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Influence of the Thermal Conditions of Fabrication and Treatment on the Optical Properties of In_2O_3 Films

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Abstract—In_2O_3 films on Al_2O_3 (012) substrates are fabricated by *dc* magnetron sputtering at various temperatures (20–600°C). The effect of annealing and the substrate temperature on the film properties are studied by the ellipsometric method and the optical transmission method. Refractive-index profiles are constructed and band gaps for direct and indirect transitions are found. It is established that annealing leads to densification of the film material and unifies the refractive index. Annealing also decreases and unifies the energies of band-to-band transitions, which can be explained by lowering the influence of barriers in annealed films. However, the band gap for direct transitions varies greater than for indirect transitions. This fact can be associated with the mechanism of indirect transitions, notably, the participation of phonons facilitates interband transitions even if they are hindered by extra barriers caused by grain boundaries. The latter can be indirect evidence of the actuality of indirect transitions in indium oxide.

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1. INTRODUCTION

The semiconductor In_2O_3 is a rather well-known and well-studied material. Nevertheless, the interest of researchers in films of this material has not ebbed, which is due to a host of unique properties. For example, being optically transparent, In_2O_3 films possess a high electrical conductivity, which is very sensitive to the composition of the surrounding medium. Herewith, the variations in the electrical conductivity are low-inertia depending on the surrounding-medium composition and are reversible. In_2O_3 films have already found a wide application as transparent contacts and gas sensors. The doping of In_2O_3 with various impurities makes it possible to vary the film properties such as the electrical conductivity, sensitivity to various gases, etc., within broad limits.

2. EXPERIMENTAL

We studied the optical properties of In_2O_3 films fabricated by *dc* magnetron sputtering [1] on Al_2O_3 (012) substrates. Deposition in an argon–oxygen atmosphere was performed at substrates temperatures of 600, 300, and 20°C for 1 h; the working current was 50 mA, and the voltage was 300 V. The optical properties of the films were studied by spectrophotometry methods in the wavelength range from 190 to 1100 nm (photon energies of 1–6 eV) and reflective multiangular ellipsometry at the wavelength of a helium–neon laser (632.8 nm). Ellipsometric measurements were performed in order to study the film structure, and spectrophotometric measurements were performed to establish the character of the band-to-band transitions and band-gap width from analysis of the fundamental absorption edge in optical transmission spectra.

2.1. Ellipsometric Measurements

We interpreted the results of measurements of the ellipsometric angles Ψ and Δ, which depend on the probing radiation wavelength λ, incidence angle φ, thickness *d*, and refractive index *n* of the transparent film, as well as the refractive index of the transparent substrate n_0, by the minimization method according to our previous procedure of comprehensive studies of thin-film coatings based on the joint use of the data of ellipsometric measurements and magnitude of optical transmission [2]. The target function had the form

$$G = M\frac{(T^{(e)} - T^{(c)})^2}{(T^{(e)})^2} + \sum_{i=1}^{M}\left(\frac{(\Psi_i^{(e)} - \Psi_i^{(c)})^2}{(\Psi_i^{(e)})^2} + \frac{(\Delta_i^{(e)} - \Delta_i^{(c)})^2}{(\Delta_i^{(e)})^2}\right).$$

The indices (e) and (c) correspond to the experimental and calculated values of Ψ and Δ, *T* is the optical transmission coefficient at a wavelength of 633 nm, and *M* is the number of measurements at various inci-

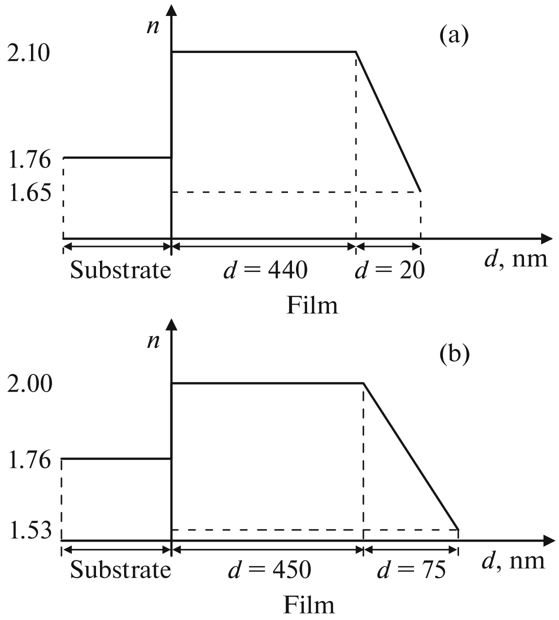

Fig. 1. Refractive-index profiles of the films deposited onto substrates with a temperature of (a) 600°C and (b) 300°C.

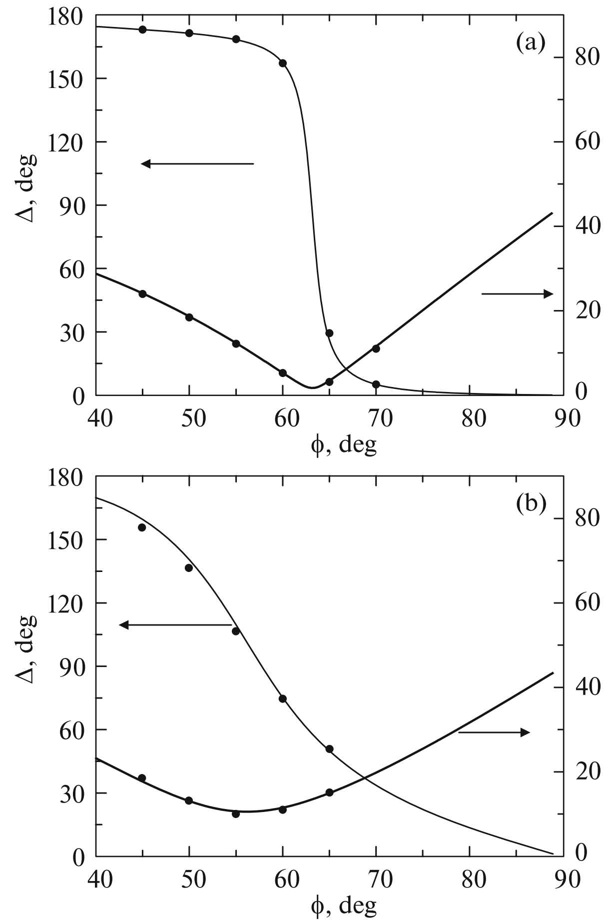

Fig. 2. Calculated (solid lines) and experimental (symbols) dependences of the ellipsometric angles Δ and Ψ on the incidence angle for films deposited onto substrates with a temperature of (a) 600°C and (b) 300°C.

dence angles of probing radiation. Transition layers on the film surface were modeled as assemblies of physically infinitely thin layers of a fixed thickness with a refractive index varying according to specified linear laws [3].

We did not take into account the birefringence of sapphire because it did not affect the result due to special sample orientation during the measurement. The studied films are transparent to light with a wavelength of 633 nm; therefore, it was sufficient to minimize the target function in coordinates (n, d).

The application of this procedure to In_2O_3 films on Al_2O_3 substrates allowed us to establish that the films deposited onto substrates with a temperature of 300°C and higher are more uniform in thickness but have a damaged surface layer. Herewith, the higher the temperature of the substrate onto which the films were deposited, the smaller the thicknesses of the film and damaged layer. On the contrary, the refractive index increases with an increase in the substrate temperature. Our results for "hot" (300 and 600°C) substrates are illustrated by refractive-index profiles with indication of the corresponding thicknesses (Fig. 1). Figure 2 shows the experimental and calculated dependences of the ellipsometric angles Ψ and Δ on the incidence angle of elliptically polarized light. They show good agreement of the experimental and calculated results. The observed dependences in variations in the optical parameters of the In_2O_3 films depending on the substrate temperature are rather regular, i.e., the higher the substrate temperature during sputtering, the denser and less imperfect the film material.

Figure 3 shows the results of processing the data of ellipsometric measurement of the In_2O_3 film deposited on a "cold" (20°C) Al_2O_3 substrate. It is seen from Fig. 3 that the layer refractive index of the material under study itself initially increases from 1.9 near the substrate–film boundary and then linearly decreases in the damaged layer from 2 to 1.8. Herewith, the film material is "loose", and its total thickness, similarly to that of the damaged layer, is larger than for the films on "hot" substrates. Our results in general agree with the above-mentioned notions. As for the increase in the refractive index in the base film material, it is apparently associated with an increase in the surface temperature of the growing film during its deposition.

Annealing unifies the properties of the studied films, the distribution of the refractive index over the thickness improves, and the thickness of the film and the damaged layer decreases, i.e., the material becomes denser. The thicknesses of all annealed films approach 400 nm, the refractive indices approach 2, and the damaged layer thickness approaches 21 nm.

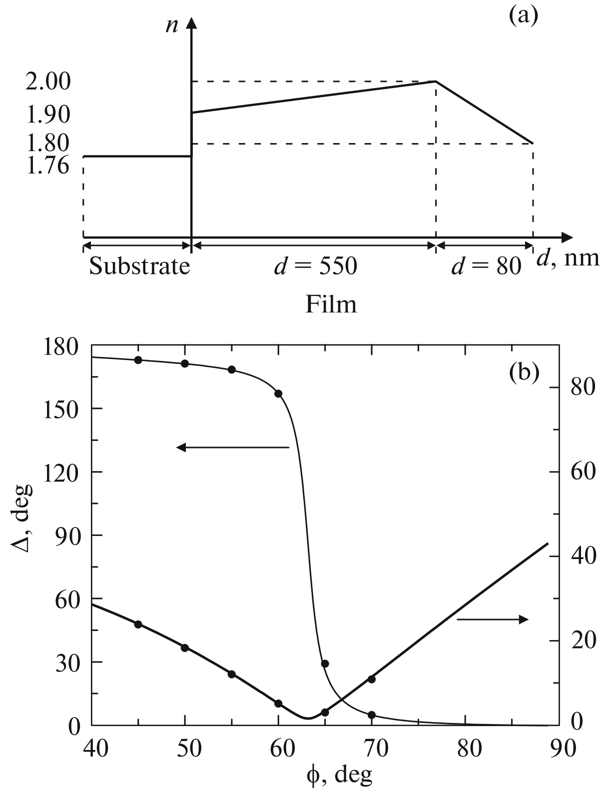

Fig. 3. Results of ellipsometric measurements of the films deposited onto substrates with a temperature of 20°C: (a) refractive-index profile and (b) calculated (solid lines) and experimental (symbols) dependences of the ellipsometric angles Δ and Ψ on the incidence angle φ.

2.2. Study of the Fundamental Absorption Edge

The study of the fundamental absorption edge depending on the substrate temperature during the deposition of In_2O_3 films is of special interest. This is associated with the discussion relative to the character of the interband transitions in these materials [4, 5].

The observed absorption spectra presented in [6, 7] evidence the presence of transitions with energy E_g^{indir} = 2.62–2.69 eV interpreted as indirect, band-to-band transitions, and direct transitions with energy E_g^{Γ} = 3.56–3.75 eV. However, the authors of [4, 5], based on calculations of the electronic structure of defect-free indium oxide, came to the conclusion that the difference in the energies of direct and indirect transitions doe not exceed 50 meV, while the observed indirect transitions are associated with imperfections of the material structure. The authors refer to the boundary effects in indium oxides and associated depleted layers (with a characteristic activation energy of 2.2–3.5 eV relative to the valence-band top) as experimental confirmation [5, 8, 9]. In connection with this fact, experiments directed at studying the fundamental absorption edge of In_2O_3 films depending on the degree of their quality seem to be important.

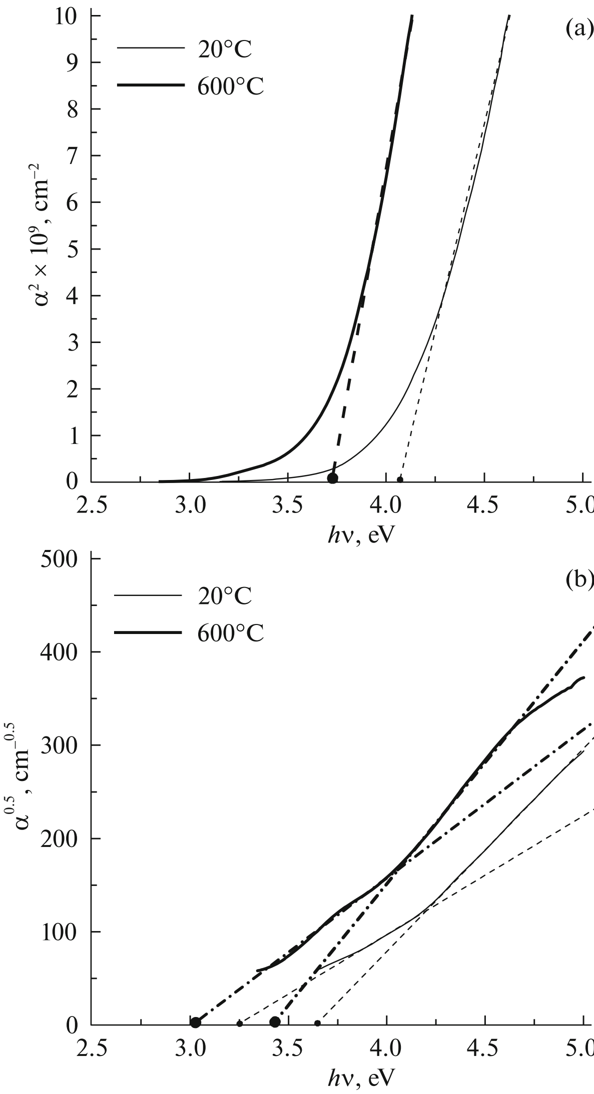

Fig. 4. Dependences of the absorptance (a) α^2 and (b) $\alpha^{1/2}$ on the photon energy for films deposited on substrates with a temperature of 20 and 600°C before annealing.

We estimated the band-gap width for direct E_g^{Γ} and indirect E_g^{indir} band-to-band transitions from the fundamental absorption edge. Figures 4 and 5 show the corresponding dependences of the absorptance α^2 and $\alpha^{0.5}$ on the photon energy calculated from the results of measurements of optical transmission and ellipsometric measurements. The energies of transitions are presented in Table 1.

It is seen from Figs. 4 and 5 and from the tabulated data that the higher the substrate temperature during film deposition, the narrower the band gap. These results are quite regular because the degree of imperfection of the film deposited onto a "hot" substrate is lower. Annealing also unifies the film properties with respect to the band-gap width. The difference in the energies of direct and indirect transitions $\Delta E = E_g^{\Gamma}$ –

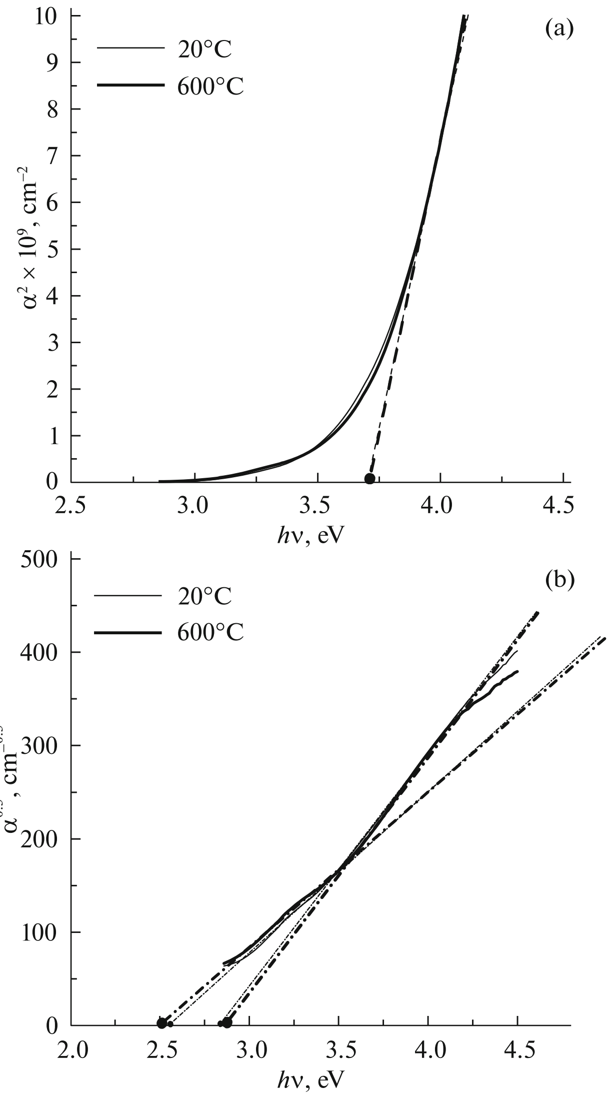

Fig. 5. Dependences of the absorptance (a) α^2 and (b) $\alpha^{1/2}$ on the photon energy for films deposited on substrates with a temperature of 20 and 600°C after annealing.

E_g^{indir} for all films is about 1 eV, which agrees with the data [10, 11] excluding unannealed films on a cold substrate. Annealing of the latter leads to lowering ΔE, and the band-gap width for direct transitions varies more greatly compared with indirect transitions, i.e., annealing preferentially affects the energy of direct transitions. This fact can be associated with the mechanism of indirect transitions because the participation of phonons facilitates interband transitions even if they are hindered by the presence of additional barriers caused by grain boundaries.

Table 1. Direct and indirect transitions in In_2O_3 films

Substrate temperature, °C	Before annealing			After annealing		
	E_g^{Γ}, eV	E_g^{indir}, eV	ΔE, eV	E_g^{Γ}, eV	E_g^{indir}, eV	ΔE, eV
20	4.07	2.94	1.13	3.71	2.69	1.02
600	3.72	2.72	1.00	3.71	2.67	1.04

3. CONCLUSIONS

It is established by the results of ellipsometric measurements that annealing leads to unification of the properties of all studied films as well as to densification of their material and improvement in its homogeneity. It should be noted that annealing has the strongest forming effect on the film deposited onto a "cold" substrate. The influence of annealing on two other films is insignificant.

The evident results of annealing are the elimination of structural defects, the rise of grain sizes, and, consequently, densification of the film material. Thus, we can explain a decrease in the energy of interband transitions by a weakening of the influence of barriers in annealed films. The smaller influence of annealing on the energies of indirect transitions is caused by the fact that phonons participating in indirect transitions have various energies and wave vectors. The latter is possibly indirect evidence of the occurrence of indirect transitions in In_2O_3 and points to the necessity of further studies directed to the establishment of electron band-to-band transitions in this compound.

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