Materials Letters 117 (2014) 108–111

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Controlling the morphology of indium tin oxide using PEG-assisted hydrothermal synthesis

Brendan G. DeLacy [a,*], Steven Lacey [a], Dajie Zhang [b], Erica Valdes [a], Kenneth Hoang [a]

[a] U.S. Army Edgewood Chemical Biological Center, Research & Technology Directorate, 5183 Blackhawk Road, Aberdeen Proving Ground, MD 21010-5424, USA

[b] Johns Hopkins University Advanced Technology Laboratory, Johns Hopkins University, Baltimore, MD, USA

ARTICLE INFO

Article history:
Received 17 October 2013
Accepted 28 November 2013
Available online 6 December 2013

Keywords:
Tin-doped indium oxide
ITO
Nanomaterials
Semiconductor

ABSTRACT

We report the synthesis of indium tin oxide (ITO) powders with varying morphologies using hydrothermal synthesis. Polyethylene glycol (PEG) 400 and sodium hydroxide (NaOH) were used to promote the formation of non-spherical morphologies. The ratio of PEG to NaOH was found to influence the morphology of the products. Nanocrystalline spheres, cubes, block-like structures, rods, and dendrites were produced in the study. All resultant products were characterized by X-ray powder diffraction, scanning electron microscopy, and scanning transmission electron microscopy. Influential factors on the growth mechanisms of ITO are discussed.

Published by Elsevier B.V.

1. Introduction

Tin-doped indium oxide (ITO) is one of the more widely used transparent conducting oxides, because of its transparent optical properties in the visible region and its attenuating properties in the infrared region. These properties are due to its electrical conductivity and inherent bandgap, typically reported as 4.0 eV [1]. Devices that incorporate ITO include liquid crystal displays [2], optoelectronic devices [3–5], heat reflecting mirrors [6], and sensors [7,8]. Thin layers of ITO are commonly deposited in these devices using costly methods such as chemical vapor deposition (CVD) and physical vapor deposition (PVD). Alternative and cheaper routes for fabricating thin films of ITO would therefore be of great interest to the optical device and optics communities. The deposition of colloidal suspensions containing ITO particles using ink-based printing, dip coating, or spin coating techniques are examples of cheaper coating methods.

Particle shape and dimensionality at the nanoscale have proven to play significant roles in modifying the optical properties of a wide range of materials, including plasmonic materials [9], quantum dots [10], and metal oxides [11]. Hence, the development of facile methods that exhibit control of particle size and morphology are highly desirable. Hydrothermal synthesis is a highly versatile method for preparing many types of nanocrystals with diverse morphologies, especially metal oxides and mixed oxides, including ITO [12–15]. However, little information can be found on the effect of hydrothermal synthesis conditions, such as the presence of surfactants or re-crystallization aids, on the morphology of ITO. Herein, we report the hydrothermal synthesis of indium tin oxide (ITO) powders with varying morphologies using polyethylene glycol (PEG) 400 as a template and NaOH as a possible re-crystallization aid. In the experiments described herein, the concentrations of PEG 400 and NaOH, relative to the concentration of In and Sn, were systematically varied to determine the impact on the size and shape of ITO particles.

2. Experimental section

Indium chloride tetrahydrate (97%), tin (IV) chloride (99%), and sodium hydroxide were obtained from Sigma Aldrich. Polyethylene glycol 400 was obtained from Alfa Aesar. In a typical synthesis, 1.46 g $InCl_3 \cdot 4H_2O$, 58.5 μL $SnCl_4$, and a variable amount of NaOH (0.32/0.80/1.6/3.2 g) were dissolved into a 10 mL solution containing high purity distilled H_2O. The solution was then magnetically stirred for 15 min in a 25 mL Erlenmeyer flask. To a Teflon-lined stainless steel autoclave of 125 mL capacity, 4 mL of the In/Sn/NaOH solution, a variable amount of PEG 400 (0/2.5/5/10/15 mL), and a variable amount of ethanol (to ensure a total volume of 54 mL), were added and magnetically stirred for 15 min. The autoclave was then sealed and heated at 190 °C for 24 h. The precipitate was transferred to a centrifuge tube, washed with 20 mL of ethanol, sonicated, centrifuged at 4000 RPM for 15 min, and the supernatant was removed. This washing/sonication/centrifugation step was then repeated with water. Finally, the precipitate was loaded in a crucible and annealed in air at 500 °C for 2 h. As controls to the above reaction conditions, experiments with no PEG present, with no NaOH present, and with no PEG or NaOH present, were also conducted. A tabulated description of all experiments is provided in Table 1. The X-ray powder diffraction (XRD) patterns were recorded on a Panalytical X'Pert Pro diffractometer with Xcelerator, using Cu anode ($\lambda = 1.5406$ Å) at 45 kV and

* Corresponding author. Tel.: +14104365282; fax: +14104368519.
E-mail address: brendan.g.delacy.civ@mail.mil (B.G. DeLacy).

0167-577X/$ - see front matter Published by Elsevier B.V.
http://dx.doi.org/10.1016/j.matlet.2013.11.114

Table 1
A description of experimental parameters and resulting ITO morphologies.

NaOH: PEG	NaOH (mmol)	PEG (mmol)	In (mmol)	Sn (mmol)	Particle shape (SEM/TEM)
0.8	32	42.3	2	0.2	Rods/dendrites
1.1	32	28.2	2	0.2	Rods/dendrites
2.3	32	14.1	2	0.2	Rods/dendrites
4.6	32	7.1	2	0.2	Rods/dendrites
2.3	32	14.1	2	0.2	Rods/dendrites
1.1	16	14.1	2	0.2	Rods/dendrites
0.6	8	14.1	2	0.2	Nanocrystalline spheres
0.2	3.2	14.1	2	0.2	Cubes/blocks
n/a	0	14.1	2	0.2	Nanocrystalline spheres/blocks
n/a	32	0	2	0.2	Rods/dendrites
n/a	0	0	2	0.2	Nanocrystalline spheres

40 mA. Scanning electron microscopy (SEM) images were taken with a JEOL model JCM-5700 scanning electron microscope. SEM and scanning transmission electron microscopy (STEM) images were also taken with a JEOL 7001FLV (JEOL, Japan) Field Emission Scanning Electron Microscope equipped with a transmitted electron detector. Samples were supported on carbon films for both scanning and scanning transmission images. The instrument was operated in high vacuum mode using an accelerating voltage of 20 keV and nominal working distance of 7.5 mm.

3. Results and discussion

In this study, our goal was to determine the effects of sodium hydroxide and PEG 400 on the formation and morphology of ITO particles. The ratio of NaOH to PEG was a primary focus in this study. Hence, the concentrations of indium and tin were held constant throughout the experiments, while the concentrations of NaOH and PEG were varied. Table 1 provides a summary of the experiments conducted in this study.

The impact of NaOH on particle morphology has been explored in the synthesis of various metal oxides including ZnO [12], CuO [13], Bi_2O_3 [14], In_2O_3 [15], and Y_2O_3 [16]. The role of NaOH in the formation of ITO particles is based on the generally accepted mechanism in which [17]

$$In^{3+} + 3H_2O \rightarrow In(OH)_3 + 3H^+ \quad (1)$$

$$In(OH)_3 \rightarrow InOOH + H_2O \quad (2)$$

$$Sn^{4+} + 3H_2O \rightarrow SnO_3H_2 + 4H^+ \quad (3)$$

The dehydration of the ITO precursors may be subsequently carried out during the annealing process in which

$$2InOOH \rightarrow In_2O_3 + H_2O \quad (4)$$

$$SnO_3H_2 \rightarrow Sn_2O_5H_2 \rightarrow Sn_4O_9H_3 \rightarrow SnO_2 \quad (5)$$

Inspection of reactions (1) and (3) highlights the influence of pH on the formation of the indium oxide precursor and the tin oxide precursor, respectively. Based on Le Châtelier's principle, the reduction of H^+ ions via the addition of OH^- drives the reaction towards the production of the indium oxide precursor and tin oxide precursor, assuming that a sufficient amount of In and Sn is present. Hence, the addition of NaOH may favor the formation of ITO. In addition to the impact of NaOH on ITO particle formation, PEG-400 was included in this study as a possible additive to induce non-spherical morphologies. Short-chain polymers, such as PEG-400, have been explored for inducing the formation of other non-spherical metal oxide particles, including ZnO nanowires [12] and copper nanorods [13]. This propensity may be explained mechanistically by the fact that the ethylene oxide chain in PEG consists of a series of oxygen atoms, each having two lone pairs of electrons. These electrons act as nucleophiles and promote the alignment of In^{3+} and Sn^{4+} along the backbone of the PEG chain in solution. Hence, the formation of indium oxide and tin oxide may occur in a linear fashion.

For the initial series of experiments, the NaOH:PEG ratio was varied (0.8, 1.1, 2.3, and 4.6) by keeping the amount of NaOH constant (32 mmol) while varying the amount of PEG (7.1–42.3 mmol). Rod and dendrite morphologies were consistently observed in these experiments. SEM and STEM images are provided in Fig. 1.

Next, the [NaOH]:[PEG] ratio was varied (0.2, 0.6, 1.1, and 2.3) by keeping the amount of PEG constant (14.1 mmol) while varying the amount of NaOH (from 3.2 mmol to 32 mmol). A wide range of particle morphologies was observed in these experiments. SEM images of particles obtained from these experiments are provided in Fig. 2.

Regardless of whether NaOH or PEG was held constant, rods and dendrites were consistently observed for those experiments in which the NaOH:PEG ratio was 0.8 or greater. As the ratio of NaOH:PEG decreased to 0.6, the particle morphology transitioned back to a nanocrystalline form. Finally, cubic and block-like structures were observed when the NaOH:PEG ratio was its lowest at 0.2, allowing PEG to have its greatest influence.

As controls to those experiments in which NaOH:PEG was varied, experiments in which there was no sodium hydroxide, no PEG, and no sodium hydroxide or PEG were also conducted. The absence of sodium hydroxide yielded nanocrystalline spheres, with the presence of some block-like structures. This result indicates that PEG plays a minor role in the formation of non-spherical ITO particles. The absence of PEG yielded rods and dendrites, indicating that NaOH plays a vital role in the formation of these structures. The absence of both NaOH and PEG-400 yielded nanocrystalline ITO particles, indicating that NaOH and/or PEG-400 are required to induce non-spherical morphologies.

The XRD patterns for rods/dendrites (NaOH:PEG=0.8), spheres/blocks (no NaOH present), and nanocrystalline (no NaOH or PEG present) ITO are provided in Fig. 3. These spectra can be indexed to ITO with a cubic body-centered crystal structure. The lattice parameters of ITO ranged from 10.1192 Å to 10.1240 Å, which closely agree with those observed in the literature (10.1234 Å (ICCD PDF reference #04-009-7769) and 10.124 Å (ICCD PDF reference #04-014-4398). For those experiments in which NaOH:PEG was 0.8 and NaOH was absent, the intensity of the XRD peaks indicates that that the rod/dendrite and cubic/block products are well crystallized. Tin oxide (TO) and indium oxide (IO) impurities were also observed for the experiment in which the [NaOH]:[PEG] ratio was 0.8. Only the IO impurity was observed for the experiment in which no NaOH and PEG were present. The crystal structures of TO and IO particles are found to be tetragonal (a=4.7421 Å and c=3.1901 Å) and rhombohedral (a=5.487 Å and c=14.51 Å), which are consistent with the ICCD PDF references #04-008-8133 and #04-005-4422, respectively.

The solubility of the ITO precursors ($In(OH)_3$ and SnO_3H_2) must be considered when formulating a hypothesis on the impact of NaOH on ITO morphology. Both $In(OH)_3$ and SnO_3H_2 are insoluble in the water/ethanol solvent used in this study. Hence, for the experiment in which NaOH and PEG were absent, the hydrothermal synthesis is a straight forward forced co-precipitation method and nanocrystalline spheres are produced. The presence of the indium oxide impurity in the nanocrystalline XRD data indicates that a small amount of $In(OH)_3$ may have precipitated out prior to the co-precipitation of the indium and tin precursors. For those experiments in which the amount of NaOH is sufficiently large (i.e. for NaOH:PEG ratios >0.8), rods/dendrites are the predominant morphology. It is hypothesized that this morphology is promoted via the dissolution of $In(OH)_3$ and SnO_3H_2 in the presence of NaOH, and the subsequent re-crystalli-