The preparation, electrical and optical properties of indium doped ZnO conductive nanoparticles

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In this paper, In-doped ZnO (IZO) nanoparticles were prepared by the solvothermal method . The structure properties of the as-prepared IZO nanoparticles were studied in detail using X-ray diffractometer (XRD) and transmission electronic microscopy (TEM), Structural characterization indicates that the IZO nanoparticles were spherical shape with the wurtzite structure and IZO-5 nanoparticles had average particle size of 60 nm. In addition, the effects of indium doping level and H_2 reduction conditions on the conductive properties of the prepared IZO nanoparticles were studied. The most optimal conductivity of IZO nanoparticles was achieved with 5 mol% indium doping. Compared with pure ZnO as prepared, before and after H_2 reduction treatment, the resistance of IZO decreased more than two and five orders, respectively. Furthermore, the IZO nanoparticles show superior optical transparent in the visible light region. Consequently, the prepared IZO nanoparticles are promising as transparent conductive filler due to the excellent electrical conductive and optical transparent properties.

(Received January 16, 2010; accepted February 02, 2010)

Keywords: IZO, Nanoparticles, Solvothermal method, Electrical conductivity, Reduction

1. Introduction

ZnO is an n-type semiconductor with a wide band gap of 3.37 eV and it has a wide range of applications including as UV absorber, catalysts, luminescent materials, surface acoustic wave devices, varistors and transparent conductors [1-7]. So-called transparent conductors have low optical absorption in the visible region of the optical spectrum and are good electrical conductors. Other transparent conductors such as SnO2: Sb, In2O3: Sn, and Cd2SnO4 are toxic and/or more costly. Thus, ZnO based materials are especially attractive on consideration of the low cost and lack of toxicity. Some applications of transparent conductors require films. Examples of these applications are transparent electrodes for optoelectronic devices, transparent heat mirrors for solar energy utilization, and coatings to heat the surface of glass windows [6-9]. Powders of transparent conductors also have important applications such as additives to polymers and paper to prevent buildup of static electricity or as functional filler in transparent thermal resistant coating or films [10-12]. Highly colored conductors such as carbon are undesirable in some of these applications.

Electrical and optical properties of undoped ZnO depend mainly on deviation from the stoichiometric composition. Either oxygen vacancies or interstitial zinc atoms are expected to be donors in pure ZnO. However, the content of oxygen vacancies or interstitial Zn atoms in zinc oxide is typically difficult to control. ZnO doped with Al, Ga and In have been studied in the past years due to the unique properties of doped ZnO such as excellent conductivity and transparency in visible light [6-15]. In particular, In is considered one of the best dopant due to its high stability and similar ionic radius with zinc. The electrical and optical properties of In-doped ZnO (IZO) can be controlled by varying the amount of dopant instead of manipulating the non-stoichiometry. In general, only the IZO films are subject to investigation. Knowledge of the electrical and optical properties of IZO nanoparticles itself is surprisingly limited and which is very important for the application of IZO nanoparticles as transparent conductive filler.

In the present paper, solvothermal method was used for preparation of IZO nanoparticles. First, the IZO nanoparticles with different In/Zn molar ratio were prepared by solvothermal reaction in methoxyethanol solution. Then, for further improving the conductive properties of the prepared IZO nanoparticles, the process of H_2 reduction has been employed. The as-prepared IZO nanoparticles were characterized using XRD and TEM. In addition, the effects of indium doping on the electrical conductive and optical properties of the IZO nanoparticles were investigated in detail.

2. Experimental procedure

2.1 Preparation of IZO nanoparticles

The chemical reagents used in this work were methoxyethanol ($H_3COCH_2CH_2OH$), zinc acetate dihydrate (Zn $(CH_3CO_2)_2 \cdot 2H_2O$), Indium (III) chloride ($InCl_3$), ethanol and distilled water. All reagents were analytical purity and used without further purification.

IZO nanoparticles were prepared by a solvothermal method similar to that described by Cimitan et al [12]. 3.52 g Zn $(CH_3CO_2)_2 \cdot 2H_2O$ and the necessary amount of $InCl_3$ to obtain the desired Zn: In molar ratio, were dissolved in 40 g of methoxyethanol (>99.5%) under stirring. The above solution was ultrasonically treated for more than 10 min and then transferred to a 50ml capacity Teflon-lined autoclave. The autoclave was sealed into a stainless steel tank and kept at 175℃ for 2 hours. Afterwards, the reactor was cooled to room temperature naturally. The resulting samples (Table 1) were collected and washed with de-ionized water and ethanol, then dried at 80 ℃ in air. For further improving the electrical conductivity of the prepared IZO particles, the products were reduced within the H_2 atmosphere at 700℃ for 30 min.

Table 1. IZO samples with different In: Zn molar ratio.

Sample no.	ZnO	IZO-1	IZO-2	IZO-3	IZO-4	IZO-5	IZO-6
In/Zn (mol %)	0	0.01	0.02	0.03	0. 04	0.05	0.06
Electrical Resistivity (Ω·cm)	7830/ $2\times10^{5*}$	1840	120	110	110	6.19/1040*	28.2

* Electrical resistivity before H_2 reduction treatment.

2.2. Characterization

To reveal the crystalline structure of IZO powders, XRD analysis was carried out on a Bruker D8 ADVANCE X-Ray diffractometer at a voltage of 40 kV with Cu-Kα radiation (λ=1.5406 Å) in the 2θ ranging from 10° to 80°. Transmission electron microscopy (TEM) of IZO samples was performed with a transmission electron microscope (Model JEM-2100, Hitachi) and the particle sizes from TEM were estimated with the software of Photoshop 7.0. The Ohm Resistances (R) of the as-prepared IZO nanoparticles were measured with a DT890A universal meter. Because the samples were in powder form, measured conductivities are affected by the powder density and contacts between grains. Thus, the conductivities of IZO nanoparticles with a fixed weight of 0.2 g were measured with a self-made Φ8 mm mould under 5 MPa pressure. The resistivity can be calculated from the equation: $\rho = R \cdot A/H$, where ρ is the resistivity (Ω·cm) of the powders, A the cross sectional area (cm^2) and H the thickness (cm) of the pressed IZO slice powders. To investigation the optical properties of the prepared IZO nanoparticles, IZO-5 nanoparticles were mixed with transparent epoxy resin (The weight ratio of IZO-5: epoxy resin was 1%) and coated on a glass sheet. Then the optical properties of the glass sheet were measured by using a UV-VIS spectrophotometer (Model Cary 5000).

3. Results and discussion

3.1 Structural characterization

The preparation of IZO by solvothermal synthesis yielded nanoscale particles suspended in methoxyethanol solution. As shown in Fig. 1, the possible reaction mechanism was proposed on the basis of experimental results and literature [12]. The formation of doped ZnO nanoparticles could be based on a hydrolytic process initiated by the OH ions that can be generated as a result of an esterification reaction of acetate ions with alcohol, as already reported. Alcohols, in fact, provide an appropriate medium for the hydrolysis of carboxylates that yield ZnO through the condensation route. Thus, the esterification of acetate with methoxyethanol could lead to the release of hydroxyl groups bound to the zinc species whose condensation leads to ZnO and water, as indicated in Fig. 1. IZO nanoparticles can be harvested from the obtained methoxyethanol solution by centrifugation or filter.

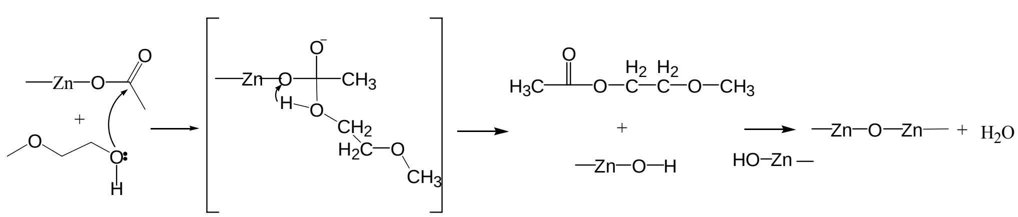

Fig. 1. Schematic representation of synthesis of doped ZnO nanoparticles.

The morphology and particle size of prepared IZO nanoparticles were observed with TEM. Fig. 2 reveals the TEM picture of IZO-5 nanopaticles, it can be seen that most of the IZO-5 nanoparticles are spherical in shape with an average particle size of about 60 nm. In addition, the photograph of IZO-5 particles shows somewhat of light agglomeration, which may be induced by the drying process. In addition, in this study, undoped ZnO particles appear white color, whereas In-doped ZnO particles appear bluish white color, and as the doped level increased, the color of IZO is enhanced. The change of the IZO color implies that the Indium element has been doped into the ZnO lattice and controlled the ZnO growth.

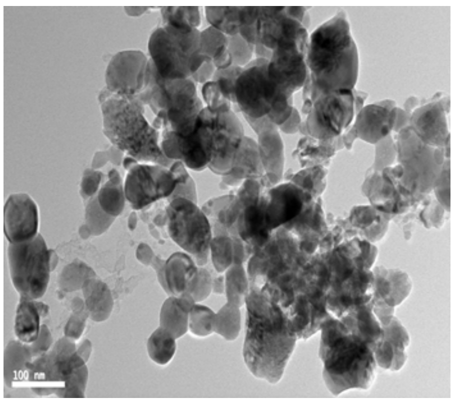

Fig. 2. TEM picture of IZO-5 nanoparticles.

Fig. 3 displays the XRD patterns of pure ZnO and IZO-5 nanoparticles. It can be seen that the XRD patterns of IZO were similar with pure ZnO, and both of those agree well with the standard wurtzite structure (JCPDS file No.05-0664). No other phases have been detected, which indicates that all indium ions come into the crystal lattice of bulk ZnO to substitute for Zinc ions. The formation of doped metal oxides with the structure of ZnO was preferred over the formation with the structure of In_2O_3 and $Zn_2In_2O_5$. Furthermore, all diffraction lines are broadened, which indicates nano-sized crystallites in the samples.

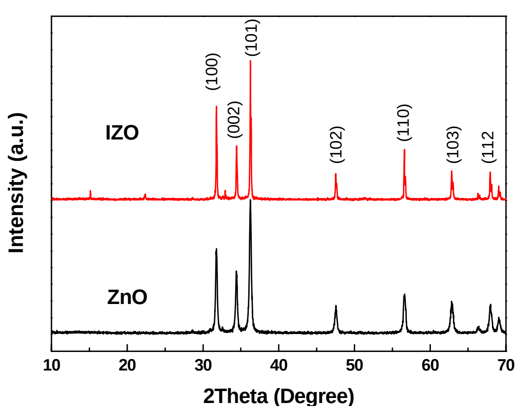

Fig. 3. XRD patterns of ZnO and IZO-5 nanoparticles.

3.2 Electrical and optical properties

As show in Fig. 4, the influences of Indium doping content on the electrical resistivity of IZO nanoparticles were investigated. It can be observed that electrical resistivity of IZO nanoparticles shows a tremendous decreasing tendency initially with increasing Indium doping content. When the Indium doping content was increased to 5 mol%, the electrical resistivity of IZO-5 nanoparticles is decreased by more than three orders compared with the pure ZnO particles, which means that the electrical conductivity is increased more than three orders. Further increasing of the Indium doped level leads to the increased electrical resistivity of IZO nanoparticles. The primary reason of the decrease in resistivity at low doping level is attributed to the increase Indium dopant concentration due to substitution of In^{3+} at the Zn^{2+} lattice site giving one extra electron which acts like a donor. However at higher doping level no more Zn^{2+} sites may be available for the substitution of dopant In^{3+} because of the limited solubility of indium in ZnO [13]. Another important reason of the decrease in resistivity was the H_2 reduction treatment. In this work, the electrical resistivity of the pure ZnO and 5 mol% In-doped ZnO, without H_2 reduction treatment, is 2×10^5 Ω·cm and 1040 Ω·cm, respectively. However, after H_2 reduction treatment, the electrical resistivity was decreased to 7830 Ω·cm and 6.19 Ω·cm, respectively. The behavior of the resistivity is related both to carrier density and Hall mobility. During H_2 reduction treatment, oxygen desorption from the particles surfaces leads to a higher carrier density and Hall mobility [13,14].

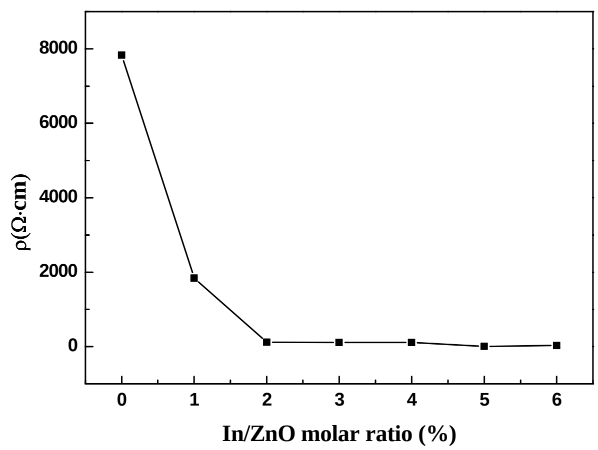

Fig. 4. The effect of In doping level on the electric resistivity of IZO nanoparticles.

In addition, the 5 mol% In-doped ZnO nanoparticles, with the best electrical conductivity, were mixed with epoxy resin and coated on a glass sheet. The prepared IZO-5 nanoparticles possess excellent dispersion property in the epoxy and almost no effect on the color of epoxy resin. Fig. 5 shows the optical transmittance spectrum of the prepared IZO-5/epoxy. The transmittance within the visible light region is almost higher than 60% (including the effect of glass substrate and epoxy resin), which reveal the superior optical properties exhibited by the IZO conductive nanoparticles produced in this work.

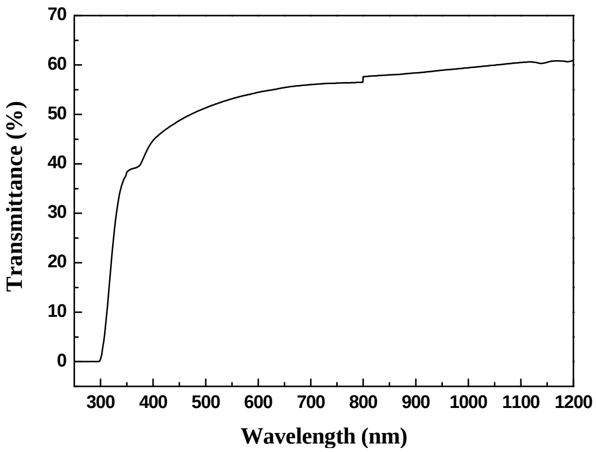

Fig. 5. The optical transmittance spectrum of the IZO-5/epoxy coated glass.

4. Conclusions

In summary, IZO nanoparticles with different In doping content have been prepared by the solvothermal method in methoxyethanol solution. The results from the XRD and TEM measurements revealed that the In-doped ZnO nanoparticles showed good crystallinity with the wurtzite structure and IZO-5 nanoparticles had an average particle size of about 60 nm with spherical like morphology. Moreover, the most optimal conductivity of IZO nanoparticles was achieved with 5 mol% indium doping. Compared with pure ZnO, before and after H_2 reduction treatment, the resistance of IZO-5 decreased more than two and five orders, respectively. Furthermore, the IZO nanoparticles show superior optical transparent in the visible light region. Consequently, the prepared IZO nanoparticles are promising as transparent conductive filler due to the excellent electrical conductive and optical transparent properties.

Acknowledgements

The financial support of this work by the Hebei Education Department Foundation of China (Grant No.: 733010) and the Hebei Province Natural Science Foundation of China (Grant No.: E2008000440).

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