Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 38 (2012) 1281–1286

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

AC transport properties of nanocrystalline SnO_2 semiconductor

P.P. Sahay [a,*], R.K. Mishra [a], S.N. Pandey [a], S. Jha [b], M. Shamsuddin [b]

[a] Department of Physics, Motilal Nehru National Institute of Technology, Allahabad 211 004, India
[b] Department of Metallurgical Engineering, Banaras Hindu University, Varanasi 221 005, India

Received 23 June 2011; received in revised form 15 August 2011; accepted 30 August 2011
Available online 6 September 2011

Abstract

Nanocrystalline SnO_2 materials were prepared by the chemical co-precipitation route by adding ammonia solution to 0.1 M solution of $SnCl_4{\cdot}5H_2O$. The resulting precipitate after thorough washing with distilled water and calcination at 600 °C for 10 h was investigated by XRD for phase identification and crystallite size determination. The materials have been found to be polycrystalline SnO_2, possessing tetragonal rutile crystal structure and nanocrystalline in grain size of approximately 30 nm. The TEM micrograph shows agglomerated particles (cluster of primary crystallites) with an average size of 37.4 nm. A corresponding selected area electron diffraction pattern reveals the different Debye rings of SnO_2, as analyzed in XRD.

The complex dielectric constant ε^* has been found to vary with frequency which is attributed to the multi-relaxation time constants of the energy states responsible for conduction mechanism. At any particular frequency, ε^* has been found to increase with temperature. The frequency dependence of loss tangent tan δ has been explained with the help of the equivalent circuit model. The observed frequency dependence of ac conductivity has been found to obey the power law: $\sigma_{ac} \propto \omega^S$, where variation of S with temperature indicates multi-hopping conduction mechanism in nanocrystalline SnO_2 samples. The complex impedance plots of Z' versus Z'' at different temperatures have been found to be single semicircular arcs with a non-zero intersection with the real axis in the high frequency region and have their centres lying below the real axis at a particular angle of depression, indicating multirelaxation processes in the material.

Keywords: SnO_2 nanoparticles; Complex dielectric constant; Loss tangent; AC conductivity; Impedance spectroscopy

1. Introduction

Tin dioxide (SnO_2) belongs to the family of an important *n*-type wide-bandgap semiconductors (E_g = 3.6 eV at 300 K). In its tetragonal rutile structure inherent oxygen vacancies act as an *n*-type dopant [1]. The unit cell parameters are a = 4.737 Å and c = 3.185 Å and its space group is $P42/mmm$. In recent years SnO_2 has attracted a lot of interests because of its wide range of applications as gas sensors [2–4], heat mirrors [5,6], transparent electrodes for solar cells [7], opto-electronic devices [8], etc. For various applications, this material has been exploited in the form of single crystals [9], compressed pellets [10], thin films [11] and thick films [12]. Very recently, nanocrystalline SnO_2 has gained prominence in technological field due to its interesting electrical and optical properties arising out of large surface-to-volume ratio, quantum confinement effect, etc. Starke et al. [13] have studied laser-ablated nanocrystalline SnO_2 material for low-level CO detection. Sensing characterization of NH_3 of nanocrystalline Sb-doped SnO_2 has been carried out by Wang et al. [14]. El-Etre et al. [15] have characterized nanocrystalline SnO_2 thin film for dye-sensitized solar cell application.

The optimization of device development based on SnO_2 material requires a better understanding of the transport properties of this material. Though a large number of studies on the dc conduction mechanism of SnO_2 have been carried out [16–19] but comparatively a little attention has been paid to the investigation of ac transport properties [20,21]. Dielectric measurements give an insight of the relaxation behaviour of the charge conduction species which, in turn, are responsible for the charge holding capacity, i.e., ac capacitance of the system. Ac conductivity measurements provide information about the interior of the materials in the region of low conductivity and are helpful in distinguishing the hopping conduction in the

* Corresponding author. Tel.: +91 532 2271260; fax: +91 532 2545341.
E-mail address: dr_ppsahay@rediffmail.com (P.P. Sahay).

0272-8842/$36.00
doi:10.1016/j.ceramint.2011.08.062

localized states from the free band conduction. Analysis of complex impedance spectra can be used to resolve the contribution of various processes such as bulk conduction, grain boundary conduction and transport across electrode–sample interface in the total conductivity of the polycrystalline system. In this paper we report a detailed study on the ac transport properties of SnO_2 nanoparticles.

To prepare active nanocrystalline powders, several chemical techniques have been investigated and reported in the literature. Among the various methods of preparing nanostructured SnO_2, co-precipitation [22], sol–gel [23], spray pyrolysis [24], hydrothermal routes [25], etc. are popular. In the present investigation, the authors have used co-precipitation method for the preparation of nanocrystalline SnO_2 materials as this method requires little manipulation and no sophisticated equipment.

2. Experimental

The nanocrystalline SnO_2 materials were prepared by the chemical co-precipitation route. The experimental details are as follows: all the chemicals used were of analytical grade. Firstly, stannic tetrachloride hydrated ($SnCl_4{\cdot}5H_2O$) was dissolved in distilled water to prepare 0.1 M solution. Ammonia solution was then added into the solution under constant agitation to form white slurry. The slurry was filtered and washed thoroughly with distilled water several times to remove the chloride ions completely from the precipitate. The resulting precipitate was dried at 90 °C and then calcined at 600 °C for 10 h in air. The dried mass was then crushed into fine powder. The structural analysis of the SnO_2 powder was carried out using PANalytical X'Pert Pro X-ray Diffractometer with CuKα radiation (λ = 1.5418 Å) as X-ray source at 40 kV and 30 mA in the scanning angle (2θ) from 20° to 80°. The morphologies and dimensions of the powders were observed by transmission electron microscopy (TEM), which were taken on a Philips model Tecnai-20 using an accelerating voltage of 200 kV.

For electrical measurements, the fine powder of SnO_2 was pressed into pellets of 12 mm diameter and 2.5 mm thickness at a pressure of ∼15 MPa using a hydraulic press. These pellets were sintered at around 600 °C for 5 h in air. The flat faces of the sintered pellets were polished and then coated with a thin layer of high temperature silver paste for making good electrical contacts. The pellet was then mounted on a home-made two-probe assembly which was inserted coaxially inside a resistance-heated furnace. The temperature of the pellets was monitored using a chromel–alumel thermocouple with the help of a Motwane digital multimeter (Model: 454). The ac measurements (impedance and phase angle) on the pellets were carried out as a function of frequency (100 Hz to 2 MHz) in the temperature range of 300–400 K by Precision Impedance Analyzer (Agilent Technologies; Model: 4294A). Throughout the measurements, the pellet in the furnace was allowed to equilibrate at each temperature for more than 10 min.

3. Results and discussion

3.1. Structural analysis

Fig. 1 shows the XRD pattern of the SnO_2 powder which matches with JCPDS File No. 72-1147. All the prominent peaks in the pattern have been found to correspond to the tetragonal rutile structure of polycrystalline SnO_2 and have been indexed on the basis of JCPDS file.

The lattice constants 'a' and 'c' for the tetragonal phase structure have been determined by the relation [26]:

$$\frac{1}{d^2} = \left(\frac{h^2 + k^2}{a^2}\right) + \left(\frac{1^2}{c^2}\right) \quad (1)$$

where 'd' is the interplaner spacing and ($h\,k\,l$) are miller indices, respectively. The lattice constants 'a' and 'c' thus calculated are 4.685 Å and 3.175 Å, respectively.

The average crystallite size (D) of the SnO_2 nanoparticles has been estimated for the three observed planes (1 1 0), (1 0 1) and (2 1 1) by using Scherrer formula [27]:

$$D = \frac{0.9\lambda}{\beta\cos\,\theta} \quad (2)$$

where λ, β and θ are the X-ray wavelength, full width at half maximum (FWHM) of the diffraction peak and the Bragg's diffraction angle, respectively. The crystallite size thus estimated has been found to be ∼30 nm.

The bright-field TEM image and the selected area electron diffraction (SAED) pattern of the synthesized SnO_2 nanoparticles are shown in Figs. 2 and 3, respectively. The TEM micrograph shows agglomerated particles (cluster of primary crystallites) with an average size of 37.4 nm which is close to the size calculated from XRD. The SAED pattern is consistent with the tetragonal rutile structure of SnO_2 featuring strong ring patterns assigned to (1 1 0), (1 0 1), (2 0 0), (2 1 1), (2 2 0), (0 0 2) and (3 1 0) planes and proves the high crystallinity of the nanoparticles.

The X-ray density (ρ_x), experimental density (ρ_a) and porosity (P) of the synthesized SnO_2 nanoparticle pellets have

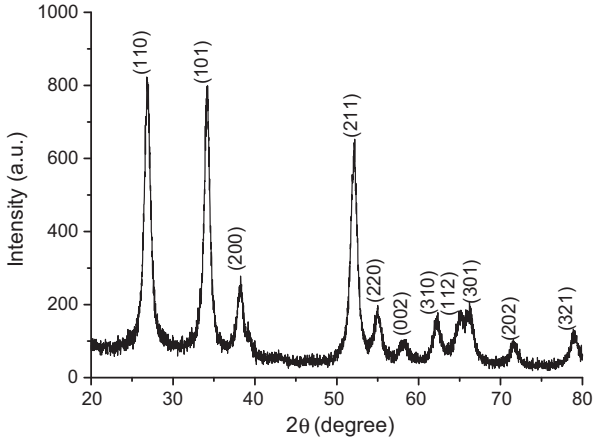

Fig. 1. XRD spectra of the SnO_2 nanoparticles.