) range from 300nm to 900nm. The optical spectra of all samples exhibits a high transmittance of 85% in the visible range when λ is above 400nm. It is observed that sharp ultraviolet absorption edges at approximately $\lambda = 380$nm, which is close to the intrinsic bandgap of ZnO (3.37eV). The tendency of curves depends on the annealing temperature. Optical transmittance at 380~ 600nm decreases with the increase of annealing temperature, but grows larger at 600℃, the reason of which is still unclear and need further study. The weak fluctuation in the curves is due to the interferences in the thin films owing to the reflection at air-ZnO and ZnO-quartz interfaces[12].

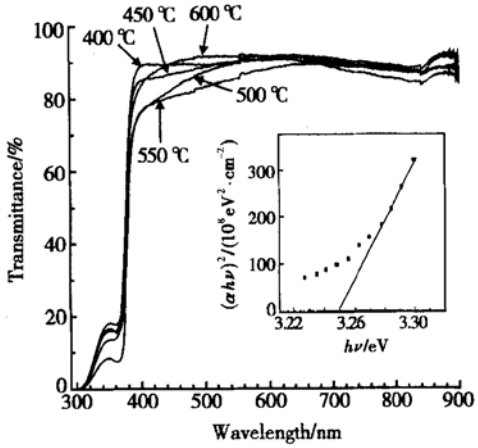


Fig. 5 Optical transmittance and absorption spectra of ZnO thin films obtained at different annealing temperatures and the inset shows a plot of $(\alpha h\nu)^2$ versus $h\nu$ for the ZnO thin films

The absorption coefficient $\alpha(\omega)$ is given by the transmittance T and film thickness d using the formula

$$\alpha(\omega) = -\ln(1/T)/d$$

where ω is angular frequency. When $\alpha(\omega)$ exceeds 10^{-4}cm^{-1}, α obeys the relationship as

$$\alpha h\nu = k(h\nu - E_g)^m$$

where E_g is the optical bandgap, k is a constant and the exponent $m = 1/2, 1, 2, 3$, depending on the types of electronic transition in k-space. To deter-

mine the optical bandgap of the ZnO thin films, taking $m = 1/2$ gives the best fit for this film. The optical bandgap, E_g, is determined for ZnO (annealed at 500℃ and film thickness $d = 157$nm) by extrapolation of linear part of the plot of $(\alpha h\nu)^2$ versus the excitation energy, $h\nu$ as inset in Fig. 5. The $E_g = 3.25$ is nearly the same as those for ZnO films deposited by CVD[18] (3.17eV), spray pyrolysis (3.26eV)[19] and sol-gel (3.21eV)[20]. The result for ZnO film by inorganic sol-gel method indicates electronic transitions of direct type.

4 Conclusion

We have successfully synthesized porous ZnO thin films by inorganic chelating sol-gel method, which used zinc nitrate, absolute ethanol and citric acid as precursor material, solvent and chelating agent respectively. The results show that the stabilitated metal chelates can be formed between Zn^{2+} and citric acid. The ZnO films are polycrystalline and the crystal structure is hexagonal wurtzite. The surface of ZnO films is porous and mainly consists of mesopores of 2.02nm and 4.97nm. Grain size of films grows large with the increase of annealing temperatures. BET surface area of ZnO film fired at 500℃ is 27.57m^2/g. The transmittances spectrum gives a high transmittance of 85% in the visible region and the optical band-gap of ZnO film (fired at 500℃) is 3.25eV.

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无机络合溶胶-凝胶法制备多孔 ZnO 薄膜*

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摘要: 利用无机络合溶胶-凝胶法制备多孔 ZnO 薄膜, 同时利用多种测试手段对薄膜的晶体结构、表面形貌、多孔和光学性能进行了研究. XRD 和 SEM 的测试结果表明, ZnO 薄膜的晶体结构为六方纤锌矿, 薄膜表面呈多孔状. 由孔径分布曲线得出薄膜的孔主要集中在介孔 2.02nm 和 4.97nm; 500℃煅烧得到的 ZnO 薄膜的比表面积是 27.57m^2/g; 在不同温度下煅烧的薄膜在可见光区域透射率均高于 85%, 光学带宽为 3.25eV.

关键词: 多孔 ZnO 薄膜; 无机络合溶胶-凝胶法; 孔径分布; 性能

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