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Charge carrier transport mechanisms in nanocrystalline indium oxide

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ABSTRACT

The charge transport properties of nanocrystalline indium oxide (In_2O_3) are studied. A number of nanostructured In_2O_3 samples with various nanocrystal sizes are prepared by sol–gel method and characterized using various techniques. The mean nanocrystals size varies from 7–8 nm to 18–20 nm depending on the conditions of their preparation. Structural characterizations of the In_2O_3 samples are performed by means of transmission electron microscopy and X-ray diffraction. The analysis of dc and ac conductivity in a wide temperature range ($T = 50$–300 K) shows that at high temperatures charge carrier transport takes place over conduction band and at low temperatures a variable range hopping transport mechanism can be observed. We find out that the temperature of transition from one mechanism to another depends on nanocrystal size: the transition temperature rises when nanocrystals are bigger in size. The average hopping distance between two sites and the activation energy are calculated basing on the analysis of dc conductivity at low temperature. Using random barrier model we show a uniform hopping mechanism taking place in our samples and conclude that nanocrystalline In_2O_3 can be regarded as a disordered system.

1. Introduction

For the last few decades, nanocrystalline indium oxide (In_2O_3) has been widely applied to fabricate photovoltaic cells [1,2], sensor modules [3,4] and transparent electrode materials for both electrochromic cells and liquid crystal display devices [5]. Despite the fact that the In_2O_3 has been studied for a long time, many of its properties are not clear yet. The current research works considering In_2O_3 mainly concentrated on its preparation and studies of its structural properties [6,7].

However application of this material in many technical devices (in particular, sensors) requires solving the following problem: what are the electrical properties of nanocrystalline In_2O_3 and how does its size influence them? The decrease of the nanocrystal size may lead to significant changes in the electrical properties of the studied material. In the present study we investigate the structural and electrical properties of indium oxide with different nanocrystal sizes on purpose to clarify charge carrier transport mechanisms.

2. Experimental details

The nanocrystalline samples of In_2O_3 were prepared by wet chemical method with subsequent heat treatment [8]. A measured amount of $In(NO_3)_3 \cdot 4.5H_2O$ was dissolved in deionized water in an ice bath and aqueous ammonia was slowly added to the stirred solution to achieve a complete precipitation of indium(III) hydroxide. The resulting gel was centrifuged, washed several times with deionized water and dried at 100 °C during 24 h. All dried powders were crushed and calcined in the same conditions: in air at 300, 500, and 700 °C during 24 h. After that the phase composition, dispersion degree, particle size and specific surface area of nanocomposites were studied.

The composition and the dispersion degree of the samples were determined by X-ray diffraction (XRD). XRD patterns were recorded using a STOE diffractometer in Bragg–Brentano configuration with monochromatic Cu (K_α) ($\lambda = 1.5406$ Å) radiation. The results were processed using STOE WinXPow software. The XRD data were also used for estimation of In_2O_3 average grain size which was calculated using the Scherrer equation. The specific surface area of the samples was estimated by the method of low-temperature nitrogen adsorption using the Brunauer–Emmett–Teller model [9]. The experiments were carried out by means of Chemisorb 2750 (Micromeritics) unit. The morphology and nanocrystal size of the In_2O_3 samples were determined by transmission electron

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microscopy (TEM) using a LEO 912 AB OMEGA microscope operated at 300 kV with 0.19 nm point resolution. For TEM observations, nanopowders were ultrasonically dispersed in ethanol and deposited on Cu grid covered with carbon film.

The thin films were prepared by stencil process. The powder was mixed with a binding substance (alcoholic solution of terpineol) and put in the form of paste on glass substrates. The thickness of the obtained thin films was equal to 1 μm. In order to measure the electrical characteristics, gold contacts with area of 1 mm^2 were vapor-deposited on the front side of the samples. The measurements of thermopower revealed that the In_2O_3 samples are n-type semiconductors.

Prior to the measurements, the samples had been placed into M9700 closed cycle helium cryostat produced by Advance Research Systems, which was evacuated to a pressure of 5 Pa using oil-free vacuum equipment manufactured by Alcatel. The conductivity was measured in the temperature range from 50 to 300 K using Keithley 6487 unit.

Frequency dependencies of conductivity were measured by an impedance analyzer HP 4192A in the frequency range from 5 Hz to 13 MHz.

3. Results and discussion

3.1. Composition and morphology of the samples

The XRD patterns of the In_2O_3 samples (see Fig. 1) show a single phase of cubic In_2O_3, and the peaks indicate its good crystallinity. The nanocrystal size increases while the annealing temperature rises. The calculated lattice parameter ($\alpha = 1.018$ nm) for the sample is in a good agreement with the known lattice parameter for crystalline In_2O_3 ($\alpha = 1.0117$ nm). The designations of the samples, annealing temperatures, nanocrystals size and specific surface areas are given in Table 1.

In order to obtain some more detailed information on the microstructure of the materials being studied, In_2O_3-300 sample with the smallest nanocrystal size was investigated using a transmission electron microscope (see Fig. 2). The TEM analysis shows that the In_2O_3 powders consist of nanoparticles, really corresponding to cubic modification. From the TEM micrographs the grain size distribution (see Fig. 3) was determined by measuring the average of two perpendicular diameters of the cross section of some hundred grains in each analyzed distribution. The most probable (more than 80%) sizes of In_2O_3 nanoparticles are within 5–10 nm which corresponds to XRD analysis (see Table 1).

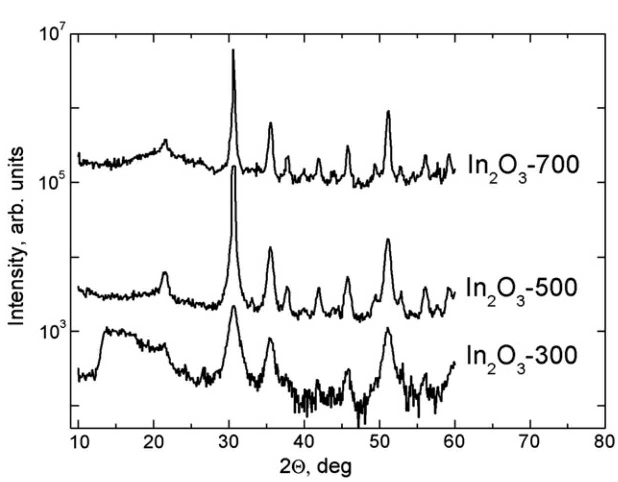

Fig. 1. X-ray diffraction patterns of In_2O_3 samples.

Table 1
The designations of samples, annealing temperatures, sizes of nanocrystals and specific surface area.

Designation of sample	Annealing temperature (°C)	Nanocrystal size (nm)	Specific surface area (m^2/g)
In_2O_3-300	300	7–8	100
In_2O_3-500	500	12–13	35
In_2O_3-700	700	18–20	10

3.2. Electrical properties: dc conductivity

Temperature dependencies of dc conductivity of In_2O_3 samples with nanocrystals different in sizes are presented in Fig. 4. It can be seen that the $\sigma_{dc}(T)$ dependencies consist of two specific regions. The first one occupies a temperature region from ~210 K to 300 K where the conductivity increases with the rise in temperature. This may suggest that a simple thermal activation process dominates the electrical conduction in the In_2O_3 samples. For the thermally activated band conduction, the conductivity (σ_{dc}) can be expressed as:

$$\sigma_{dc} = \sigma_0 \exp(-E_A/k_BT) \tag{1}$$

where E_A denotes the thermal activation energy of electrical conduction, σ_0 represents a parameter depending on the semiconductor nature and k is the Boltzmann constant. The conductivity decrease and the activation energy increase are observed with the reduction of the nanocrystal size (the activation energy values are represented in Table 2). The dependence described by Eq. (1) is typical for charge carrier transport over delocalized states in semiconductors [10]. In the case of electron transport over the conduction band the thermal activation energy of electrical conductivity is defined as the energy difference between the bottom of the conduction band E_C and Fermi level E_F extrapolated to absolute zero temperature. Since there are potential barriers on the boundaries of nanocrystals the activation energy of conductivity E_A must also be defined by potential barriers' heights E_B. In the case of the existence of potential barriers at the grain boundaries and thermionic emission [11], drift charge carrier mobility μ is thermally activated [12,13]:

$$\mu \propto \mu_0 \exp(-E_B/k_BT) \tag{2}$$

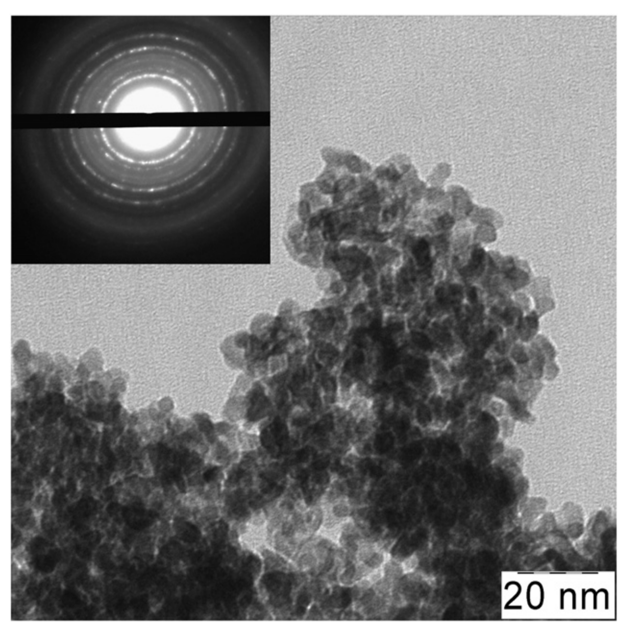

Fig. 2. TEM image of In_2O_3-300 sample. The inset of this figure represents the electron diffraction pattern.