Optical and photoelectrical features in nanocrystalline indium oxide

Ekaterina FORSH[1,2], Mikhail MARTYSHOV[1,3], Pavel FORSH[1,3], Pavel KASHKAROV[1,2,3]
[1]*National Research Center "Kurchatov Institute"*
[2]*Moscow Institute of Physics and Technology*
[3]*Faculty of Physics, Lomonosov Moscow State University*
forsh_ea@nrcki.ru

***Abstract* — Spectral dependencies of absorption coefficient and persistent photoconductivity in nanocrystalline indium oxide (In_2O_3) are studied. Nanostructured In_2O_3 samples with various nanocrystals size are prepared by sol-gel method and characterized using various techniques. The mean nanocrystals size varies from 7–8 nm to 39–41 nm depending on the preparation conditions. Structural characterization of the In_2O_3 samples is performed by means of transmission electron microscopy and X-ray diffraction. The analysis of ultraviolet – visible absorption spectroscopy shows that nanostructuring leads to the change in optical band gap: optical band gap of the In_2O_3 samples (with an average nanocrystal size from 7 to 41 nm) is equal to 2.8 eV. We find out the correlation between spectral dependence of photoconductivity and optical properties of nanocrystalline In_2O_3: sharp increase in photoconductivity was observed to begin at 2.8 eV energy equal to the optical bandgap in the In_2O_3 samples, and reached its maximum at energies of 3.2–3.3 eV.**

***Index Terms* — absorption, nanocrystalline indium oxide, persistent photoconductivity, ultraviolet – visible absorption spectroscopy.**

I. INTRODUCTION

Indium oxide (In_2O_3) is a wide band gap n-type semiconductor possessing high electrical conductivity and optical transparency [1]. The optical and electronic properties of indium oxide make this material suitable for numerous applications such as optoelectronics, gas sensors, solar cells, holographic recorders, thin film transistors, photocatalysts etc [2-8]. However nanocrystalline indium oxide with few-nanometers nanocrystal size may exhibit properties different from the bulk material. Therefore a study of the optical and photoelectrical properties of the nanocrystalline In_2O_3 is very important.

It is well known [9] that there are fundamental (2.89 eV) and optical band gap E_g (3.70 eV) in single-crystalline In_2O_3 (direct optical transitions from the valence band maximum to the conduction band minimum are parity forbidden because of the band structure symmetry) and that the first strong transitions occur from valence bands 0.81 eV below the valence band maximum. But there are no data on the optical band gap width in nanocrystalline indium oxide. Furthermore direct measurements of spectral dependences of absorption coefficient in nanocrystalline In_2O_3 was not carried out. Optical band gap can also be determined from analysis of the photoconductivity spectral dependence. At the same time detailed studies of the spectral dependence of the photoconductivity of nanocrystalline indium oxide also were not carried out.

In this work spectral dependencies of photoconductivity and absorption coefficient in nanocrystalline indium oxide with small nanocrystals size are studied in detail, value of the optical band gap of the nanocrystalline In_2O_3 is defined. The high quality nanocrystalline In_2O_3 thin films with different nanocrystal size (7 – 40 nm) have been investigated in our work.

II. EXPERIMENTAL DETAILS

The In_2O_3 nanocrystalline samples were prepared by sol-gel method and then annealed at various temperatures (T=300-700 °C) during 24 h as described in our previous work [10]. Depending on the annealing temperature the samples are called In_2O_3-300, In_2O_3-500 and In_2O_3-700. After that the phase composition, dispersion degree, particle size and specific surface area of nanocomposites were studied.

The structure of the samples was examined using X-ray diffraction (XRD) and transmission electron microscopy (TEM). The XRD and TEM data were also used for estimation of In_2O_3 average grain size. The specific surface area of the samples was estimated by the method of low-temperature nitrogen adsorption using the Brunauer-Emmet-Teller model [11].

The thin films were prepared by stencil process. The thickness of the obtained thin films was equal 1 μm.

Transmission and reflection measurements in wide spectral interval (λ=190 –1100 nm) were made using Perkin-Elmer spectrometer (model Lambda 35) with resolution 1 nm. Incident beam was normal to the surface of the samples.

Samples for photoconductivity measurements had two gold planar electrodes spaced at a distance of 0.5 mm. All structures demonstrated ohmic behavior in the range of 0–10 V applied voltages. In order to measure the spectral dependence of photoconductivity, the samples have been illuminated by monochromatic light in the range of 300 – 700 nm by using a spectrometer with a high-power Xenon filament. The intensity of light irradiation was 70 mW/cm^2.

The value of the photoconductivity ($\Delta\sigma_{ph}$) was defined as the difference between the conductivity of the sample during illumination (σ_{ill}) and dark conductivity (σ_d):

$$\Delta\sigma_{ph} = \sigma_{ill} - \sigma_d .$$

III. RESULTS AND DISSCUSSION

The XRD and TEM analyses of the In_2O_3 samples show a single phase of cubic In_2O_3. The XRD peaks indicate its good crystallinity. The nanocrystals size increases while the annealing temperature rises [12]. The designations of the samples, annealing temperatures, nanocrystals size and specific surface areas are given in Table I.

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

Sample	Annealing temperature (ºC)	Nanocrystal size (nm)	Specific surface area (m^2/g)	E_g, eV
In_2O_3-300	300	7-8	100	2.8
In_2O_3-500	500	12-13	35	2.8
In_2O_3-700	700	18-20	10	2.7

To determine optical band gap of the In_2O_3 samples, the reflectance and transmission spectra were measured and then the absorption coefficient was calculated using the formula [13]

$$\alpha = \frac{\left[\ln\left(T/(1-R)^2\right)\right]}{h},$$

where R and T are the reflectance and transmittance coefficients, respectively, h is film thickness of nanocrystalline In_2O_3 (Fig. 1(a)).

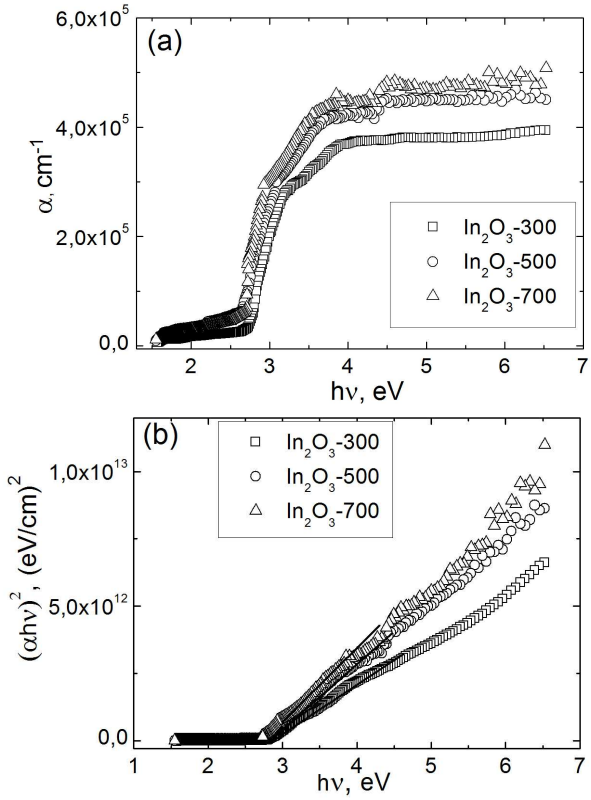

Fig. 1. Absorption coefficient spectra (a) and a plot of $(\alpha h\nu)^2$ versus $h\nu$ (b) of nanocrystalline In_2O_3.

Fig. 1(b) shows a plot of $(\alpha h\nu)^2$ versus $h\nu$ that corresponds to direct allowed transitions in semiconductor materials. So one can see that the direct allowed transitions with photon energy of 2.8 eV are observed in nanocrystalline indium oxide (Table 1). However as it is known [9] there should exist fundamental (2.89 eV) and optical band gap (3.70 eV) in single-crystalline In_2O_3. Really according to the theory the direct optical transitions from the valence band maximum to the conduction band minimum are parity forbidden and the first strong transitions occur from valence bands 0.81 eV below the valence band maximum. According to the data in the Table I in nanocrystalline indium oxide the optical band gap is close to the fundamental one in the bulk In_2O_3, while transitions with photon energy above E_g are allowed. This fact can be explained by the removal of the prohibition of the electronic transitions in the nanocrystalline In_2O_3 due to breaking of the local symmetry.

Moreover, nonzero value of the absorption coefficient is observed for all In_2O_3 samples for the quantum energy $h\nu$<2,8 eV (see Fig. 1(a)) that may be due to the presence of energy distributed localized states in the band gap of the investigated In_2O_3 samples.

The spectral dependences of nanocrystalline indium oxide photoconductivity (normalized to unity) are shown in Fig. 2. When the photon energy is 2.7 – 2.8 eV (depending on the nanocrystals size) a sharp increase of the photoconductivity begins. This energy threshold is equal to the optical band gap energy as defined above. While photon energy increases the photoconductivity quickly reaches a maximum (at the energies of 3.2 – 3.3 eV, depending on the nanocrystals size), and then decreases. This reduction can be explained by the small lifetimes of the nonequilibrium charge carriers in the surface layer of the semiconductor due to the strong surface recombination (photons with energy $h\nu > E_g$ is preferentially absorbed near surface).

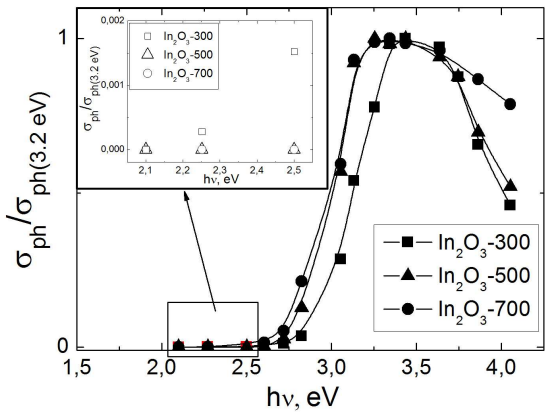

Fig. 2. The spectral dependences of photoconductivity of nanocrystalline indium oxide (normalized to unity). The inset shows the spectral dependences of photoconductivity of investigated samples at energies of 2,1 – 2,5 eV.

In addition, the relative photoconductivity (the ratio of the photoconductivity to its maximum value) decreases with growth of nanocrystal size. This reduction in photoconductivity obviously can be explained by the decrease of the relative change in the free electrons concentration under the illumination with the nanocrystals size growth.

As can be seen from the inset in Fig. 2 the photoconductivity for the sample In_2O_3- 300 is nonzero at photon energies lower than the optical band gap. This sample is photosensitive to green light (photoconductivity

has been registered since the photon energy was 2.25 eV). Apparently, the photoconductivity at $2.25 < h\nu < E_g$ is associated with the presence of localized states in the band gap of this sample. It should be noted that there are evidently localized states in the band gaps of the samples In_2O_3- 500 and In_2O_3- 700, however the photoconductivity at energies $h\nu < E_g$ is not visible on a background of the relatively high dark conductivity of these samples.

IV. CONCLUSION

The results of this study indicate that nanostructuring leads to the change in optical band gap: optical band gap of the In_2O_3 samples (with an average nanocrystal size from 7 to 40 nm) is equal to 2.8 eV may be due to the removal of the prohibition of the electronic transitions in the nanocrystalline In_2O_3 due to breaking of the local symmetry The nonzero value of the absorption coefficient for all In_2O_3 samples for the quantum energy $h\nu$<2,8 eV is observed. It may indicate the presence of energy distributed localized states in the band gap of the investigated In_2O_3 samples.

There is a correlation between spectral dependence of photoconductivity and optical properties of nanocrystalline In_2O_3. Sharp increase in photoconductivity was observed to begin at 2.8 eV energy equal to the optical bandgap in the In_2O_3 samples, and reached its maximum at energies of 3.2 - 3.3 eV. The photoconductivity increase with photon energy growth from 2.8 eV to 3,2 eV can be associated with an increase of the optical absorption near the absorption edge. Subsequent photoconductivity decrease with growth of photon energy at $h\nu$> 3,2 eV can be explained by the increasing role of surface recombination.

It was found out that the samples with low dark conductivity were photosensitive not only to UV light but to visible light, in particular the In_2O_3-300 sample with a smallest nanocrystal size (7 - 8 nm) was photosensitive to green light (photoconductivity was registered since the photon energy was equal to 2.25 eV), which can be explained by the generation of electrons from localized levels located in the bandgap.

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