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Synthesis and Characterization of Indium Oxide Nanoparticles

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ABSTRACT

Nanoparticles of indium oxide, a transparent conducting oxide with a band gap close to GaN, were synthesized by pulsed laser ablation of a pure indium metal target. X-ray diffraction and transmission electron microscopy confirmed that nanocrystalline indium oxide particles with a mean diameter of 6.6 nm with a cubic crystal structure were formed. Photoluminescence spectroscopy shows a strong emission peak at 3.78 eV with a weak size dependence.

Materials research focused on the synthesis and characterization of structural, electronic, or optical properties of thin film and bulk transparent conducting oxides, popularly called TCOs, has experienced a resurgence of interest in the past few years. Recent overviews[1] of the many fascinating aspects of these materials have addressed issues related to synthesis/processing, the nature of charge carriers and electronic characteristics, dopant effects, and theoretical models for projecting performance limits. Of the many possible TCOs, the most studied, and certainly of greatest technological importance thus far, are the oxides of zinc, tin, and indium (e.g., indium−tin oxide (ITO)) although cadmium stannates and fluorine-doped TCOs have shown impressive figures of merit based on electrical conductivity and optical absorption measurements. Clearly, the motivation for investigating the TCOs is their remarkable combination of high transparency in the visible region and high conductivity.[1−3]

Indium oxide and the closely related indium tin oxide are two important TCOs that are useful in applications such as electrooptic modulators, low-emissivity windows, solar cells, flat-panel displays, and electrochromic mirrors and in dissipating static electricity from the windows on xerographic copiers.[4,5] The wide band gap of indium oxide (direct gap of 3.55−3.75 eV) is also remarkably close to GaN, another popular current electronic and optical material. While several synthesis and processing methods (sputtering, spray pyrolysis, CVD) have been employed for making thin films of TCOs, research on nanoparticles and quantum dot structures is still quite sparse. The possibility of using nanostructures of TCOs for UV lasers and detectors and as gas sensors for ozone and nitrogen dioxide is appealing. For instance, the gas sensing ability of indium oxide has been shown to increase significantly by decreasing its particle size.[6] In the present work we report the results of synthesis, structural, and optical properties of indium oxide nanoparticles formed by pulsed laser ablation of an indium metal target. X-ray diffraction, transmission electron microscopy, and photoluminescence were among the characterization methods used.

Indium metal with a purity of 99.9999% was laser ablated in a stainless steel chamber while maintaining a pressure of 25 Torr with an air flow rate of about 0.6 L/min. The laser source was the fourth harmonic of a pulsed Nd:YAG laser ($\lambda = 266$ nm) with a pulse width of 10 ns, repetition rate of 10 Hz, and a pulse energy of typically 50 mJ. The laser beam was focused down to a spot of ∼1 mm diameter on the indium target to cause the ablation. The reaction product was collected downstream on a microporous cellulose nitrate membrane filter. The procedures and experimental conditions were generally similar to our previous work on the synthesis of GaN nanocrystals.[7,8] The reaction product was characterized using X-ray diffraction (XRD), transmission electron microscopy (TEM), and photoluminescence (PL) spectroscopy.

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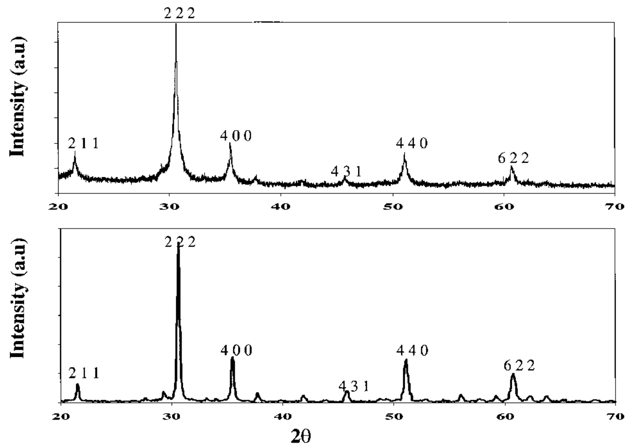

Figure 1. (a) XRD of indium oxide nanoparticles synthesized by reactive laser ablation and (b) XRD of indium oxide bulk powder. The numbers above the peaks correspond to the (*hkl*) values of the cubic structure.

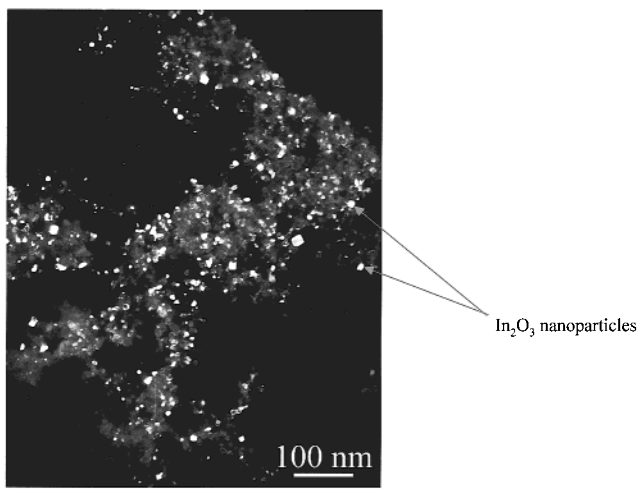

Figure 2. Representative TEM dark field image of indium oxide nanoparticles synthesized by reactive laser ablation. The mean particle diameter is 6.6 nm with a standard deviation of 3.3 nm.

XRD data were collected with a Scintag XDS-2000 powder X-ray diffractometer using Cu Kα radiation. A quartz single-crystal zero-background specimen holder was used to minimize the background signals. The sample was prepared by dispersing the powder onto the quartz specimen holder. The crystalline peaks in the XRD data of the sample matched the diffraction data of cubic indium oxide obtained from the PDF files and it also matched with the peaks of bulk commercial (Alfa Aesar) indium oxide powders, as shown in Figure 1. These data confirmed that the laser-ablated product was indeed indium oxide and the structure and morphology of the reaction product was then further analyzed by TEM methods using a Philips CM-12 TEM operated at 100 kV. The sample was prepared by first ultrasonically dispersing the powder in methanol for 2 min. The resulting methanol-powder mixture was then dispersed onto a holey carbon-coated 400 mesh copper grid. The methanol evaporated in the dry environment, leaving a distribution of particles on the carbon film. The dark-field TEM image (Figure 2) of the laser-ablated indium oxide sample shows nanocrystals with a mean diameter of 6.6 nm and a standard deviation of 3.3 nm, along with some amorphous material. NIH IMAGE software (version 1.60) was used to develop a characteristic particle size histogram from the dark field TEM image. Figure 3 shows the particle size distribution of the laser-ablated indium oxide sample. For comparison, the exciton Bohr diameter for indium oxide is estimated to be in the range between 2.6 and 5 nm.[9,10] Since the indium oxide particles from the ablated sample are of the order of the Bohr exciton diameter, they are likely to show only a weak size dependence.[11] TEM analysis of the commercial powder shows that sample to consist of large particles approximately 1 μm in diameter, interspersed with networks of small particles ranging from 30 to 100 nm in diameter.

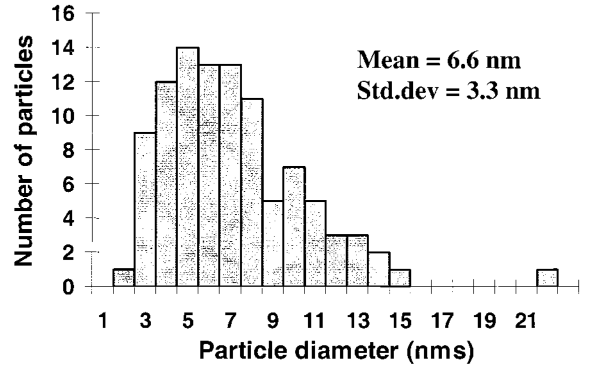

Figure 3. Characteristic particle size histogram from the dark field TEM image. The mean particle diameter is 6.6 nm with a standard deviation of 3.3 nm.

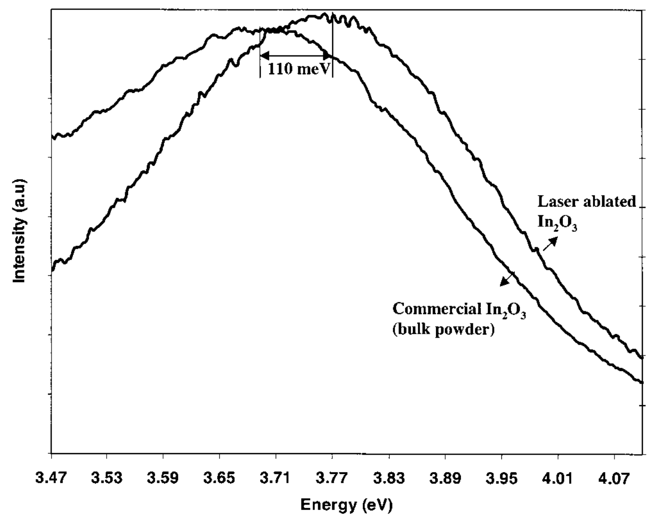

Figure 4. Room-temperature photoluminescence (PL) spectra of the laser-ablated sample and the commercial indium oxide powder. The laser-ablated sample shows a weak blue shift of 110 meV, consistent with a mean particle size on the order of the Bohr exciton diameter.

Photoluminescence spectroscopy was performed on the indium oxide nanoparticles using appropriate spectrometers having a resolution of ∼1 nm. Optical excitation was provided by a xenon arc lamp dispersed by a monochromator. Spectra were recorded with another monochromator at room temperature. Figure 4 shows the PL spectra of the commercial indium oxide powder, and the laser-ablated sample. Both the samples were excited at 250 nm. As can be seen from the figure, the commercial indium oxide powder (bulk system) shows a spectrum with the PL onset peaking around 3.67 eV, and in the laser-ablated sample the peak position is blue shifted to 3.78 eV, a shift of approximately 110 meV. If a weak size dependence is assumed, the size of the particles for an energy shift of 110 meV can be calculated using[11]

$$\Delta E = \frac{\hbar^2 \pi^2}{2MR^2}$$

where ΔE is the shift in energy equal to 110 meV, $M = m_e^* + m_h^* = 0.3m_0 + 0.6m_0$,[10] and R is the radius of the particle. Using the appropriate values in the above equation, the average size of the particles is determined to be 4 nm in diameter. The calculated value is in good agreement with the TEM results for the laser-ablated indium oxide sample (6.6 nm in diameter), thus indicating the blue shift to have a weak size dependence.

In summary, we have synthesized nanoparticles of indium oxide, an important TCO material, and characterized its structural, morphological, and optical properties. XRD and TEM analysis showed the particles to be cubic, with a mean diameter of 6.6 nm. The weak size dependence revealed by a blue shift of about 110 meV in the PL spectra is consistent with a particle size on the order of the Bohr exciton diameter. Future more detailed experiments will be needed to sort out the origin of the luminescence. In addition, the effect of nanoparticle size on the optical, electrical conductivity, and gas sensing properties of indium oxide and related TCO materials is also worthy of future research.

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