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Preparation of indium-tin oxide (ITO) nano-aciculae by a simple precipitation near boiling point and post-calcination method

Shu-Guang Chen[a,b], Chen-Hui Li[a,b,*], Wei-Hao Xiong[a], Lang-Ming Liu[b], Hui Wang[b]

[a]*State Key Lab of Plastic Forming Simulation and Die and Mould Technology, Huazhong University of Science and Technology, Wuhan, Hubei 430074, People's Republic of China*

[b]*Zhuzhou Smelter Group Co. Ltd., Zhuzhou, Hunan 412004, People's Republic of China*

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Abstract

ITO nano-aciculae (needle-like nanometer crystals) were prepared by post-calcination of ITO precursor nano-aciculae, which were synthesized by a simple precipitation near boiling point method. Transparent conductive film formed of ITO nano-aciculae was prepared by a simple coating process. ITO precursor nano-aciculae, ITO nano-aciculae and films were characterized with morphology, phase structure, optical and electrical properties, etc. The cross-sectional diameters of most of ITO nano-aciculae were mainly in the range of 20 to 60 nm, and the aspect ratios were mostly in the range of 4 to 12. Moreover, the ITO nano-aciculae had smaller cross-sectional diameters and bigger aspect ratios in comparison with the ITO precursor nano-aciculae on the whole. ITO precursor nano-aciculae were composed of very subtle nano-wires of 3 to 4 nm in cross-sectional diameter, and the nano-wires were regularly arranged to be parallel to the axial direction of ITO precursor nano-aciculae. However, ITO nano-aciculae were composed of caky subunits (flaky grain) whose flat surfaces were perpendicular to the axial direction. ITO precursor nano-aciculae were composed of $In(OH)_3$ and $Sn_3O_2(OH)_2$, and growth of nano-wires in ITO precursor nano-aciculae was along the [1 0 0] direction of $In(OH)_3$. ITO nano-aciculae were ITO solid solution being not well-crystallized. ITO nano-aciculae were interlaced with each other and formed an alveolate meshwork (meshed texture). The average transmittance of the film was about 85% in a wide visible light range of 400 to 1000 nm, and the sheet resistance of the film was 4.3 kΩ/□. The ITO nano-aciculae film was used as low and middle-grade transparent conductive film.

Keywords: ITO; Nano-aciculae; Film

Indium-tin oxide (ITO) is not only transparent to visible light but also high in electrical conductivity, and transparent electroconductive films from ITO play an important role in the optoelectronics industry [1–3]. There are several methods for preparing transparent electroconductive films, and one of them is by coating an electroconductive ink on a substrate. The films formed by coating process are somewhat low in electrical conductivity compared to the films formed by sputtering process. However, films of complex shape can be deposited on large-area substrates with such a simple and cheap coating process. Conventional electroconductive inks are known to be pastes that are obtained by dispersing electroconductive filler comprising spherical or granular ultra-fine ITO powders in a solvent containing a resin dissolved therein [4]. Of electroconductive inks, those have a smaller content of electroconductive filler therein are more economical, and it is necessary that the films obtained by coating those inks have a satisfactory physical strength. However, cracking of the films obtained by coating inks using spherical or granular ultra-fine ITO powders as fillers is a common problem, and the content of fillers added into inks is relatively large. If ITO powder fillers used in electroconductive inks had an acicular (needle-like) or flaky

* Corresponding author. Postal address: Department of Materials Science and Technology, College of Materials Science and Engineering, Huazhong University of Science and Technology, Wuhan, Hubei 430074, People's Republic of China. Tel.: +86 13873338339; fax: +86 7338393167.
E-mail address: hustcsg@sina.com (C.-H. Li).

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shape, these fillers can interlace to increase the physical strength of the films with the formation of a meshwork and the content of the fillers used in inks can be reduced. Moreover, current-carrying paths in electroconductive films are formed by the contacts between ITO fillers, and acicular or flaky fillers have increased chance for the creation of such current-carrying paths. So acicular ITO powders have their peculiar advantages over spherical or granular ultra-fine ITO powders, and it should be an interesting and meaningful issue to synthesize acicular ITO powders.

In the present work, ITO nano-aciculae having a high aspect ratio (defined as the ratio of axial length to cross-sectional diameter) were prepared by a simple precipitation near boiling point and post-calcination method. Transparent conductive film formed of such ITO nano-aciculae was prepared by a simple coating process. ITO precursor nano-aciculae, ITO nano-aciculae and film were characterized with morphology, phase structure, optical and electrical properties, etc.

1. Experimental

1.1. Preparation of ITO precursor nano-aciculae and ITO nano-aciculae

23 grams of indium ingot was dissolved into aqueous hydrochloric acid, and the solution was adjusted to 2 l. To the solution, 7 g of stannic chloride ($SnCl_4 \cdot 5H_2O$) was added to prepare a starting acidic aqueous solution which was charged into a glass beaker. In a separate step, 300 g of 25% aqueous ammonia was diluted with 2700 g of deionised water and the resulting alkali was precipitator. The temperature of the acidic solution was raised to boiling point and held at 99±1 °C, and the precipitator was added in drops to the solution over a period of 3 h to achieve a final pH of 7 and the solution was stirred at the same time. Moreover, deionised water at boiling point was added to the solution to make up for the evaporation of water every 10 min during the precipitation process. The resulting slurry was centrifugal filtered, washed with deionised water and azeotropic distilled with *n*-butanol, and ITO precursor nano-aciculae were obtained. Finally, ITO precursor nano-aciculae were calcined in air at 450 °C for 1 h, and ITO nano-aciculae were prepared.

1.2. Preparation of a conductive film formed of ITO nano-aciculae

10 grams of ITO nano-aciculae and 100 mL ethanol were mixed by ultrasonic vibrations and milled to prepare a dispersion. By adding colloidal silica and ethanol to the dispersion, a slurry was prepared which contained 2% of ITO nano-aciculae and 0.2% of silica. A glass plate was spin coated with the slurry and dried at 300 °C for an hour to form a transparent conductive film.

1.3. Characterizations

Transmission electron microscopy (TEM) images were carried on FEI G2 20 TEM. Field emission scanning electron microscopy (FESEM) images were taken on FEI Sirion 200 SEM. The X-ray powder diffraction (XRD) patterns were recorded on a Riguku D/max-rA X-ray diffractometer (λ=1.54056 Å) with Ni-filtered CuK_α radiation at a scanning speed of 1°/min. Optical transmission spectra in the UV and visible ranges were determined on a Shimadzu UV-2100 spectrophotometer scanning from 200 to 1000 nm. The thickness of the film was measured on the transversal fracture face of the glass plate coated with a conductive film using FEI Sirion 200 SEM, and the sheet resistance of the film was measured by a four-probe method at room temperature.

2. Results and discussion

Fig. 1(a) and (b) showed the typical TEM images of ITO precursor nano-aciculae and ITO nano-aciculae, respectively. On the whole, ITO nano-aciculae inherited the acicular shape of ITO precursor nano-aciculae after post-calcination, and the former had smaller cross-sectional diameters and bigger aspect ratios in comparison with the latter. Statistical approaches were applied to ITO precursor nano-aciculae in 10 observed fields similar to Fig. 1(a), and the frequency distributions of the cross-sectional diameter and aspect ratio were shown by Fig. 2. In the same way, the frequency distributions of the cross-sectional diameter and aspect ratio of ITO nano-aciculae were obtained and shown by Fig. 3. It was found that the cross-sectional diameters of most of ITO precursor nano-aciculae were in the range of 20 to 100 nm evenly, and the aspect ratios were mainly in the range of 3 to 8. The cross-sectional diameters of most of ITO nano-aciculae were mainly in the range of 20 to 60 nm, and the aspect ratios were mostly in the range of 4 to 12.

Fig. 4 showed TEM images of subtle microstructures of ITO precursor nano-aciculae and ITO nano-aciculae. It was very interesting to know that ITO precursor nano-aciculae were composed of very subtle nano-wires of 3 to 4 nm in cross-sectional diameter, and the nano-wires were regularly arranged to be parallel to the axial direction of ITO precursor nano-aciculae. Though ITO nano-aciculae inherited the acicular shape of ITO precursor nano-aciculae on the whole, the subtle microstructures of the former were very different from the latter. It seemed that ITO nano-aciculae were composed of caky subunits whose flat surfaces were perpendicular to the axial direction, and it should be due to dehydration and recrystallization during post-calcination process.

Fig. 5 showed the XRD patterns of ITO precursor nano-aciculae and ITO nano-aciculae. Two sharp diffraction peaks in Fig. 5(a) located at 22.26°2θ and 45.43°2θ could be