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Preparation and optical properties of Sn- and Ga-doped indium oxide semiconductor nanoparticles

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ABSTRACT

Indium tin oxide (ITO) nanoparticles and gallium-doped indium tin oxide (GITO) nanoparticles with various molar ratios of dopants were prepared by a solution method in oleylamine. Characterization of crystal, morphology, and optical properties was carried out using X-ray diffraction (XRD), transmission electron microscopy (TEM), ultraviolet–visible (UV–Vis), photoluminescent (PL), and Fourier transform infrared spectroscopy (FT-IR). XRD patterns show that with increasing of Sn, the crystal structure of ITO nanoparticles varies gradually from standard cubic bixbyite In_2O_3 to amorphous and to standard tetragonal SnO_2, whereas the GITO nanoparticles retain the crystal structure of ITO. The smallest particle size is around 10 nm, and the morphology of the particles is nearly spherical. The smallest particles, though coated with oleylamine, tend to aggregate forming larger flower-like particles. Defect level emission at the present of dopants was observed in the PL spectra of the ITO and GITO nanoparticles.

1. Introduction

Metal oxide semiconductors (MOS) have been widely studied and used due to its strong corrosion resistance, good chemical stability, easy preparation, and low costs [1]. MOS nanoparticles have excellent optical transmission performances in the visible region and low resistivity, especially indium tin oxide and zinc oxide. MOS nanoparticles are readily to be processed into thin films, ceramics and composites due to their small particle sizes. Numerous preparation methods have been developed for MOS nanoparticles, such as heat treatment technology [2], laser induced technology [3], solvent thermal method [4], microwave assisted synthesis [5], and microemulsion method [6], etc. It should be noticed that solution method has the advantages of simple operation, low cost, and so forth, and are frequently used for the preparation of MOS nanoparticles [7–11].

At present, MOS nanoparticles with high crystallinity, uniform composition and narrow particle size distribution have been the focus regarding to MOS research. Among the most studied MOS, indium tin oxide (ITO) is a typical one with the lowest resistivity and the highest transmittance in the visible light region [12]. Electronic devices using MOS as semiconductor layers have the advantages beyond common electronic devices, such as resistant to oxidation, small size, low power consumption, sensitive reaction [13,14], etc. MOS, especially ITO, have been widely used in flat panel displays [15], solar cells [16–19], light-emitting diodes [20], field-effect transistors [21–24] and other devices.

As a non-renewable natural resource, indium is relatively rare to obtain, so it is urgent to find elements that can partially replace indium without reducing the performance of the materials significantly. Indium oxide doped with Sn, Zn, Ga, and other elements are more investigated ones recently, such as ITO [25,26], indium zinc oxide (IZO) [27], zinc tin oxide (ZTO) [28], which are also the MOS material with more potential applications in optoelectronics. However, many problems still need to be further studied in the synthesis and properties of this kind of MOS nanomaterials.

In this work, metal acetylacetonates and oleylamine were used as starting materials and the reaction solvent, respectively, to synthesize ITO and gallium-doped indium tin oxide (GITO) nanoparticles at a certain temperature. Crystallinity, morphology, and optical properties of the ITO and GITO nanoparticles were characterized.

2. Experimental

2.1. Materials

Tin bis(acetylacetonate) dichloride ($Sn(acac)_2Cl_2$, 98%) and oleylamine ($C_{18}H_{37}N$, > 50%) were purchased from Tokyo Chemical Industry (TCI). Indium acetylacetonate ($In(acac)_3$, > 99.9%) and gallium acetylacetonate ($Ga(acac)_3$, > 99.9%) were purchased from

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Aldrich and Alfa Aesar, respectively. Other reagents were purchased from local suppliers. All chemicals were used without further purification.

2.2. Synthesis of nanoparticles

ITO nanoparticles were synthesized using solution method with an In/Sn molar ratio of 5:1, 4:2, 3:3, 2:4, and 1:5, respectively. The amount of oleylamine as a solvent was determined by calculating the molar ratio of (In+Sn):oleylamine=1:48. Taken the ITO nanoparticles with an In/Sn molar ratio of 5:1 as an example, the preparation process is as follows.

Indium acetylacetonate (0.3000*g*), tin bis(acetylacetonate) dichloride (0.0565*g*) and oleylamine (11.2151*g*) solution were added in a 50 mL three-neck round bottom flask. The system was magnetically stirred and heated to 220 °C, and then reacted for 8 h under nitrogen condition. At the end of the reaction, the viscosity of the solution became larger and the color changed to gray. After the reaction, the product was washed three times with a mixture of ethyl alcohol and hexane in a volume ratio of 5:1, and then dispersed by sonication and separated by centrifuge. After the supernatant was removed, the product was obtained. The product was divided into two parts, one of which was vacuum dried for XRD measurement, and the other of which was dispersed in dichloromethane for measurement of UV–Vis absorption, photoluminescence (PL) and transmission electron microscopy (TEM).

The preparation of GITO nanoparticles was similar to that of the ITO nanoparticles. For GITO nanoparticles, the In/Sn molar ratio was 5:1 and the molar content of gallium was 3%, 5%, and 10%, respectively.

2.3. Characterization

The crystallization performance of ITO and GITO was characterized using a DMAX-RB X-ray diffractometer (XRD) with Cu Kα radiation working in the reflection mode at 40 kV and 150 mA with a scanning rate of 10° min^{-1}. The UV–Vis absorption spectrum was measured on a JASCO V570 spectrophotometer. The fluorescence emission spectrum was measured on an FL-4500 spectrophotometer. The morphology of ITO and GITO in the films was observed by an FEI-F20 transmission election microscope.

3. Results and discussion

3.1. Crystal properties of ITO nanoparticles

Fig. 1 shows XRD patterns of the ITO samples with different In/Sn molar ratios. For the ITO nanoparticles with an In/Sn molar ratio of

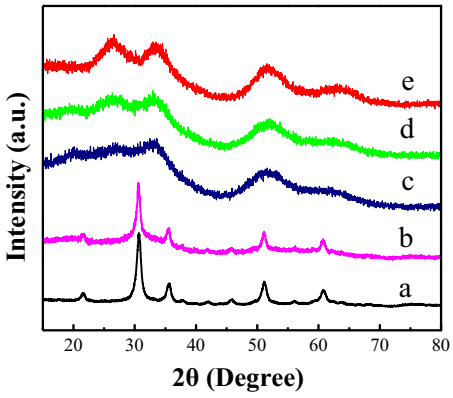

Fig. 1. XRD patterns of the ITO nanoparticles with different In/Sn molar ratios; a. 5:1, b. 4:2, c. 3:3, d. 2:4, e. 1:5.

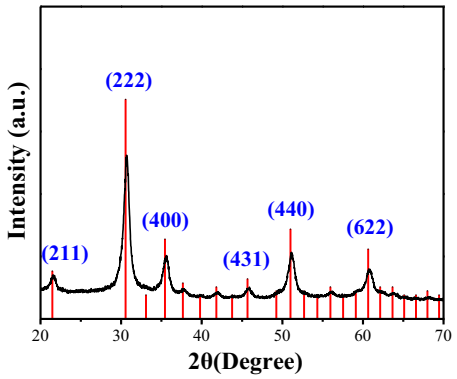

Fig. 2. XRD pattern of the ITO nanoparticles with an In/Sn molar ratio of 5:1.

5:1 and 4:2, narrow and sharp diffraction peaks at 30.26, 35.38, 51.10, and 60.72° appear, which correspond to the (222), (400), (440), and (622) planes of the standard cubic bixbyite In_2O_3 (JCPDS No. 06-0416), respectively. The sample of ITO with an In/Sn molar ratio of 3:3 is amorphous. The samples of ITO with an In/Sn molar ratio of 2:4 and 1:5 show broad diffraction peaks at 26.58, 33.38, and 51.96°, which correspond to the (110), (101) and (211) planes of the standard tetragonal SnO_2 (JCPDS No. 77-0448), respectively. This result indicates that the crystallinity of ITO changes with different molar ratio of In/Sn.

To study the influence of In/Sn molar ratio on the crystal properties and particle size, the XRD pattern of the ITO nanoparticles with an In/Sn molar ratio of 5:1 is shown in Fig. 2. The strong and sharp characteristic peaks match well with standard cubic bixbyite In_2O_3, suggesting good crystallization of the sample. There is no significant diffraction peaks of SnO_2, indicating that the product is indium tin oxide solid solution. However, the characteristic peaks shift slightly to large angles, which is mainly due to the difference in ionic radius of In and Sn. The replacement of larger In^{3+} ions (r=0.81 Å) with smaller Sn^{4+} ions (r=0.71 Å) could lead to the decrease in lattice spacing of the samples. The lattice constant of (222) plane calculated is 10.091 Å, which is slightly decreased compared to the lattice parameter of In_2O_3 (a_0=10.120 Å). The result shows that the doping of Sn leads to the increase of the lattice defects in indium oxide. The crystallite size of the ITO nanoparticles with an In/Sn molar ratio of 5:1, which was determined using the Debye-Scherrer equation [29], is 9.60 nm.

3.2. Optical properties of ITO nanoparticles

The UV–Vis absorption spectra of ITO with various doping ratios are shown in Fig. 3. All the ITO samples exhibit sharp strong absorption peaks at around 230 nm, indicating that the particle sizes of the ITO products are nearly uniform. The second peaks locate at 272,

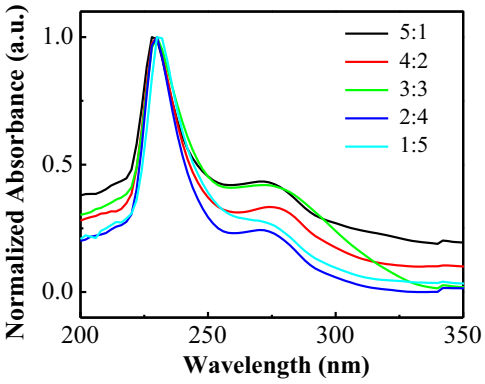

Fig. 3. UV–Visible absorption spectra of ITO nanoparticles with different In/Sn molar ratios.