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Fundamental and applied aspects of physical characteristics of polycrystalline samples of oxide semiconductor $(In_2O_3)_{1-x} : (SrO)_x$

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The electrical and structural characteristics of polycrystalline samples of indium oxide with varying levels of strontium doping have been studied. These characteristics allow the formation of unusual sensory properties of the oxide functional material, which are manifested in a broadband photoconductivity effect and increased sensitivity to the effects of humidity and oxidizing gases. It has been established that the maximum photoconductivity effect is realized in the high-resistance state of the samples, which is achieved by selecting a coordinated content in the material of impurity acceptor states and intrinsic electrically active defects in the form of oxygen vacancies. It is shown that the photosensitivity of the samples is manifested due to the formation of a spatial relief of the conduction band, which even at a high level of doping ($x = 0.1$) can be suppressed without changing the cationic composition of the sample by significantly increasing the concentration of oxygen vacancies within the framework of the sample heat treatment procedure at a relatively low temperature $T = 300-400^\circ$C.

Keywords: oxide semiconductors, doping, donor and acceptor states of defects, photoconductivity, oxidizing gases.

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1. Introduction

Strontium-doped indium oxide is a very promising model material with unique physical properties. Pure indium oxide is a wide-band semiconductor. Its band gap is estimated at 2.7−3.75 eV based on optical and calculated data [1]. However, owing to the electrical activity of intrinsic defects, polycrystalline samples are characterized by a relatively high conductivity at room temperature. The minimum concentration of free carriers is estimated at $10^{-17}\,\mathrm{cm}^{-3}$ [2,3].

The concentration of conduction electrons may be increased significantly by doping indium oxide with a group IV element (tin, Sn). Film samples of this chemical compound (ITO) are used widely to establish electrical connections in solar batteries, monitors, and various optoelectronic devices, since they are characterized by high electrical conductivity and optical transparency [4,5]. A considerable amount of research attention is paid presently to the development of process technology and the study of thin-film and multilayer heterostructures and new materials based on doped indium oxides for application in, e. g., active microelectronic components [6–11].

When indium oxide is doped with a group II element (strontium), the effect is opposite: acceptor states form, and conductivity is reduced. Since *p*-type conductivity in indium oxide is not observed in practice, the resistance of samples increases monotonically by several orders of magnitude as the strontium doping level increases from zero to $x = 0.1$ [12]. A highly resistive state of samples is established this way. It, in turn, may be disrupted by increasing the concentration of intrinsic defects in the form of oxygen vacancies, which act as shallow donors. Technologically, the oxygen content is adjusted in the course of heat treatment of a sample in an oxygen-containing gaseous atmosphere (e. g., in air or in low vacuum at temperature $T = 300-400^\circ$C). Let us note another intriguing fact. With sufficiently extensive heat treatment in vacuum, the concentration of oxygen in a sample decreases, and a gradual transition from the characteristics of a compensated semiconductor to those a heavily doped one with high conductivity, which has no noticeable temperature dependence, is observed [12]. This virtually corresponds to the condition of a degenerate electron gas, where Fermi energy E_F is significantly higher than kT. Of practical use is the fact that the topological transition between the heavily doped and heavily compensated semiconductor states occurs without alteration of the cationic composition.

As was demonstrated earlier [3], the reduction in conductivity due to strontium doping enhances significantly (by more than an order of magnitude) the sensitivity of conductivity of polycrystalline $(In_2O_3)_{0.9} : (SrO)_{0.1}$ samples to the effects of oxidizing gases and humidity. One of the reasons for this is that doping reduces the initial conductivity, which then sets the background for its variation. In addition, if doping is performed by substituting a certain fraction of trivalent indium atoms with divalent strontium, relatively weakly bound oxygen atoms emerge at least on the surface of crystallites, which lower the energy cost of atomic exchange of the material with the external gas environment.

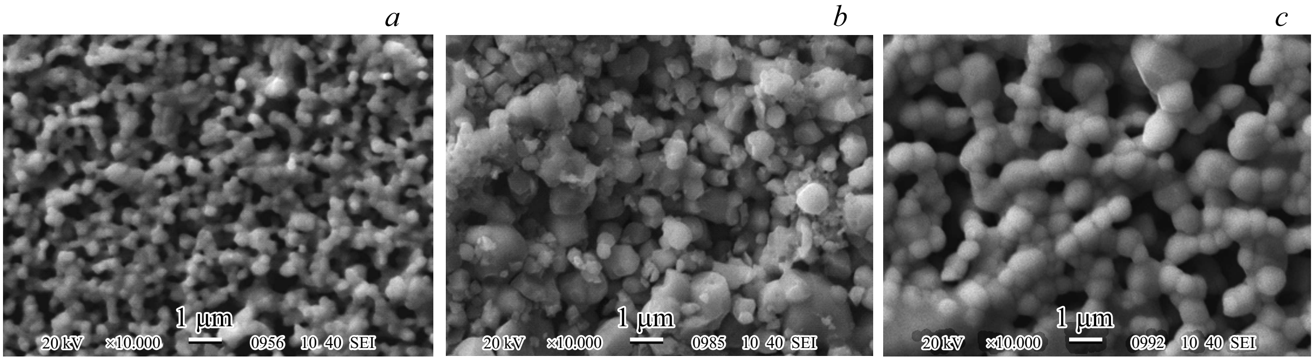

Figure 1. SEM images of the microstructure of polycrystalline indium oxide samples with different weight content of SrO,%: *a* — 0, *b* — 8, *c* — 10.

The effect of doping of indium oxide with foreign atoms is largely expected and qualitatively understandable within the traditional tight-binding approach. In quantitative terms, the process of formation of the compensated state is less well understood, since it requires a very high level of doping ($x > 0.1$). The reason may lie in the oxide nature and the defect crystal structure of polycrystalline samples that depends on the technology of their fabrication. In the present study, we discuss in detail the specifics of doping of samples using the example of the $(In_2O_3)_{1-x} : (SrO)_x$ photoconductivity effect, which is manifested most clearly in the highly resistive state of the material [13].

2. Method of fabrication, microstructure, and electrical characteristics of $(In_2O_3)_{1-x} : (SrO)_x$ samples

Traditional ceramic technology was used to fabricate the samples. In_2O_3 and $SrCO_3$ powders were mixed in the required weight ratio in distilled water and compacted into pellets with a thickness of 3 mm and a diameter of 10 mm under a pressure of 100 MPa. The samples were then subjected to heat treatment at a temperature of $T = 1150°C$ in air for 10 h. The microstructure of the obtained samples is shown in Figure 1.

It can be seen from Figure 1 that the samples are characterized by a granular crystalline microstructure and significant porosity. Figure 2 presents the dependence of the electrical conductivity of these samples on the degree of strontium doping.

The variation range is ~ 7 orders of magnitude. The dependence is nonuniform. One may distinguish three sections with different rates of conductivity variation. Within the initial section, the conductivity changes by an order of magnitude as the weight content of SrO increases from zero to 1%. An order-of-magnitude change in conductivity within the second (flatter) section corresponds to an increase in SrO percentage from 2 to 8%. As the SrO content increases further from 8 to 12% within the third section, the conductivity drops sharply again (approximately by 4 orders of magnitude). One of the reasons behind the nonuniform dependence of conductivity on the weight content of SrO is the formation of an additional material phase in the samples. As was demonstrated earlier, an additional $SrIn_2O_4$ phase, which is a chemically stable dielectric with a spinel structure, forms in the used fabrication process if indium oxide contains $> 4\%$ SrO. This phase becomes more prominent as the SrO content increases [3]. It should be noted that the number of strontium atoms needed to form the stoichiometric composition ($SrIn_2O_4$) is two times lower than the number of indium atoms. The used process of fabrication from a mixture of powders is exactly the one that allows for the formation of relatively large (microscopic) inclusions of the second phase. The macroscopic properties of samples are expected in this case to be affected by a random potential induced by structural disorder. One manifestation of such an influence is the fact that the dependence of conductivity on the weight content

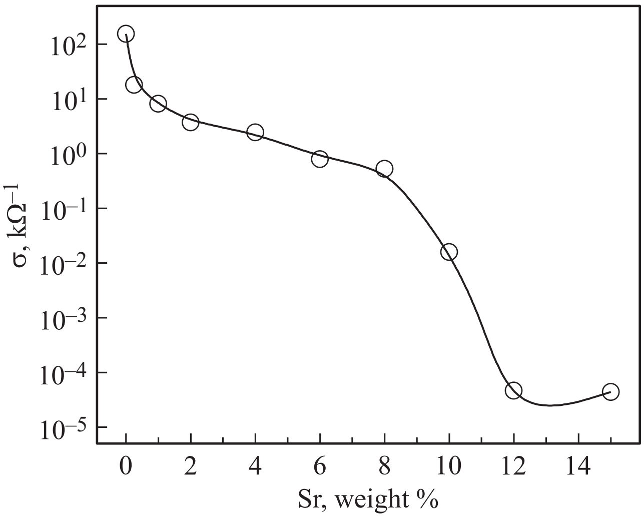

Figure 2. Dependence of the electrical conductivity of polycrystalline indium oxide samples on the degree of doping (weight content of SrO in the material).

of strontium is non-monotonic within the SrO percentage range of 12–15%.

3. Photosensitivity of $(In_2O_3)_{1-x}:(SrO)_x$ samples (experiment and discussion)

Figure 3 shows the dependence of effect magnitude $\Delta\sigma/\sigma_0 = (\sigma_{\text{light}}-\sigma_{\text{dark}})/\sigma_{\text{dark}}$, where σ_{light} and σ_{dark} are the sample conductivities under illumination and without it. A low-power three-color RGB LED was used to illuminate the sample surface. The energy of red, green, and blue light quanta is estimated at 1.8, 2.4, and 2.7 eV, respectively.

Owing to the spatial heterogeneity of the highly resistive state, the photoconductivity of samples was examined by the two-probe method in the set voltage mode. Contact pads with a relatively large area ($\sim 4\,\text{mm}^2$) were formed along the edges of the irradiated surface of the samples using silver conductive adhesive (Electrolube). To negate the influence of solvent vapors on the measured values, the samples with contact pads applied to them were subjected to heat treatment at a temperature of 300°C for 20 min in vacuum and in air. The photosensitivity measurements were performed at room temperature.

It follows from Figure 3 that the conductivity response to irradiation is relatively weak at a low doping level (with the sample material containing $< 8\%$ of SrO). The photosensitivity reaches its maximum as the so-called highly resistive state is established, which is generally consistent with the considered physical mechanism.

Within the initial section, doping proceeds via partial substitution of indium atoms with strontium without alteration of the crystal structure type. Strontium atoms form deep acceptor states in this case. The inset in Figure 3 shows a relatively small photoconductivity peak at $x = 0.05$, which is less pronounced under red and green illumination, but becomes prominent when the sample is irradiated with blue light. Therefore, the photoconductivity peak may be regarded as evidence of the presence of deep (up to 2.7 eV) Sr acceptor levels and, at the same time, a random spatial potential relief induced by defects in the crystal structure.

At an SrO weight content of 8–12% in samples, the concentration of conduction electrons decreases strongly due to their localization both at deep acceptor levels and in potential relief wells. In the parlance of band theory, the Fermi energy of electrons shifts under these conditions below the percolation level [14]. Similar conditions have been modeled earlier in classical semiconductors by compensating precisely the numbers of donor and acceptor impurities (see, e. g., [15]). A significant photoconductivity effect was then observed in the compensated semiconductor.

In the present case, the pattern is similar, although the magnitude of potential relief is much greater. The response of the sample conductivity to irradiation is maximized at an Sr concentration of approximately 12%. It can be seen from Figure 3 that the amplitude of this response to irradiation with blue light with a higher quantum energy grows faster than the corresponding amplitudes for green and red illumination; when the amount of Sr reaches 15%, the response amplitude decreases, despite a slight increase in the „dark“ resistance of the sample, even under irradiation with blue light. It may be assumed that the ultimate reason for such behavior lies in an increase in the number of structural defects of the material. It is impractical to raise the degree of doping further. At the same time, lowering the Fermi level at a lower doping level (e. g., at $x = 0.1$) via heat treatment of the sample in air for the purpose of reducing the concentration of shallow donors is a viable way to reduce the material conductivity and enhance significantly the magnitude of the photoeffect [13].

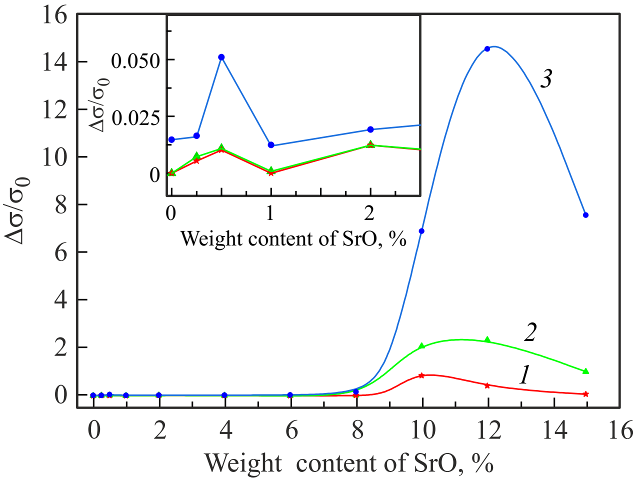

Figure 3. Photosensitivity of the conductivity of samples to irradiation with red (*1*), green (*2*), and blue (*3*) light as a function of the weight content of SrO.

4. Conclusion

We note in conclusion that if the granular structure of polycrystalline $(In_2O_3)_{1-x}:(SrO)_x$ samples is disregarded, their macroscopic electrical characteristics are formally characterized quite accurately within the classical continuous medium approaches. However, a physical model taking into account only the effects of oxidation at the boundaries of granules [16,17] has been used earlier to characterize nonlinear current–voltage characteristics in this material, and the formation of nanothick heterojunctions has also been discussed [18]. Apparently, several different versions of this material may be obtained by varying the size of initial powders and the sintering temperature.

On the practical side, it is worth noting that the photosensitivity of the samples in the visible spectral range is quite high and broadband. Since the process of production of the examined material is simple, polycrystalline samples of indium oxide with 10–12% of SrO may be used to construct photoresistors for monitoring, e. g., the intensity of illumination of objects. As for more complex and frequency-selective optoelectronic instruments, the considered physical mechanism may be used to manufacture devices based on thin films and purpose-made micro- and nanosized heterostructures.

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Conflict of interest

The authors declare that they have no conflict of interest.

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