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Morphological, structural, and gas-sensing characterization of tin-doped indium oxide nanoparticles

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Abstract

Tin-doped indium oxide (ITO) nanoparticles with stable cubic phases were synthesized using a sol–gel combustion method that includes gelation and combustion in organic fuel. The influence of SnO_2 on the phase and morphology of the In_2O_3 nanoparticles were studied by X-ray diffraction, scanning electron microscopy, and high resolution transmission electron microscopy (TEM), along with selected area electron diffraction. ITO nanoparticles with 11–20 nm crystallite size and 69–46 m^2/g specific surface area were obtained. The lattice constant was nearly 10.12 Å, with orientation along the (222), (400), and (110) planes for all proportions of the doped SnO, indicating a stable cubic phase with high conductivity. The TEM micrograph of the ITO nanoparticles and powder revealed spherical morphology. The microstructure of the cured In_2O_3: Sn with Sn concentrations of 5, 10, 20, and 50 wt% demonstrated that the ITO nanoparticles clustered more densely with the increase in Sn concentration. The gas-sensing ability of the synthesized powders was demonstrated through the sensing of ethanol vapor at 200 °C.

Keywords: Sol–gel combustion; Sn-doped indium oxide; Structural; Electrical

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1. Introduction

Tin-doped indium oxide (ITO) powder/films have been used to manufacture transparent conductive coatings. ITO is an advanced semiconducting material with potential applications in touch panel contacts, electrodes for LCD/electro-chromic displays, defogging aircraft windows, gas sensors, and antistatic window coatings [1–4]. Research and development studies on ITO have been focused on the synthesis and properties of its powder [1–3]. Different forms of ITO powder with low-dimensional and quasi-one-dimensional structured semiconducting particles, such as nanosphere [5], nanocircle [6], nanorod [2], nanowire [7], and nanotube [8], have been of great technological interest for devices requiring larger surface areas. However, high electrical conductivity is observed only in the stable cubic phase [9–11]. Various methods are available for preparing ITO powder, such as co-precipitation [5,12], vapor–liquid–solid [13], sol–gel [14], and emulsion techniques [8,15]. The high electrical conductivity property of ITO is caused by the creation of a conducting carrier-oxygen vacancy with the addition of the dopant (Sn) within the In_2O_3 matrix.

Sol–gel combustion is a novel method, with a unique combination of both the chemical sol–gel technique and the combustion process [16]. This method is based on the gelation and subsequent combustion of an aqueous solution containing salts of the desired metals and organic fuel such as urea, which leads to a voluminous and fluffy product with large surface area. This process offers several advantages, including inexpensive precursors, a simple preparation method, a final output of nanosized powder, and so on. The present study investigates the possibility of obtaining ITO nanopowder with a uniform particle size through the sol–gel combustion process.

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When Sn is added above the solubility limit, metastable secondary phases may appear to form a new composite material. However, detailed studies on the behavior of Sn on substitution in nanocrystalline ITO powder with a wide range of Sn^{4+} content above the solubility limit have not been performed. In this study, ITO powder with various levels of Sn content was synthesized by sol–gel combustion. The structural and micro-structural characterization of the nanocrystalline ITO powder were examined and reported. Gas-sensing measurements were carried out on ethanol vapor.

2. Experimental

Powders of In_2O_3:Sn with various Sn concentrations were prepared through sol–gel combustion. $Sn(NO_3)_2 \cdot 5H_2O$ (99.99%), $In(NO_3)_3 \cdot 7H_2O$ (99.99%), and NH_2CONH_2 (50%) were purchased from Sigma-Aldrich and used without further purification. In and Sn solutions were prepared by dissolving 4.752 g of $In(NO_3)_3 \cdot 7H_2O$ and 0.648 g of $Sn(NO_3)_2 \cdot 5H_2O$ in 20 mL of deionized (DI) water, respectively. The quantity of the metal ions in the solution was adjusted to achieve the final ratio of ternary oxide (In_2O_3/SnO_2) at 95:05, 90:10, 80:20, and 50:50. An aqueous urea solution was prepared by dissolving 0.4 g of urea in 10 mL of DI water. The prepared urea solution was then added dropwise to the In/Sn solution under constant stirring until a sol was formed. The bath temperature was maintained at 30 °C. This sol was heated at 120 °C for 20 min and then placed in a muffle furnace for 20 min until a dry gel was obtained. The samples were then ignited in a furnace at 350 °C, in which an auto-combustion process occurred, and a burnt powder was formed. The obtained burnt powder was subsequently calcined at 400 °C for 1 h.

The structural properties of the ITO nanoparticles were investigated using an X-ray diffractometer (Model Philips Expert Pro). The X-ray diffraction (XRD) pattern was recorded in the range of 10° to 80°, operating at a voltage of 40 kV and a current of 40 mA. Morphological studies were performed using scanning electron microscopy (SEM) with a Hitachi S-3400 N. Structural analysis was carried out by transmission electron microscopy (TEM) using a 200 kV Tecnai-20 G2 TEM instrument. The selected area electron diffraction (SAED) pattern was also recorded. Gas-sensing measurements were carried out in a chamber comprising a vacuum coating unit, a temperature controller, and a Keithley 2000 multifunction meter.

For the measurement of gas sensitivity, the sensing elements based on ITO nanocrystalline powders were fabricated in a conventional manner [10]. The powders were pressed into pellets under a pressure of 15 MPa and then Al lead was mounted on both sides of the pellet to form the sensing element. The gas sensing measurements were carried out in a static chamber with a volume of 25 L. The operating temperature of the sensor was measured by adjusting the current flow through the heater, and temperature was controlled using a Cr–Al thermocouple. Sensor sensitivity was defined as follows:

$$s = \left(\frac{R_{vac} - R_{gas}}{R_{gas}}\right) \tag{1}$$

Resistance was measured by the half-bridge technique [17]. The operating temperature of the ethanol sensor was optimized for the highest response of the test gas. The optimized temperature was tested for 1000 ppm of ethanol.

3. Results and discussion

Fig. 1(a–d) shows the XRD patterns of the ITO powders containing 5%, 10%, 20%, and 50% SnO_2 annealed at 400 °C. The result suggested that the crystallinity of the In_2O_3 powders decreased with dopant concentrations. All ITO powder particles showed preferred orientation along the (222) direction. The relative intensity of the (222) peak decreased with increasing Sn concentration [18]. Particles with adequate energy were oriented along a thermodynamically favorable (222) direction. As the concentration of In_2O_3 decreased, the energy of the doped particles increased, and the particles moved more actively toward thermodynamically stable sites.

The observed (d) values matched perfectly with that of the cubic lattice of JCPDS standard card no. 89-4598. No additional peaks corresponding to additional phases were observed; hence, no impurities existed. This result indicates that the ITO phase formation was completed during the combustion process. Notably, a single phase material was obtained through the solid-state reaction route only after prolonged calcinations of the reaction mixture at relatively high temperatures with multiple intermediate grindings.

The particle size was determined by the X-ray line broadening method using Scherer's equation:

$$D = \frac{0.94\lambda}{\beta \cos\theta} \tag{2}$$

where D is the particle size, λ is the wavelength of the X-ray radiation source (1.5406 Å for Cu-Kα radiation), β is the corrected peak full width at half-maximum, and θ is the peak position. The calculated values of the crystallite size are listed in Table 1.

The crystallite size of the as-prepared powders varied slightly with increasing Sn content (Fig. 2a) within the range of 11–20 nm. Similarly, the crystallite size increased slightly within a very narrow limit with increasing annealing temperature. Small amounts of Sn (up to 5% Sn) cause a decrease in the lattice constant, thereby leading to a decrease in bond length. As the Sn content increases, the bond length slowly increases due to the distortion of In–Sn–O. This distortion increases the lattice constant (Fig. 2b) and decreases the crystal density of the crystal structures. Fig. 2c shows the peak intensity ratio of the (222)/(440) planes for various Sn concentrations. The peak intensity ratio decreases with decreasing Sn concentration. The lattice constants and bond lengths, crystallite size, and crystalline density were calculated, and the refinement values are shown in Table 2. The variation in bond length, which increases at the tetrahedral site and decreases at the octahedral site of the ITO powder obtained in 50:50 proportions, may be attributed to the relative value of occupancy of In to Sn at the site.