Available online at www.sciencedirect.com

SciVerse ScienceDirect

Acta Materialia 60 (2012) 1072–1078

Acta MATERIALIA

www.elsevier.com/locate/actamat

Quantum confinement effects and band gap engineering of SnO_2 nanocrystals in a MgO matrix

M.B. Sahana [a], C. Sudakar [a,*], A. Dixit [a], J.S. Thakur [a], R. Naik [a], V.M. Naik [b]

[a] Department of Physics and Astronomy, Wayne State University, Detroit, MI 48201, USA
[b] Department of Natural Sciences, University of Michigan–Dearborn, Dearborn, MI 48128, USA

Received 14 June 2011; received in revised form 6 November 2011; accepted 6 November 2011
Available online 15 December 2011

Abstract

Nanocrystal formation of SnO_2 in $xSnO_2$–$(100 - x)$MgO (x in mol.%) nanocrystalline composite thin films is reported. SnO_2 and MgO exhibit strong immiscibility behavior below 750 °C, leading to controllable particle size of SnO_2 in the MgO matrix by changing their composition. The particle size of SnO_2 can also be controlled by increasing the annealing temperature. Above 750 °C MgO and SnO_2 react to yield a MgO–Mg_2SnO_4–SnO_2 composite in which the size of the SnO_2 nanophase increases with increasing temperature. By controlled choice of the composition and annealing conditions the band gap of SnO_2 can be continuously increased from 3.89 to 4.5 eV. We discuss this behavior in terms of the quantum confinement effect. The method provides a generic approach to tuning the band gap in nanocomposite systems over a wide energy range.

Keywords: Band gap engineering; SnO_2–MgO composite thin films; Nanocrystalline films; Quantum confinement

1. Introduction

Semi-conducting oxide nanostructures are promising building blocks for future generation photovoltaic devices, opto-electronics and magneto-electronics applications [1,2]. SnO_2 is an important n-type intrinsic semiconducting wide band gap ($E_g = 3.6$ eV) oxide. Tuning the optical and electrical properties of SnO_2 is important for several applications, including transparent conductors, dye sensitized solar cells, lithium ion battery materials, catalysts, gas sensing, and field emission and field effect transistors. SnO_{2-x} is considered to be one of the promising anode materials for Li ion batteries due to their high volumetric and gravimetric capacities [3–5]. SnO_2-based composite oxides, e.g. magnesium–tin composite oxides, are considered as alternative anode materials for use in Li ion batteries due to buffering of the volume changes during Li insertion and due to its large Li ion capacity at low potentials [6–8]. Materials with a tunable band gap are most appropriate for both photovoltaic and photo-catalytic applications and SnO_2 is one of the promising materials for these applications [9]. The suitability of these materials depends on the crystallite size, which strongly influences the optical properties and the associated changes in physical properties.

The value of the band gap E_g influences many fundamental properties of semi-conducting oxides. The band gap can be tuned by forming oxide alloys, as demonstrated in materials such as MgZnO and CdZnO [9]. Alternately, the band gap can be increased by reducing the size of a nanocrystallite to that of or smaller than its exciton Bohr radius [10,11]. The challenge is to find a semi-conductor material with a suitable band gap which can be made in nanostructured form. Further, understanding the interplay between the nanoscale structure and the optical properties of semi-conducting materials is crucial. Although several studies have been reported on the band gap tunability of particles by decreasing their size, investigations on composite nanocrystalline materials are sparse. Interestingly, the

* Corresponding author. Present address: Department of Physics, Indian Institute of Technology, Madras, Chennai 600 036, India.
E-mail address: csudakar@iitm.ac.in (C. Sudakar).

1359-6454/$36.00
doi:10.1016/j.actamat.2011.11.012

material properties of nanostructured composites often differ from the individual bulk components because of strong surface interactions between closely packed nanoparticles, a large surface to volume ratio and quantum confinement effects due to the very small size.

In an earlier study of SnO_2–Fe_2O_3 composite thin films we showed that the band gap could be tuned from 2.3 to 3.89 eV by changing the ratio of SnO_2 to Fe_2O_3 [12]. Due to strong phase separation instability, the change in band gap was found to be related to the size of Fe_2O_3 nanocrystallites. In this article we report that the optical band gap of SnO_2–MgO composites can be continuously increased from 3.89 to 4.5 eV, which is attributed to quantum confinement effects in nanophase SnO_2 in a MgO matrix. A generic approach to tailoring the band gap of a semi-conductor over a wide range by controlling the particle size in a nanocomposite system is proposed.

2. Experimental details

SnO_2–MgO nanoparticle thin films were prepared by a metal–organic decomposition technique. We prepared heterogeneous nanocomposites starting from a uniformly mixed precursor solution. $x$$SnO_2$–$(100-x)$MgO thin films (0.5–1 μm thick) having a range of compositions ($x = 0$–100) were prepared by spin coating the metal–organic precursors. Sn(IV) ethylhexanoate ($Sn(C_{16}H_{30}O_4)$) and Mg methoxide ($Mg(OCH_3)_2$), 7–8% in methanol, were used in preparing the precursor solutions. About 50–100 wt.% xylene solution was added to the precursor solution to obtain a homogeneous solution for spin coating. The $x$$SnO_2$–$(100-x)$MgO films were prepared by dispensing the homogeneous metal–organic precursor solution *c*-plane (0 0 0 1) sapphire substrates (2–3 cm^2 area) polished on two sides. Sapphire substrates polished on two sides were used so that the optical transmission spectra of the thin films could be recorded using an ultraviolet/visible spectrometer. Also, the band gap of sapphire (8.8 eV) is larger than that of MgO (7.2 eV) [13]. The substrate was spun at 5000 r.p.m. for 15 s, followed by baking in air at 500 °C. This process of coating was repeated 10 times to obtain ~1 μm thick films. In the following text we use the notation Snx–Mg$(100-x)$ to represent a composite sample with $(100-x)$ mol.% MgO in x mol.% SnO_2. We found that the SnO_2 and MgO phases were completely immiscible below 750 °C. The particle size of the SnO_2 and MgO phases can be controlled by tuning the composition (the ratio of SnO_2 to MgO) and post-deposition annealing conditions. The temperatures for the post-annealing treatment were varied from 600 °C to 950 °C in steps of 50 °C in an ambient air atmosphere. Our studies established that the band gap in these composite materials can be tuned from that of SnO_2 (3.89 eV) to a band gap of 4.5 eV by modifying the particle size and crystallinity of the SnO_2 nanoparticles in MgO. We attribute the observed particle size-dependent band gap tunability to quantum confinement effects.

3. Results and discussion

The crystal structure and composition of these films were determined using X-ray diffraction (XRD). The

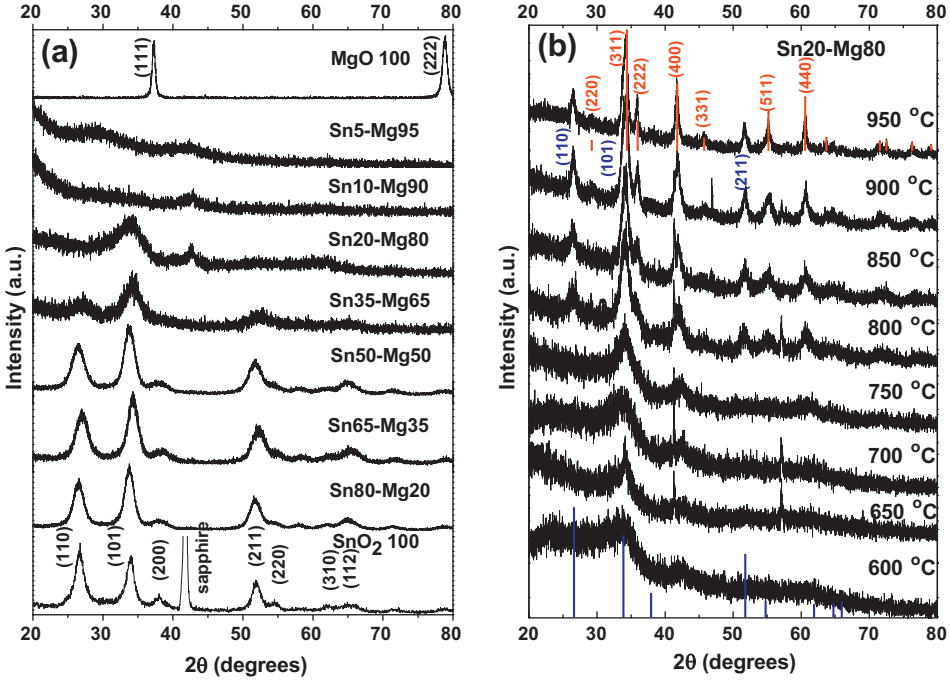

Fig. 1. (a) XRD of $x$$SnO_2$–$(1-x)$MgO (Sn$x$–Mg$(100-x)$) ($x = 0$–100 mol.%) thin films. (b) XRD patterns of 20SnO_2–80MgO annealed at 600–950 °C in steps of 50 °C. The (*hkl*) reflections of SnO_2 (blue lines on the 600 °C X-ray plot), and Mg_2SnO_4 (red lines on the 950 °C X-ray plot) are given by the vertical lines in. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)