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Relaxation of Photoconductivity in Nanocrystalline Indium Oxide

E. A. Forsh[a, b], A. S. Ilyin[c], M. N. Martyshov[a, c], P. A. Forsh[a, c], and P. K. Kashkarov[a, b, c]
[a] *National Research Center "Kurchatov Institute", pl. Akademika Kurchatova 1, Moscow, 123182 Russia*
[b] *Department of Nano-, Bio-, Information, and Cognitive Technologies, Moscow Institute of Physics and Technology, Institutskii per. 9, Dolgoprudnyi, Moscow oblast, 141700 Russia*
[c] *Physical Department, M.V. Lomonosov Moscow State University, Moscow, 119991 Russia*
e-mail: forsh_ea@nrcki.ru

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Abstract—Photoelectric properties of nanocrystalline indium oxide synthesized by the sol–gel method with nanocrystal sizes of 7–20 nm have been studied. An increase in the conductance by UV-light illumination of several orders of magnitude and the retention of this high-conducting state after the light is switched off is revealed. The kinetics of photoconductivity decay in air, vacuum, and argon at room temperature is studied; it is found that the photoconductivity decay is described by an expanded exponent. A conclusion about the determining role of oxygen molecules in the phenomenon of residual photoconductivity is made. A model is proposed which explains permanent photoconductivity decay in nanocrystalline indium oxide. A correlation between structural and photoelectric features in the object under study is found.

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INTRODUCTION

Indium oxide (In_2O_3) is an important material for various engineering applications, such as photodetectors, photoconvertors, and sensors of a resistive type [1–3]. Despite the fact that indium oxide has been studied for a long time, its many properties have not been fully studied. In particular, the unsteady-state photoconductivity in In_2O_3 has not been studied completely. A residual photoconductivity, i.e., a light-induced change in the conductance retaining after light is switched off, was observed in polycrystalline, amorphous, and mesoporous In_2O_3 [4–6]. At the same time, the phenomenon mentioned has not been observed for a nanocrystalline indium oxide with small sizes of nanocrystals, which is the most promising material for all industrial applications. In the case of nanocrystalline objects, the photoconductive properties substantially differ from those for a bulk material. The surface, acting as a region of the capture and recombination of charge carriers, substantially contributes to the conductance of nanomaterials. The authors of [4–6] came to a conclusion about the key role of oxygen in the phenomenon of long-term decay of photoconductivity. However, no experiments concerning the influence of the atmosphere on the photoconductive properties of In_2O_3 have been carried out. No model has been proposed which could approximate and explain the long-term decay of the photoconductivity.

The major existing works contain experimental facts on the interaction between light parameters (photon energy, radiation wavelength, and exposure duration) and the material under study [7, 8]. At the same time, the correlation between the properties of materials (size of particles, area of specific surface, and composition of the surface) and the photoelectric properties of the material has not been studied.

In this work we first present experimental data concerning the phenomenon of a residual photoconductivity in nanocrystalline indium oxide with small sizes of nanocrystals, a theoretical model which explains the long-term decay of photoconductivity is proposed, and the correlation between structural and electric properties of the materials under study is revealed.

SAMPLES AND EXPERIMENTAL TECHNIQUE

Nanocrystalline samples of indium oxide were obtained by the sol–gel method with subsequent annealing at various temperatures (T = 300–700°C) for 24 h (the synthesis of samples is described in detail in [9]) and deposited onto a glass substrate. The thickness of the layers obtained amounted to 1 μm.

The phase composition and degree of dispersity of powders were determined by X-ray diffraction on aDRON-4 device using radiation of the line K_α of copper. The area of the sample's specific surface was estimated using the technique of low-temperature adsorption of nitrogen, and the calculations were carried out according to the Brunauer–Emmett–Teller model [10]. The experiments were carried out in a single-point mode on a Chemisorb 2750 device (Micrometrics). The sample microstructure was studied using transmission electron microscopy by FEI Tecnai $G_2$30

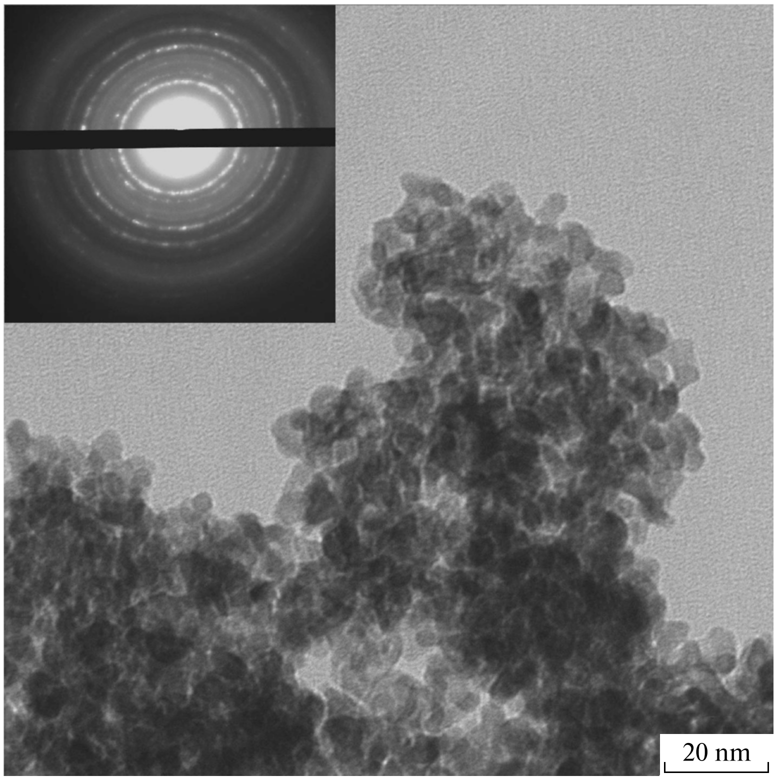

Fig. 1. Microphotograph of a sample. The insert shows a picture of electron diffraction.

TEM/STEM. The data obtained were used to determine the sizes of In_2O_3 nanocrystals.

In order to measure the electrical characteristics, gold contacts were deposited onto an upper surface of the films using a vacuum universal station VUP-5. An In_2O_3 sample was placed into a nitrogen cryostat, which allowed us to carry out the measurements at both atmospheric pressure and at vacuum of ~10^{-4} Torr. The conductance of the samples was measured by a Keithley 6487 peak amperemeter. The voltage was applied to the sample from a source built into the peak amperemeter. The sample was illuminated by an UV light-emitting diode of 1 W power with a wavelength of 380–385 nm. The value of the photoconductivity ($\Delta\sigma_{ph}$) was determined as a difference of the conductances of the sample by illumination (σ_{ill}) and dark conductance (σ_d); i.e.,

$$\Delta\sigma_{ph} = \sigma_{ill} - \sigma_d. \quad (1)$$

Table 1. Conditional designations, temperature of annealing, average sizes

Sample	Temperature of annealing, °C	Size of nanocrystals, nm	Specific surface, m^2/g
In_2O_3-300	300	7–8	100
In_2O_3-500	500	11–12	35
In_2O_3-700	700	18–20	10

EXPERIMENTAL RESULTS AND DISCUSSION

An analysis of X-ray diffraction and transmission electron microscopy data for samples annealed at various temperatures has shown that all the samples are characterized by a cubic modification of crystalline indium oxide. In this case, the sizes of nanocrystals are larger the higher the temperature of annealing is. Figure 1 shows a microphotograph of an In_2O_3-300 sample (with the smallest size of nanocrystals) obtained on a transmission microscope. Sample designations, temperatures of annealing at which they were obtained, and the sizes of nanocrystals determined by the method of X-ray diffraction and the calculated values of the specific surface of the samples are collected in Table 1.

A change in conductance of the indium oxide samples under study illuminated by UV light at room temperature in air atmosphere is shown in Fig. 2. When the light was switched on, the conductance of the materials increased by more than three orders for 10 s and then gradually continued to increase with time. When the light was switched off, the conductance began to decrease but did not reach its initial value; i.e., so-called residual photoconductivity was observed (the difference in the material's conductances before and after illumination). In this case, when the nanocrystal size increases, the photosensitivity (the ratio of

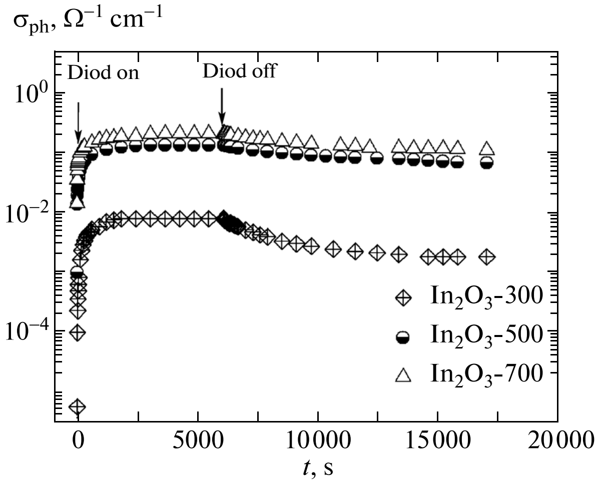

Fig. 2. Time dependence of the electroconductance of nanocrystalline In_2O_3-300 sample upon illumination by a UV-diode.

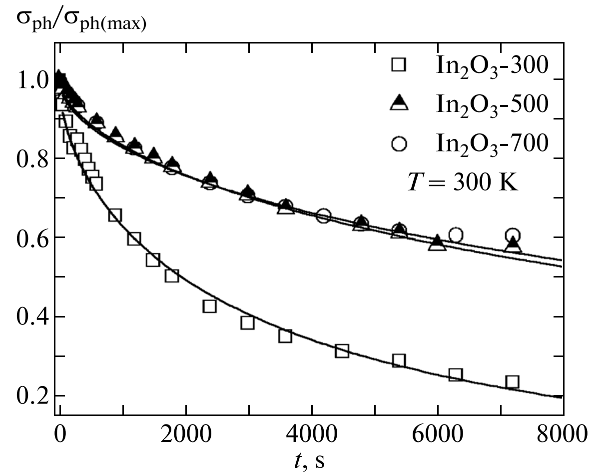

Fig. 3. Kinetics of decay of the photoconductivity of nanocrystalline In_2O_3 in air atmosphere at room temperature.

photoconductivity to dark conductance) decreases and the residual photoconductivity increases (see Fig. 3).

The spectra presented in Fig. 3 may be approximated by an exponent expanded in time:

$$\sigma_{ph} = \sigma_0 \exp[-(t/\tau)^\beta], \quad (2)$$

where σ_0 is the preexponential factor, τ is an efficient time of relaxation of photoconductivity, and β is the exponential factor. The values of parameters τ and β are presented in Table 2. It is seen that the value of parameter τ strongly depends on the sizes of nanocrystals and increases with their increase. In this case, parameter β is not practically changed from sample to sample and is in the vicinity of a value of 0.6.

In order to more substantially study the influence of atmosphere composition on the photoelectric properties of nanostructured indium oxide, the kinetics of photoconductivity decay were measured in vacuum and argon and are presented in Fig. 4 (as an example, the In_2O_3-300 was chosen; for all other samples a similar picture was observed, the differences only being in the values of relaxation times). It is seen that the decay in vacuum and argon proceeds much more slowly than in air. This may prove that oxygen molecules play the determining role in the observed phenomenon of long-time decay of the photoconductivity.

It is known [11] that the placement of an undoped ZnO film into argon atmosphere results in an increase in the conductance due to the increase in both concentration and mobility of charge carriers. The increase in the concentration and mobility of charge carriers is associated, according to [11], with oxygen desorption from the surface of nanocrystals. We suggest that the same process may also take place in our nanocrystalline In_2O_3 samples. Therefore, In_2O_3 films were annealed at 200°C in argon for 2 h (argon volume fraction in the balloon was no less than 99.999%, while the oxygen volume fraction was not more than 0.00015%). Then the films were cooled in argon to room temperature. After this, air was admitted into the cryostat instead of argon and time dependences of photoconductivity decay were measured. As a result of annealing in argon, the conductance of nanocrystalline In_2O_3 increased by two orders, while the activation energy decreased to units of meV.

Thus, we may suggest that a substantial part of oxygen located at the surface of nanocrystals is removed during the annealing in argon. It is seen from time dependences of photoconductivity decay after annealing and illumination in argon (Fig. 5) that the decay of photoconductivity is also described by an expanded exponent ($\tau = 2.6 \times 10^6$ s, $\beta = 0.43$); however, it proceeds much more slowly than without annealing in argon (curve *3* in Fig. 4) ($\tau = 3.6 \times 10^3$ s, $\beta = 0.63$). Thus, we can conclude that desorption–adsorption of oxygen atoms at the surface of nanocrystals plays the dominant role in our samples of nanocrystalline In_2O_3.

However, it is impossible to explain the long-time decay of photoconductivity by only the adsorption of oxygen atoms at the surface of nanocrystals, because in air the decay of photoconductivity should proceed quickly due to the presence of a great number of oxy-

Table 2. Values of photoconductivity relaxation times and of exponential factor In_2O_3

Sample	τ, s	β
In_2O_3-300	3.6×10^3	0.63
In_2O_3-500	2.1×10^4	0.57
In_2O_3-700	1.9×10^4	0.55

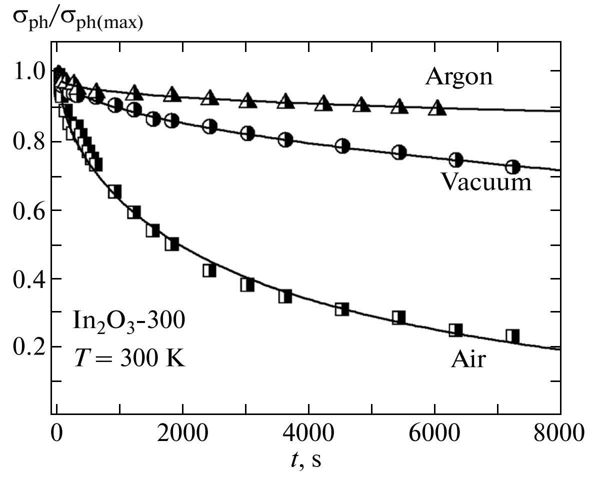

Fig. 4. Kinetics of decay of the photoconductivity in atmosphere of air and argon and in vacuum at room temperature for In_2O_3-300 sample.

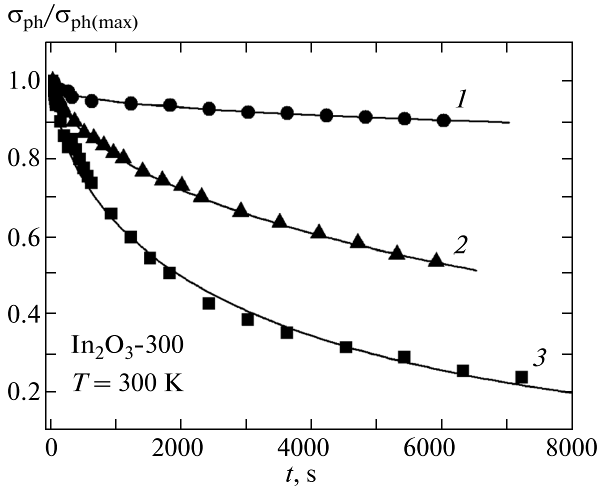

Fig. 5. Decay of photoconductivity for nanocrystalline In_2O_3-300: (*1*) in air, (*2*) in air after annealing in argon, and (*3*) in argon after annealing in argon.

gen atoms in the atmosphere, which is not observed (see Figs. 3–5).

The expanded in time exponential relaxation in disordered structures is usually associated with atomic diffusion depending on time. In particular, the structural relaxation in amorphous hydrogenized silicon is associated with the diffusion of hydrogen atoms depending on time according to a power law [12, 13]. We suggest that in our case, similar to the case of amorphous silicon, the diffusion of oxygen atoms depends on time according to a power law. Just oxygen diffuses at the film surface, jumping over surface states.

As a possible model explaining photoelectric peculiarities of the materials under study, we can propose the following one. It is known that ions of O_2^- are located at the grain boundaries of indium oxide nanocrystals [14]. By the illumination of samples, the generated holes are captured; as a result O_2^- transfers into a neutral state in accordance with $O_2^- + h \rightarrow O_2\uparrow$. In such a neutral state, O_2 is easily desorbed from the surface of nanocrystals. As a result, after the end of illumination, nonequilibrium electrons remain, which increases the concentration of charge carriers. According to Table 1, the sample with the smallest size of nanocrystals has the greatest number of surface states among all other samples, which means that a greater amount of oxygen is desorbed due to illumination by UV light, which in turn will lead to a greater increase in the conductance as a result of illumination when compared to other samples of nanocrystalline indium oxide.

Since after diode disabling a reverse process of oxygen adsorption (in air) takes place, the conductance of samples starts dropping. It is clear that, in the case of vacuum and argon, the residual photoconductivity should distinctly increase, because a reverse process of oxygen adsorption at the surface of nanocrystals will not occur (the oxygen released from nanocrystals will be pumped out).

It is possible to write for small deviations of the electron concentration from equilibrium:

$$\frac{d\Delta n}{dt} = -v(t)\Delta n, \qquad (3)$$

where $v(t)$ is the rate of achieving an equilibrium state.

According to the model used for amorphous silicon, the rate $v(t)$ should be proportional to the rate of oxygen displacement D/a^2, where a is the length of a jump and D is the coefficient of oxygen diffusion.

The results of studies of [13] show that

$$D = D_0(\omega_0 t)^{-\alpha},$$

where ω_0 is the frequency of a jump while α is the dispersion parameter.

Then, for the rate of achieving an equilibrium state, we can write

$$v(t) = \frac{D_0}{a^2}(\omega_0 t)^{-\alpha}. \qquad (4)$$

By integrating Eq. (3) under the condition of (4), we obtain

$$\Delta n = n_0 \exp[-(t/\tau)^{\beta}],$$

where $\beta = 1 - \alpha$.

By taking into account that

$$\sigma_{ph} = e\Delta n \mu_e,$$

where μ_e is the mobility of electrons, we obtain

$$\sigma_{ph} = \sigma_0 \exp[-(t/\tau)^{\beta}],$$

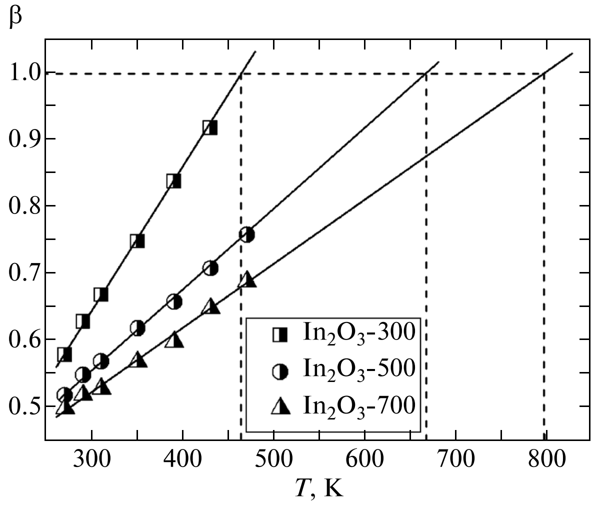

Fig. 6. Temperature dependence of the exponential factor for nanocrystalline In_2O_3 samples.

Thus, the exponential decay of the photoconductivity expanded in time follows immediately from the dispersion mechanism of oxygen diffusion.

By analogy of the dispersion transport of charged particles, we suppose that the dispersion diffusion of oxygen atoms is the result of an energy distribution of localized states at which oxygen moves. If the localized states strongly differ in energies, then the penetration of oxygen into the film will proceed more slowly. Furthermore, if the dispersion of the coefficient of diffusion D is the result of an exponential energy distribution of the localized states $\exp(-E/k_BT_0)$, where k_BT_0 is the distribution width, then the theory [14] predicts

$$\beta = 1 - \alpha = T/T_0.$$

Figure 6 shows the temperature dependences of the exponential factor β for nanocrystalline In_2O_3 films. It can be seen from the dependences presented that $T_0 \approx$ 465 K for In_2O_3-300, $T_0 \approx 670$ K for In_2O_3-500, and $T_0 \approx 800$ K for In_2O_3-700. It is seen that the differences in k_BT_0 for all three samples cannot explain such a great difference in the rates of the photoconductivity decay for samples with different sizes of nanocrystals. Therefore, we assume that a decrease in the residual photoconductivity with a decrease in the sizes of nanocrystals may be associated with the differences in the values of efficient time of relaxation of the photoconductivity τ.

CONCLUSIONS

Our investigations allowed us to detect an increase in the conductance of indium oxide by several orders by enabling a UV-diode for 10 s and a residual photoconductivity after light disabling. In this case, when the size of nanocrystals increases, the value of the photoconductivity decreases, which is explained by a decrease in the desorbed oxygen atoms as a result of UV-illumination by a decrease in the area of specific surface of the samples. We have shown that the long-time decay of the photoconductivity is described by the law of an expanded exponent and have explained it by the diffusion of oxygen associated with the energy distribution of localized states at which oxygen moves. A direct correlation between the structural and electron relaxations in nanocrystalline indium oxide is found. We think that the proposed model may be applied for many disordered systems.

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REFERENCES

1. M. N. Martyshov, E. A. Forsh, A. V. Marikutsa, et al., J. Nanoelectron. Optoelectron. **6**, 452 (2011).
2. E. A. Forsh, A. V. Marikutsa, M. N. Martyshov, et al., Nanotech. Russ. **7** (3–4), 164 (2012).
3. H. L. Hartnagel, A. L. Dawar, A. K. Jain, and C. Jagadish, *Semiconducting Transparent Thin Films* (Institute of Physics, Bristol, 1995).
4. A. Dixit, R. P. Panguluri, C. Sudakar, et al., Appl. Phys. Lett. **94**, 252105-1 (2009).
5. T. Wagner, C.-D. Kohl, S. Morandi, et al., Chem. Eur. J. **18**, 8216 (2012).
6. B. Pashmakov, B. Claflin, and B. Fritzsche, Solid State Commun. **86**, 619 (1993).
7. V. Brinzaria, M. Ivanova, B. K. Chob, M. Kameic, and G. Korotcenkov, Sensors Actuators B: Chem. **148**, 427 (2010).
8. D. Zhang, C. Li, S. Han, et al., Appl. Phys. A **76**, 1–4 (2003).
9. E. A. Forsh, A. V. Marikutsa, M. N. Martyshov, et al., Zh. Eksp. Teor. Fiz. **138**, 738 (2010).
10. S. Brunauer, *The Adsorption of Gases and Vapors* (Science, 2008).
11. H. Akazawa, Appl. Phys. Express **2**, 081601 (2009).
12. J. Kakalios, R. A. Street, and W. Jackson, Phys. Rev. Lett. **59**, 1037 (1987).
13. H. Scher and E. W. Montroll, Phys. Rev. B **12**, 2455 (1975).
14. N. Barsan and U. Weimar, J. Electroceram. **7**, 143 (2001).

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