URBACH'S RULE CRITERIA IN ALUMINA IRRADIATED WITH IONS

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Irradiation of dielectrics with ions is available for aims of the optical, mechanical and other properties modification. The defect localized states effect on alumina optical absorption properties depends on ability of incorporated elements to substitute the lattice cations. The complex energetic spectrum of the defect localized states demands the generalized approaches which characterize the radiation induced disorder in materials as a whole. The Urbach's rule criteria for the absorption spectra of alumina irradiated with the silicon, chromium and titanium ions ($\Phi=10^{17}$ cm^{-2}, E_i=100 keV) were investigated. The induced defect, their clusters and hard solid solution effect on the Urbach's equation parameters was determined. Analysis the reasons of the absorption change was given. Absorption spectra of irradiated alumina were subjected the Urbach's rule as all it criteria were fulfilled. This is stipulated by the static disorder in crystalline lattice induced by substitution defects, intrinsic defects and cluster formation on its base. A common focal point in absorption spectrums situated at 4.4 eV was fixed. This Urbach's focus is determine by the processes of defects clusterization, the energetic characteristics of clusters and depend on ability of the implanted ions to form the hard solid solutions in alumina. A correlation between the interband and exponential absorption parameters indicates to synthesis in Al_2O_3 a new strongly defect material having band gap width near the 4.5 eV and absorption edge stipulated by the defect cluster levels.

Introduction

Irradiation of dielectrics with ions is available for aims of optical and other properties modification. Induced defects and their complexes with implanted atoms are stipulate continuous localized states spectra in the optical band gap (BG) [1-3]. That demands a generalized approaches which characterized the radiation induced disorder in materials as a whole [4, 5]. The principle of static and dynamic disorder components allows to reveal the role of atomic reordering in optical absorption change and to estimate its contributions in a quantitative sense [4-9]. The absorption edge of the most crystalline and noncrystalline materials submit to generalize Urbach's equation [4-10]. Its parameters depend on induced defects (ID) concentrations [5, 6, 10], on stoichiometry [6, 7], on portion of the amorphous or crystalline structures components [9-11], on phase and composition proportion [7, 12, 13]. Absorption spectrums show the fanlike behaviour with temperature change and the variation of static disorder parameter stipulated by the structural nonuniformity [4-10]. Urbach's rule allow to investigate in materials an exciton-phonon interaction with temperature, doping levels and ID parameters changes [5], at the structural and phase transitions [7, 9, 13]. With it assistance may to establish the contribution of doping and ID contents to electronic building changes, to estimate the BG width and to determine the distribution defects localized states (LS) [7-13].

Purpose of this work is investigation the Urbach's rule criteria for absorption spectra of alumina, irradiated with the silicon, chromium and titanium ions having a different ability to substitute the lattice cations, determination the ID effect on Urbach's rule parameters and analysis the reasons of absorption change.

Experimental procedure

Irradiation of single crystals and polycrystalline alumina with ions (fluences $\Phi=10^{17}$ cm^{-2}, E_i=100 keV) was conducted In pulse-frequency regime. Spectral dependency of the absorption coefficient $\alpha(h\nu)$ was approximated by generalize Urbach's rule

$$\alpha(h\nu)=\alpha_{00}\exp[(h\nu-h\nu_0)/E_u], \quad (1)$$

where E_u–Urbach's energy depending from disorder degree (~Φ). The focus parameters α_{00}, $h\nu_0$ do not depend from Φ [4-9]. Values E_u and α_0 were calculated in the energy intervals $\Delta(h\nu)$. where $\ln\alpha \sim h\nu$ according to simplified formula

$$\alpha(h\nu)=\alpha_0\cdot\exp(h\nu/E_u). \quad (2)$$

For testing Urbach's rule criteria dependency $\alpha_0(E_u)$ was calculated using focal parameters according to

$$\alpha_0=\alpha_{00}\exp(-h\nu_0/E_u), \quad (3)$$

Isoabsorption optical gap $E_g^{\alpha'}$ was determined by energy $h\nu$ at $\alpha(h\nu)=\alpha'$ [4, 9, 12]. Values $E_g^{\alpha'}$ and E_u estimated from spectrums $\alpha(h\nu, \Phi)$ at the fixed α' was compared with dependency $E_g^{\alpha'}(E_u)$ calculated at focus parameters according to [9, 12]

$$E_g^{\alpha'} = h\nu_0-\ln(\alpha_{00}/\alpha')\cdot E_u \quad (4).$$

Besides $\alpha(h\nu)$ was approximated by the law

$$\alpha h\nu \sim (h\nu-E_g)^{1/2} \quad (5)$$

for interband direct allowed transitions via optical gap E_g [13]. Dependency $\alpha(h\nu)$ in frame of semiclassical model adjusted for amorphous and strongly defect materials was calculated on the equation

$$\alpha(h\nu)=\alpha_0''\cdot\exp[-(h\nu-E_{g0})^2/(2\cdot\sigma^2)], \quad (6)$$

where α_0'' is determined by materials constants, E_{g0}- average band gap, σ^2 – it dispersion [11].

Result and discussion

Urbach's rule in α-Al_2O_3 at $h\nu \le 6.0$ eV do not fulfil as E_g=8-9 eV [14]. After γ-, electron and neutron irradiations the exponential absorption not exists too. After irradiation with ions the defects (concentration $N>10^{20}$cm^{-3}) and implanted atoms, its space localization in matrix change the electronic building greater [1-3]. BG width is constricted on 3-5 eV. Urbach's rule is fulfills far off absorption edge at the $h\nu \ll E_g$.

As Φ grows E_u enlarges and intervals of LS are shifted from $\Delta(h\nu)$=1.5-3.2 eV to 1.8-3.5 eV (Ti^{n+} ions) and from 1.6-3.2 eV to 2.0-4.1 eV (Cr^{n+}) (fig.1). That is stipulated by intersection of a rectilinear regions where (1, 2) is carry out (fig.1). The convergence region (assignable by rectangle) is a focal point of spectrums $h\nu_0$=4.40±0.08 eV (α_{00}=8500±440 cm^{-1}). Fan-liked character of $\alpha(h\nu, \Phi)$ is stipulated by the ion Induced by quasidynamic disorder in Al_2O_3. It parameters are determined by ability of ions to form the substitution defects and their clusters. Difference between the replacement degree of Cr^{n+} and Ti^{n+} in lattice cations (0.55 against 0.9 [15]) stipulates difference in ID accumulation kinetic and exponentially distributed LS parameters [1-3, 16]. A common

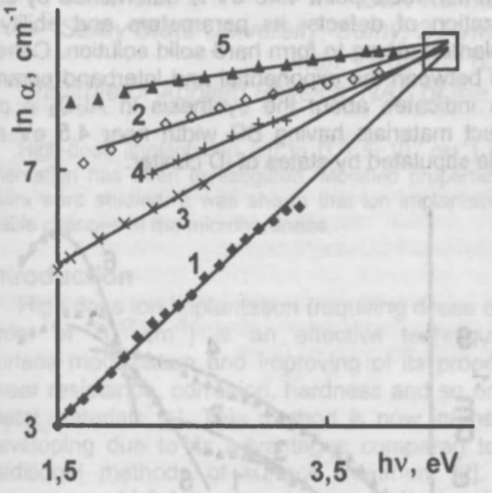

Fig.1. Absorption spectrums of polycor (1-4) and single crystals alumina (5) after irradiation with ions Ti^{n+} (1,2), Si^{n+} (3,4) and Cr^{n+} (5); $\Phi=10^{16}$ (1), $5\cdot10^{16}$ (3), $7\cdot10^{16}$ (4), 10^{17} cm^{-2} (2, 5).

focus in α(hν) is connected with effectiveness ID clusterization, cooperation LS, induced clusters, and their recharging [2, 16]. After Cr^{n+} implantation recharging $Cr_{Al}^{3,4+}\to Cr_{Al}^{2,3+}$ (ε=1.5-3.1 eV) and $Cr_{Al}^{3+}\to Cr_{Al}^{2+}$ (ε=4.0-5.0 eV) is obtained [2]. Low values E_u at Ti^{n+} implantation are stipulate the input into distribution from Ti_{Al}^{3+} (ε=2.2-2.6 eV [17, 18]) and interstitials $(Ti)_i^{2+}$ (ε=3.0-3.8 eV [17]). Influence clusters $Ti_{Al}^{3+}...Ti_{Al}^{3+}$ (ε=1.5-1.7, 2.2-2.4 eV [16]) and complexes with anion vacancies and $Ti^{3+(4+)}$ (ε=2.3-2.6 eV [16]) is less importance. Recharging $Ti_{Al}^{3+}\to Ti_{Al}^{4+}$ into clusters $Ti_{Al}^{n+}...Ti_{Al}^{n+}$ effects on parameters change too [16]. The Cr^{n+} and Ti^{n+} ions give the equivalent input in focus formation. The focal point $h\nu_0$=4.40 eV is situated between the LS of defects $Cr_i^{3(+)}$ (ε≈3.9 eV [2]), Ti_i^{2+} (ε≈3.0, 3.7 eV [17]) and Cr_{Al}^{3+} (ε=4.7-4.8 eV [2]), Ti_{Al}^{3+} (ε=4.5-4.6 eV [17,18]). A close value its energies may be reason of the common focus formation in spectra. As spectrums of alumina irradiated Si^{n+} (substitution is zero [15]) have same focal point may to consider that ability of ion to substitute lattice cations play secondary role in focus formation. Besides, may to conclude that in Al_2O_3 after ions irradiation forms a new materials with BG E_g=4.2-4.4 eV and edge at ε=2.0-4.1 eV belong to cluster states.

The parameters change may be stipulated the compositional component of disorder effect too. It is generated by partial replacement of the chemical elements in compounds. The contribution into common disorder from ID accumulation, compositional and stoichiometric staff may to separate by optical methods [7, 12]. The E_u values at Cr^{n+} ion implantation are on 0.3-0.4 eV higher than after irradiation with Ti^{n+} and Si^{n+} ions (fig.1). That may to connect with differ effect the compositional disorder on properties. This type of disorder is stipulated by synthesis of the hard solution on base of the substitution defects Cr_{Al}^{n+} and Ti_{Al}^{n+}, which differ on its concentration and optical activity [1-3, 16-18]. The contribution into properties from stoichiometry changes is lesser for case of Cr^n.

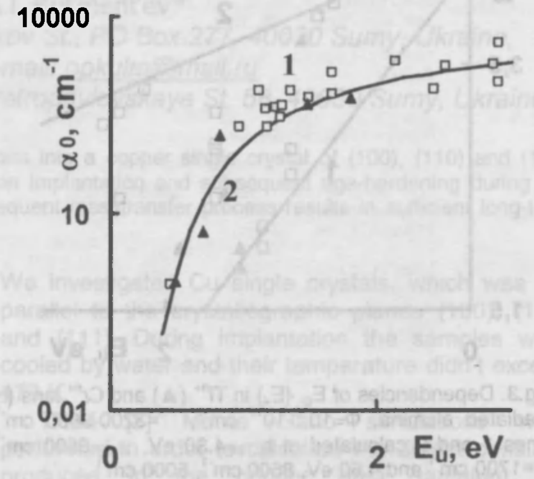

Fig.2. Dependencies of α_0 from E_u in the Al_2O_3 after irradiation with Ti^{n+} (▲) and Cr^{n+} ions (□). Parameter α_0 (curve 2) was determined from (2) and (3) on the experimental data (1), $h\nu_0$=4.40 eV and α_{00}=8500 cm^{-1}.

The second criteria of Urbach's rule realization (1) is dependence α_0=f(E_u) obtained from the spectrums α(hν) according to (2) and (3) ($h\nu_0$=4.40 eV, α_{00}=8500 cm^{-1}) (fig.2). The best-case accordance was received for polycor in intervals Δ(hν)=1.5-3.0 and 3.2-4.1 eV ($\Phi=10^{16}$-10^{17} Ti^{n+}/cm^2) and Δ(hν)=2.1-3.0 and 3.5-4.2 eV ($\Phi=5\cdot10^{16}$ Cr^{n+}/cm^2). The values α_0 situated below curve 2 corresponds to small absorption α=300-1000 cm^{-1} induced after irradiation $\Phi<5\cdot10^{16}$ cm^{-2} at energies hν=1.5-2.5 and 2.3-4.0 eV. Values α_0 distributed above curve 2 respond to spectrums of polycor irradiated at $\Phi\geq10^{17}$ Cr^{n+}/cm^2. Last fact is stipulated by more effectiveness accumulation of the states at ε=2.0-4.2 and 4.0-4.5 eV induced by defect clusters [2].

The third criteria is interrelation between the isoabsorption gap and Urbach's energy $E_g'(E_u)$ (fig.3). The values E_g' were calculated from spectrums at α'=3200-3600 cm^{-1}. The functions $E_g'(E_u)$ were compared with dependencies obtained on (4) for the focal parameters. The lines 1 and 2 form the boundaries for experimental set $E_g'(E_u)$. That is confirms the correctness the Urbach's focus (fig.1, 3). Near the line 2 concentrate the values calculated in Δ(hν)=2.2-3.5, 2.5-4.3, 4.0-4.5 eV ($\Phi=10^{17}$ Cr^{n+}/cm^2) and Δ(hν)=1.5-3.0 eV ($\Phi=10^{16}$ Ti^{n+}/cm^2). Parameters obtained in Δ(hν)=1.5-2.5, 3.5-4.2 eV and situated near 1 are correspond to $\Phi<5\cdot10^{16}$ Cr^{n+}/cm^2 and $\Phi=10^{17}$ Ti^{n+}/cm^2.

Between the $E_g'(E_u)$ stipulated by LS and $E_g(E_u)$ calculated on (5) for direct interband transitions in ranges Δ'(hν)=2.5-4.0 and 4.0-4.8 eV is exist the correlation (fig.4). This interconnection is appears in most materials [8-13]. Calculated on (4) lines 1, 2 restrict the experimental set 3 $E_g(E_u)$ (fig.4). A correlation between the exponential and interband absorption add the Urbach's criteria and confirms that ion irradiation forms in Al_2O_3 the strongly defective mate

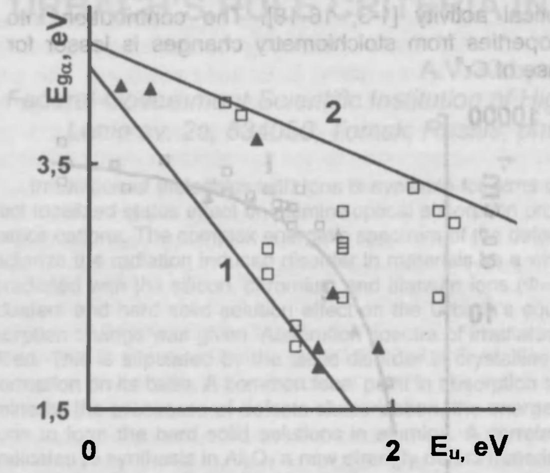

Fig.3. Dependencies of $E_g\cdot(E_u)$ in Ti^{n+} (▲) and Cr^{n+} ions (□) irradiated alumina. $\Phi=10^{16}$-10^{17} cm^{-2}, [illegible]'=3200-3600 cm^{-1}. Lines 1 and 2 calculated at $h\nu_0$=4.30 eV, α_{00}=8500 cm^{-1}, [illegible]'=1700 cm^{-1} and 4.50 eV, 8500 cm^{-1}, 5000 cm^{-1}.

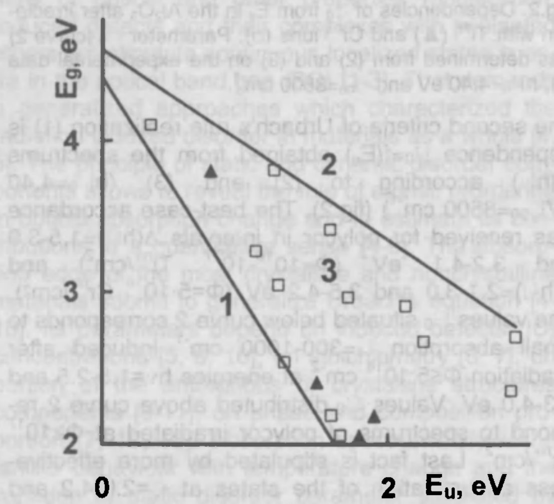

Fig.4. Dependencies of $E_g\cdot(E_u)$ (1, 2) and $E_g(E_u)$ (3) in Ti^{n+} (▲) and Cr^{n+} ions (□) irradiated alumina. $\Phi=10^{16}$-10^{17} cm^{-2}, $\Delta'(h\nu)$=2.5-4.0, 4.0-4.8 eV; $h\nu_0$=4.40 eV, α_{00}=8800 cm^{-1}, [illegible]'=2000 cm^{-1} (curve 1) and 4.60 eV, 9000 cm^{-1}, 4800 cm^{-1} (2).

rials having the maximal BG width 4.4-4.6 eV, current it value 2.0-4.4 eV for direct transitions and absorption edge stipulated by the ID clusters states [illegible]=2.0-4.2 eV. Spectrums $\alpha(h\nu)$ of alumina irradiated Cr^{n+} и Ti^{n+} in intervals $\Delta''(h\nu)$ may to approximate the equation (6) (fig.5). Ranges $\Delta''(h\nu)$ include the [illegible](hν) in which Urbach's rule is fulfils. The average gap E_{g0} coincides with focus energy $h\nu_0$=4.4 eV of spectrums. Dispersion [illegible] stipulated by ID disorder is near to E_u. Value E_{g0}=4.4 eV lies in the interval 4.30-4.60 eV which was used in calculation according to (4) for boundaries restricted the sets $E_g\cdot(E_u)$ and $E_g(E_u)$ (fig.3, 4). In the $\Delta''(h\nu)$=3.6-4.3 and 4.1-5.0 eV spectrums obey the law (6) at E_{g0}=4.7-4.8 eV, where absorption was caused the complexes of ID (fig.5, curves 5, 6). These relations are peculiar to most materials having a similar structural disorder [9-11].

Thus, absorption spectrums of alumina irradiated with ions obey the Urbach's rule as its criteria are fulfils. That stipulated by the static disorder in lattice induced by replacement defects and its clusters. Common focal point 4.40 eV is determined by clusterization of defects, its parameters and ability of implanted atoms to form hard solid solution. Correlation between the exponential and interband parameters indicates about the synthesis in Al_2O_3 a new defect materials having BG width near 4.5 eV and edge stipulated by states of ID cluster.

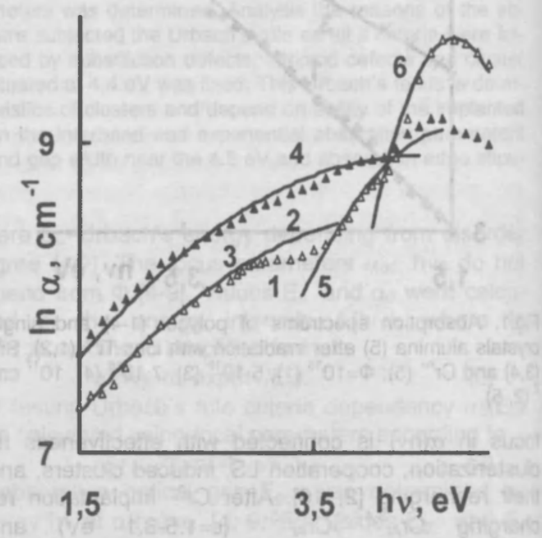

Fig.5. Absorption spectrums of polycor irradiated Cr^{n+} ions at fluences $\Phi=5\cdot10^{16}$ (1), 10^{17} cm^{-2} (2) and it approximation (3-6) by equation (6).

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