Novel Ga-doped ZnO nanocrystal ink: Synthesis and characterization

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A B S T R A C T
Ga-doped ZnO (GZO) nanocrystals were synthesized via the hot-injection method for the first time. The characterizations of its structure, composition, morphology, and absorption properties were conducted by using powder X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM) and UV–vis absorption spectroscopy. The results indicated that GZO nanocrystals were single phase polycrystalline within a range of 5–10 nm. Optical measurements illustrated that GZO nanocrystals have a tunable band gap from 3.35 to 3.81 eV, depending on the Ga doping level. GZO nanocrystals were dispersed in nonpolar solvents to form a nanocrystal ink which could remain stable after a month of storage. The GZO thin film was fabricated by spin coating the GZO nanocrystal ink and annealing in air. The electrical resistivity of the film was measured to be 7.5 × 10−2 Ω cm. This method, which eliminated the requirement of high vacuum and high temperature, was a promising alternative for transparent conducting oxide (TCO) fabrication.

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1. Introduction

ZnO doped with group-III elements, such as Al and Ga, has been regarded as a promising alternative transparent conducting oxide (TCO) to Sn-doped In2O3 (ITO), owing to its low material cost, nontoxicity, high transparency, and high chemical stability [1,2]. Among them, Ga-doped ZnO (GZO) has outstanding optical and electrical properties because of its low reactivity to oxygen and the similarity between the ionic radius of Ga3+ (0.062 nm) and Zn2+ (0.072 nm) [3]. Different types of deposition techniques have been reported to produce GZO thin films, such as magnetron sputtering [4–7], chemical vapor deposition [8,9], and pulsed laser deposition [10,11]. A new method for fabricating thin films is based on the synthesis of nanocrystals that are dispersed in an “ink”, which has been reported in CuIn1−xSex [12], Cu2ZnSnS4 [13] and Cu2ZnSnSe4 [14]. This method eliminates the need of high vacuum and high temperature, which is promising for the large scale fabrication of cost-effective TCO. But to the best of our knowledge, there is no report on the synthesis of GZO nanocrystals. Using the hot-injection method, GZO nanocrystals with sizes of 5–10 nm was obtained. The structures, compositions, morphologies and optical properties were characterized extensively. Furthermore, GZO nanocrystals were dispersed in nonpolar solvents to form a stable ink solution. Its thin film was fabricated by spin casting the GZO nanocrystal ink and annealing in air. Surface morphology and electrical conductivity of the film were also discussed.

2. Experimental

2.1. Typical synthesis of GZO nanocrystals

All of the chemical reagents and solvents in the experiment were used without further purification. 6.4 mL octadecene (90%) and 6.6 mL oleylamine (OLA, 70%) were added to a 100 mL two-neck flask followed with vacuum pumping and N2 bubbling. The solution was kept at 100 °C for 15 min. 0.05 mmol gallium(III) acetylacetonate (Ga(acac)3, analytic-grade), 0.95 mmol zinc(II) acetylacetonate (Zn(acac)2, analytic-grade), and 10 mL xylene were mixed in another 100 mL two-neck flask under N2 atmosphere and vigorous stirring. When the mixture was completely dissolved, it was immediately injected into the former flask. The temperature was then raised to 300 °C and kept for 30 min under vigorous stirring. The product was collected by standard polar/nonpolar solvent precipitation technique, using a high-speed centrifuge.

2.2. Structural and optical characterization of GZO nanocrystals

The element composition and proportion were analyzed with an Oxford INCA energy-dispersive X-ray spectroscopy (EDS) detector. The crystal structure of GZO nanocrystals was characterized by powder X-ray diffraction (XRD) using Cu Kα radiation (λ = 1.54 Å). Transmission electron microscopy (TEM) and selected area electron
diffraction (SAED) images were taken by using a JEM 2100 microscope at 200 kV accelerating voltage. A Lambda 20 UV–vis spectrometer was used to carry out UV–vis absorption spectra to evaluate the optical properties of GZO nanocrystals.

2.3. Fabrication and characterization of the GZO thin film

GZO nanocrystals were dispersed in nonpolar solvents such as a mixture of hexane and octane to form a stable ink solution with 5 wt.% concentration. The GZO thin film was fabricated by spin casting its nanocrystal ink onto a Si substrate at 1000 rpm. Subsequently, the GZO thin film was annealed for 1 h in air at 350 °C. The morphology of the film was taken by a Zeiss Ultra 55 scanning electron microscope (SEM) and the electrical resistance of the film was measured by using a four-point probe. Film thickness was found using a Dektak 6M stylus profiler.

3. Results and discussion

Fig. 1 shows the XRD pattern of the as-synthesized nanocrystals of different Ga doping ratio together with the standard pattern of ZnO (JCPDS 36-1451). The six major peaks are identified to be (100), (002), (101), (102), (110) and (103). The crystal domain size estimated from full width at half maximum (FWHM) of the strongest (101) peak by the Scherrer equation is 8 nm. Upon calculation, with the increase of the Ga doping ratio, the interplanar spacing of the GZO (101) plane shifts from 0.2468 nm to 0.2473 nm, which is probably due to the expansion of the crystal volume. Such an abnormal enlargement contradicts some observations of others [15] and further study in this issue is needed.

Fig. 2. Elemental composition measured by EDS of GZO nanocrystals.

Fig. 3. TEM images together with SAED patterns of GZO nanocrystals dispersed in chloroform for (a-c) 5 mol%Ga and (d-f) 7.5 mol%Ga.

Fig. 4. UV–vis absorption spectra of GZO nanocrystals together with the obtained band gap.
Fig. 2 indicates that the Ga doping content in GZO nanocrystals rises with the increase of the Ga input molar ratio, as determined by EDS. Considering the error of the EDS detector (approximately ±2 at.%), the slightly Ga doping content deviated from the input ratio may be due to different reactivity of metal precursors.

Fig. 3(a) and (d) presents the TEM images of GZO nanocrystals doped with 5 mol%Ga and 7.5 mol%Ga, respectively. Their diameters are mainly in the 5–10 nm range. Additionally, the morphology of GZO nanocrystals is mainly polyhedral in shape. The high resolution images of GZO nanocrystals [Fig. 3(b) and (e)] reveal the interplanar spacing of the (100) plane to be 0.284 nm in the 5%Ga-doped sample and 0.286 nm in the 7.5%Ga-doped sample, which corresponds well with the calculation from XRD. Furthermore, indicated by the presence of diffraction spots of (100), (002), (101), (102), (110), and (103) planes, the SAED images [Fig. 3(c) and (f)] illustrate the nanocrystals' nature of polycrystalline.

Fig. 4 shows UV–vis absorption spectra of absorbance unit versus wavelength (λ) and the optical band gaps of GZO nanocrystals with different Ga input molar ratios. The band gaps for the five samples in the experiment are calculated to be 3.35, 3.61, 3.70, 3.77, and 3.81 eV, respectively, indicating that a tunable band gap in the GZO nanocrystal can be gained by increasing Ga doping level. Moreover, UV–vis spectra illustrate that GZO nanocrystals have a tunable optical band gap from 3.35 to 3.81 eV depending on the Ga doping level. GZO nanocrystals were then dispersed in a mixture of hexane and octane to form a stable ink solution. The nanocrystal ink is stable after one month of storage. SEM images and electrical property of the GZO thin film further prove our method a promising alternative to the large scale production of cost-effective TCO.

4. Conclusions

In this paper, we reported for the first time that GZO nanocrystals were synthesized in the solution via the hot-injection method. EDS, XRD, TEM, and SAED reveal their composition, structure and morphology. The diameter of GZO nanocrystals basically ranges from 5 nm to 10 nm. Moreover, UV–vis spectra illustrate that GZO nanocrystals have a tunable optical band gap from 3.35 to 3.81 eV depending on the Ga doping level. GZO nanocrystals were then dispersed in a mixture of hexane and octane to form a stable ink solution. The nanocrystal ink is stable after one month of storage. SEM images and electrical property of the GZO thin film further prove our method a promising alternative to the large scale production of cost-effective TCO.

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References


Fig. 5. (a) Photo of 5% doped GZO nanocrystals dispersed in hexane/octane at concentration of 5 wt.%. (b) SEM image of the as-annealed GZO thin film.