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Density of states and interband light absorption in Y_2O_3 and Sc_2O_3 thin films

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The long-wavelength edge of the fundamental absorption band of thin Y_2O_3 and Sc_2O_3 films obtained by the method of discrete evaporation in vacuum is investigated. On the basis of its temperature dependence, the excitons - phonon interaction is investigated, which made it possible to interpret the absorption edge as the absorption of self-trapped excitons. To analyze the experimental results, we used a model of a heavily doped or defective semiconductor in the quasi-classical approximation. The use of this model made it possible to estimate the radius of the ground electronic state a and the screening radius r_s and the concentration of free charge carriers N in the films under study.

Key words: yttrium oxide, scandium oxide, thin film, fundamental absorption edge.

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Introduction

Due to their optical and operational properties, Y_2O_3 and Sc_2O_3 thin films are very promising for antireflection of optical parts, the manufacture of optical filters and other multilayer systems [1-3]. The Y and Sc oxides have a number of important common properties, which are based on their crystallographic identity [4], as well as the similarity of the outer unfilled electron shells ($3d^14s^1$ in Sc and $4d^15s^1$ in Y). Although the optical properties of these films were studied earlier [5-7], their properties in the region of the fundamental absorption edge and the features of the interaction of excitons with crystal lattice vibrations in these films have been studied in detail. In this regard, in this work, we investigate the long-wavelength edge of the fundamental absorption band of thin Y_2O_3 and Sc_2O_3 films and analyze it using the model of a heavily doped or defective semiconductor in the semiclassical approximation.

I. Experimental technique

Thin films of Y_2O_3 and Sc_2O_3 0.3 -1.0 μm thick on fused silica ($\nu\text{-SiO}_2$) substrates were obtained by discrete

evaporation in vacuum (10^{-6} Torr) followed by annealing in air at 1000°C . Oxides Y_2O_3 of the ИТО-И brand and Sc_2O_3 of the E brand were used as the initial raw material. X-ray diffraction studies revealed the presence of a polycrystalline structure of the films with a preferred orientation in the plane (222), (400), and (440). Typical diffraction patterns for Y_2O_3 films are presented by us in [8]. All diffraction maxima are identified in accordance with the rules for selecting the space group T_h^7 , which indicates the cubic structure of the films obtained.

The absorption spectra were measured on a photometric setup based on an МДР-12 monochromator and recorded with an ФЭУ-18А photomultiplier, the signal from which was fed through a resonant amplifier and an analog-to-digital interface converter to an IBM/PC computer for spectrum recording. Films for measuring optical absorption were placed in a cryostat, where the temperature varied within 85-350 K. The results obtained were normalized to the spectral sensitivity of the setup. To take into account the reflection and scattering of light, the measurements were carried out for films of various thicknesses. The scanning of wavelengths by the monochromator was carried out using a stepper motor, which was controlled by a computer through a control unit.

II. Results and discussion

Our spectral studies show that in the regions $h\nu < 5.60$ eV for thin Y₂O₃ films and $h\nu < 5.80$ eV for thin Sc₂O₃ films the spectral behavior of the absorption coefficient α is described by the Urbach empirical rule [9]. Analytically, Urbach's rule is written by the expression [10]:

$$\alpha = \alpha_0 \exp\left[-\frac{\sigma}{kT}(h\nu_0 - h\nu)\right], \quad (1)$$

$$\sigma = \sigma_0 \frac{2kT}{h\nu_\phi} \ln \frac{h\nu_\phi}{2kT}, \quad (2)$$

where α_0 , $h\nu_0$ and σ_0 are the approximation parameters, σ is the value characterizing the slope of the dependence $\ln \alpha = f(h\nu)$ for the corresponding temperature, $h\nu_\phi$ - in some cases corresponds to the average energy of phonons that interact with excitons and make the main contribution to the fundamental absorption edge. The strength of the exciton-phonon interaction g is related to the approximation parameter σ_0 by the relation $\sigma_0 = (2/3)g^{-1}$ [10].

Typical absorption spectra of Y₂O₃ and Sc₂O₃ thin films in the temperature range 85-300 K are shown in Fig. 1 and Fig. 2.

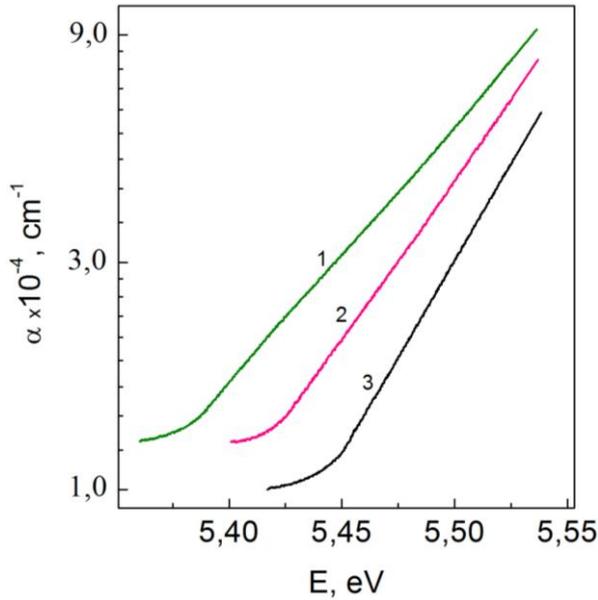


Fig. 1. Edge absorption spectrum of Y₂O₃ thin films: T= 264 (1), 207 (2), and 110 K (3).

It is known that such a shape of the absorption edge arises when there is a noticeable exciton-phonon interaction [10]. The nature and strength of the exciton-phonon interaction determine the nature of the existing exciton states and, consequently, the nature of the physical processes that occur during the formation of excitons.

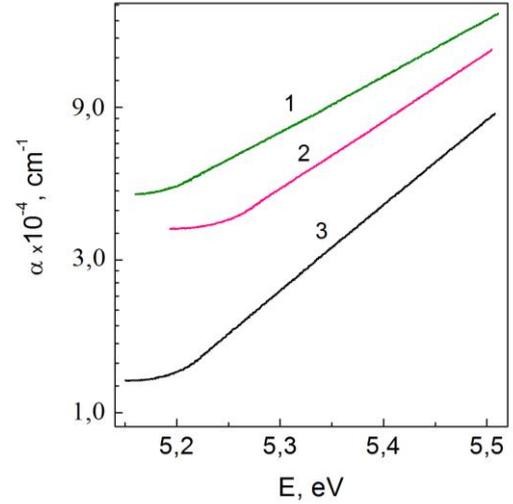


Fig. 2. Edge absorption spectrum of Sc₂O₃ thin films: T= 295 (1), 112 (2) i 85 K (3).

The exponential shape of the fundamental absorption edge also manifests itself in the case of heavy doping or strong defectiveness of the samples. In the general case, the screened Coulomb interaction is considered [11], which arises due to the defectiveness of the crystal structure, including defects and phonons in the discharge. Taking into account that the films under study have a polycrystalline structure, the presence of structural defects should also be taken into account in their analysis. In this case, the absorption edge is approximated by the dependence

$$\alpha = \alpha_0 \exp\left[-\frac{1}{\gamma}(h\nu_0 - h\nu)\right], \quad (3)$$

where γ is a parameter characterizing the disordering of the crystal lattice [12]:

$$\frac{1}{\gamma} = \begin{cases} \sigma/kT, & \alpha \geq \alpha' \\ 1/\gamma, & \alpha < \alpha' \end{cases} \quad (4)$$

In expression (4), the upper expression describes the "phonon" disorder, the lower one describes the "defect" disorder due to structural defects (vacancies, dislocations, impurities).

Our results in the temperature range 85-300 K showed that the spectral behavior of the $\alpha(h\nu)$ dependence remains similar. As can be seen from Fig.1 and Fig.2, the spectral dependences of the absorption coefficient in coordinates $\ln \alpha = f(h\nu)$ for the corresponding films are well described by a linear dependence. The intersection point of the extensions of the obtained straight lines makes it possible to determine the approximation parameters α_0 and $h\nu_0$.

Based on the values of σ determined from the graph $\ln \alpha = f(h\nu)$ for the temperatures under study with (2), $h\nu_\phi$ and σ_0 were determined, which, together with α_0 and $h\nu_0$ for the corresponding films, are given in Table 1. The obtained values of the effective phonon energy $h\nu_\phi$, in accordance with [13], fall on the high-energy boundary of fundamental phonon vibrations caused by the translational motion of YO₆ (or ScO₆) polyhedra and metal ions located between the polyhedra and more weakly bonded to oxygen atoms.

Table 1.

Parameters of the energy spectrum of Y_2O_3 and Sc_2O_3 thin films.

Thin film	$\alpha_0, 10^4 \text{ cm}^{-1}$	$h\nu, \text{ eV}$	$h\nu_{\phi}, \text{ eV}$	σ_0	g	g_{def}
Y_2O_3	1.35	5.58	0.028	0.12	5.56	1.01
Sc_2O_3	2.65	5.70	0.034	0.11	6.06	1.09

Taking into account that, in the theoretical substantiation of Urbach's rule (3), the condition $\sigma_0 < 1$ is accepted as a criterion for self-trapping [10], based on the obtained values of σ_0 for these films, we can speak of the possibility of self-trapping of excitons in thin Y_2O_3 and Sc_2O_3 films. Based on the obtained values of σ_0 , the total constant of the exciton-phonon g and excitons-defect interaction g_{def} were determined, the values of which are also given in Table. 1. The determination of the value of the exciton-phonon interaction g was carried out taking into account that the structural disordering of the crystal lattice of Y_2O_3 and Sc_2O_3 in the temperature range under study is constant. It is known [14] that for semiconductors $g < 1$, for alkali-halide compounds $g \geq 1$. This indicates that the degree of ionicity is dominant in the determination of g as compared to the degree of covalence in Y_2O_3 and Sc_2O_3 .

Based on the theoretical model of a heavily doped or defective semiconductor in the quasi-classical approximation [15], the density of states associated with fluctuations in the concentration of charged anion vacancies decreases exponentially into the energy gap

$$\rho(E) = \frac{m^{*3/2} \Delta^{1/2}}{4\pi^2 \hbar^3} \left(\frac{\Delta}{E} \right)^{3/2} \exp\left(-E^2/\Delta^2\right), \quad (5)$$

where Δ is the root-mean-square potential that determines the smearing of the bands due to the disordered arrangement of vacancies:

$$\Delta = \left(\frac{4\pi N r_s e^4}{\epsilon^2} \right)^{1/2}, \quad (6)$$

where N is the concentration of vacancies, and the screening radius

$$r_s = \frac{a}{2} \left(\frac{\pi}{3} \right)^{1/6} \frac{1}{(Na^3)^{1/6}}, \quad (7)$$

and the radius of the ground state

$$a = \frac{\hbar^2 \epsilon}{m^* e^2}, \quad (8)$$

m^* is the effective mass of charge carriers, ϵ is the dielectric constant of the sample.

The physical meaning of the rms potential Δ is determined by the fact that the rms fluctuation of the number of impurities or defects in the volume r_s^3 is of the order of $(N r_s^3)^{1/2}$, and the potential energy of an electron in the field of such fluctuations is $\Delta \approx (e^2/\epsilon r_s)(N r_s^3)^{1/2}$. As shown in [15], fluctuations of the scale r_s make the main contribution to the rms potential. The ground state energy in the well is above the well bottom by an amount of the order of $E_s = \hbar^2/m r_s^2$.

To find the quantities included in expressions (5) – (8), we use the results of previous studies [16, 17]. In particular, the values of the refractive index n necessary for determining the dielectric constant $\epsilon = n^2$ were determined by extrapolating the dependence $n(h\nu)$ determined for the region of transparency and weak absorption [16] to the studied energy region. The value of the effective mass of free charge carriers is $m^* = 0.388$ in thin Y_2O_3 films and $m^* = 0.438$ in thin Sc_2O_3 films taken by us from [17]. Assuming, according to [18], that the disordering parameter of the crystal lattice is $\gamma \approx \Delta$, we estimate the parameters of the quasi-classical model of the change in the density of states.

Analyzing the results obtained, it should be noted that the Bohr radius a in semiconductors can be quite large. So, according to the results of [15] in $n\text{-InSb}$, the radius is $a \approx 60$ nm, although according to [18] in $\text{fianites } 0.9\text{ZrO}_2\text{-}0.1\text{Y}_2\text{O}_3$ the radius is $a = 0.4$ nm, and according to [19] in thin films of $\beta\text{-Ga}_2\text{O}_3$, depending on heat treatment atmosphere a varies from 0.6 to 0.8 nm. The values we obtained are quite close to the results [18, 19], and values of this order are more likely to be characteristic of oxide compounds. It is characteristic that for thin Y_2O_3 and Sc_2O_3 films the screening radius r_s in the investigated temperature range $r_s > a$, and for Y_2O_3 films this difference is somewhat larger.

Table 2.

Model parameters of a heavily doped or defective semiconductor in the quasi-classical approximation for Y_2O_3 and Sc_2O_3 thin films.

Thin film	T, K	$\Delta, \text{ eV}$	$N, \text{ cm}^{-3}$	$r_s, \text{ nm}$	$a, \text{ nm}$
Y_2O_3	264	3.28×10^{-2}	1.51×10^{18}	1.4	0.9
	207	2.97×10^{-2}	7.59×10^{17}	1.6	
	110	2.65×10^{-2}	5.77×10^{17}	1.7	
Sc_2O_3	295	7.98×10^{-2}	7.44×10^{18}	1.0	0.7
	112	6.21×10^{-2}	4.85×10^{18}	1.0	
	85	5.74×10^{-2}	4.03×10^{18}	1.1	

The results of the rms potential Δ obtained by us are in good agreement with the results of studies of other oxide compounds. In particular, according to [18], in cubic zirconias $\Delta=7.22 \times 10^{-2}$ eV, and according to [19] in thin β -Ga₂O₃ films, the value of Δ varies from 4.78×10^{-2} eV to 23.30×10^{-2} eV. In this case, this value for thin Sc₂O₃ films is more than twice the value of Δ for thin Y₂O₃ films.

Our estimates of the concentration of free charge carriers N indicate that with an increase in temperature, this value increases both in Y₂O₃ films and in Sc₂O₃ films. In this case, this tendency is more pronounced in Y₂O₃ films. It is known [20] that in heavily doped or defective, degenerate semiconductors, the concentration of charge carriers is from 10^{16} to 10^{18} cm⁻³. Concentrations up to 10^{20} cm⁻³ are sometimes observed. The values of N obtained by us indicate that for thin films of Y₂O₃ and Sc₂O₃ there is such a concentration of free charge carriers, which is characteristic of heavily doped or defective degenerate semiconductors, for which we used a quasi-classical approximation.

Conclusions

The study of the temperature dependence of the fundamental absorption edge of thin Y₂O₃ and Sc₂O₃ films showed that the spectral behavior of the absorption coefficient in them is well described by the Urbach empirical rule. The presence of a strong exciton-phonon interaction is established, which leads to the appearance of localized exciton states at the edge of fundamental absorption, the formation of which occurs through the capture of excitons by local deformations of the crystal lattice. To explain the experimental data, we used theoretical concepts based on the model of a heavily

doped or defective semiconductor in the quasi-classical approximation. The use of this model made it possible to estimate the radius of the ground state a , the screening radius r_s , and the concentration of free charge carriers in the films under study. It is shown that, upon going from Y₂O₃ films to Sc₂O₃, the ground state radius a and the screening radius r_s decrease and the concentration of free charge carriers N increases.

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Густина станів та міжзонне поглинання світла в тонких плівках Y_2O_3 і Sc_2O_3

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Досліджено довгохвильовий край смуги фундаментального поглинання тонких плівок Y_2O_3 і Sc_2O_3 , одержаних методом дискретного випаровування у вакуумі. На основі його температурної залежності досліджено екситон-фононну взаємодію, що дало можливість інтерпретувати край поглинання як поглинання автолокалізованих екситонів. Для аналізу експериментальних результатів використано модель сильно легovanого або дефектного напівпровідника у квазикласичному наближенні. Використання даної моделі дозволило оцінити радіус основного електронного стану a , радіус екранування r_s і концентрацію вільних носіїв заряду N у досліджуваних плівках.

Ключові слова: оксид ітрію, оксид скандію, тонка плівка, край фундаментального поглинання.