Optical Properties of Alumina Implanted with Cobalt Ions

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Abstract – Irradiation dielectrics with ions is available for development of new technologies of solid state electronic elements. Advantage the ion implantation for synthesis of nanoparticles is their self-organization in matrix, control the content and distribution the implanted species, possibility to exceed limit solubility it element in matrix. Defects and nanoparticles effects on optical properties depend on ability of atoms to substitution lattice atoms. In this work the optical absorption characteristics of polycor and single crystal alumina irradiated with cobalt ions (100 keV, $\Phi = 10^{15}$–10^{17} cm^{-2}) and annealed ($P = 0.1$–10^5 Pa, $T_{an} = 300$–1800 K) were investigated. The defects and their clusters effect on properties was established. Defects accumulation with exponentially distributed levels 1.5–4.2 eV is stipulates formation common focal point of spectrums. Properties change indicates about new defective materials in alumina with band gap width near 5.4 eV.

1. Introduction

Irradiation the dielectrics with ions is available for development of new technologies of solid state electronic elements [1–6]. Silicon nanocrystals is available for nanoelectronics aims as it possesses high luminescent ability [1]. The cobalt ions Co^{n+} implantation into dielectrics do not inferior in effectiveness nanoparticles (NP) synthesis [1–6]. Implantation of Co^{n+} in materials is utilizes for modification its electrical [5, 6] and magnetic properties of [2, 3, 6]. Dielectrical properties of Al_2O_3 allow to form a more dense massive the quantum points in NP [4]. The effect from induced defects (ID) and NP localized energetic states on properties depend on ability of incorporated elements to substitution a lattice atoms [1, 4]. That stimulates the investigation of ID formation [3–10]. It is demand the approaches with generalized microscopic parameters of structural disorder in materials [11]. These approaches allow establish effect on the properties and electronic building from the disorder degree created in materials by ID, its clusters and NP. The distribution localized states (LS) induced by structural heterogeneities allow determining the ID formation effect on NP parameters.

Purpose of this work is investigation the absorption of polycrystalline alumina (polycor) and single sapphire crystals irradiated with cobalt ions, determination the degree effect of ID, implanted Co^{n+}, complexes on its base and NP on properties of Al_2O_3.

2. Result and discussion

Irradiation of single crystals and polycor with Co^{n+} (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 Urbach rule [11, 12]:

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

where E_U is the Urbach energy depending from disorder degree; X is the parameter of static disorder depending on Φ. Factor α_{00} and energy $h\nu_0$ are the focus parameters [11, 12]. Values E_U and α_0 were calculated in energy intervals $\Delta(h\nu)$ (where $\ln \alpha \sim h\nu$) according to a simplified formula. Analysis $\alpha(h\nu)$ with framework of semiclassical model for interband absorption of the amorphous and strongly defective materials was fulfilled according [11]

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

where α_0'' is the prexponential factor, E_{g0} is the average band gap (BG) for transitions between allowed bands (E_g obeys to gauss distribution regarding E_{g0}), and σ^2 is the dispersion of E_g values stipulated by the induced disorder. Decomposition of spectrums $\alpha(h\nu)$ on elementary gauss components:

$$\alpha_i = \alpha_0' \exp[-(h\nu - \varepsilon_i)^2/(0.833\gamma^2)], \qquad (3)$$

where ε_i and γ are the band energy centre and half-width was allowed to determine the contribution in absorption from local defects LS.

Local band parameters identified with transitions in Co^{n+} ions ($n = 2, 3$) in compounds are submitted to common dependencies from coordination and local symmetry, its charge state [13–15]. Intensity of bands of Co^{n+} in tetrahedral coordination is in 10^2–10^4 more than in stable octahedral ones [13–15]. Energies ε_i, stipulated by electronic transitions in replacement defects $Co_{Al}^{2,3+}$ in Al_2O_3 are in intervals $\varepsilon = 1.85$–1.95 and 2.80–2.90 eV [16].

Ion implantation stimulates the vacancies $V_{O,Al}$ and interstitials Al_i accumulation, effected on coordination, charge state and optical activity of Co^{n+} ions [2, 7, 8]. Isolated Co_{Al}^{3+} are forms at $\Phi \leq 10^{16}$ cm^{-2} and Co^{n+} are localized in octahedral sites [4, 6]. Amor-

tization is achieved at $\Phi \geq 5 \cdot 10^{16}$ cm^{-2} [4, 5]. Spectrums $\alpha(h\nu)$ indicates about larger effect of ID clusters, their fragmentation, enhance Co precipitate formation and coalescence Co^{n+} into NP [2–6].

Effectiveness of LS accumulation by the Co^{n+} implantation is higher than at same condition of irradiation Al$_2$O$_3$ with Si^{n+}, Cr^{n+} and Ti^{n+} ions (Fig. 1) [1, 7, 8, and 10].
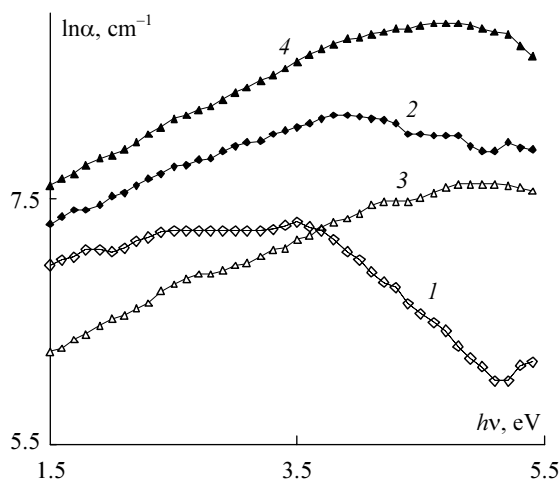
Fig. 1. Absorption spectrums of single alumina irradiated with Si^{n+} (1), Cr^{n+} (2), and Co^{n+} ions (3, 4). Fluences $\Phi = 5 \cdot 10^{16}$ (3) and 10^{17} cm^{-2} (1, 2, 4)

That is stipulated by effectiveness of disorder in crystalline lattice and accumulation the absorbed dose of Co^{n+} ions on its smaller run length in Al$_2$O$_3$ [10]. Local bands identified with Co$_{Al}^{n+}$ do not appear explicit in $\alpha(h\nu)$ (Fig. 1, curves 3, 4). Urbach rule fulfillment indicates on exponential distribution of LS induced by ID and NP (Figs. 1, 2) [8].

Growth E_U values with Φ and shift intervals $\Delta(h\nu)$ from 1.5–3.1 to 1.8–3.8, 3.1–4.1 eV in polycor and from 1.5–2.7, 2.4–4.2 to 1.5–4.1 eV in single alumina lead to intersection a rectilinear parts of spectrums (Fig. 2). That may be connected with redistribution of Co^{n+} from octahedral to tetrahedral coordination as its concentration enlarges [13–16]. Fan-liked character of $\alpha(h\nu, \Phi)$ is stipulated by ion induced quasidynamic disorder in Al$_2$O$_3$ [8, 12, 17]. The convergence region (assignable by rectangle) is a focal point of spectrums $h\nu_0 = (5.37 \pm 0.09)$ eV $[\alpha_{00} = (13360 \pm 940)$ cm$^{-1}]$. Common focal point for poly- and single crystals indicates about general character of ID effect on disorder in lattice (Fig. 2). Accumulation V$_O$ [concentration $N = (2–7) \cdot 10^{19}$ cm^{-3}] and its recharge F$^+ \rightarrow$ F^0 give the same contribution in focus at $h\nu_0 = 5.37$ eV formation (A $\rightarrow$ A transitions at $\varepsilon = 5.4$ eV in F$^+$-centre [16]).

Alternative approach to quantitative estimation of ion induced structural disorder in Al$_2$O$_3$ was showed that $\alpha(h\nu, \Phi)$ according to semiclassical model for interband absorption in intervals $\Delta''(h\nu)$ were approximated by equation (2) (Fig. 3).
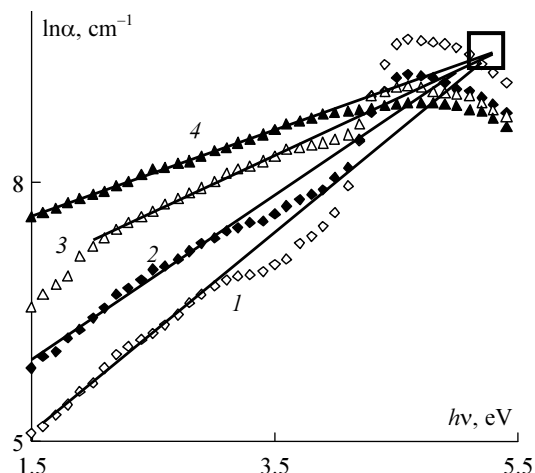

Fig. 2. Absorption spectrums of polycor (1–3) and single alumina (4) irradiated with Co^{n+} ions. Fluences $\Phi = 10^{16}$ (1), $5 \cdot 10^{16}$ (2) and 10^{17} cm^{-2} (3, 4)

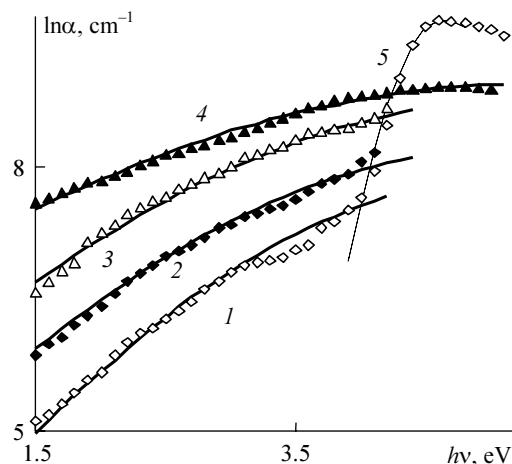Intervals $\Delta''(h\nu)$ are overlap with $\Delta(h\nu)$ where $\ln \alpha \sim h\nu$ (Figs. 2, 3).

Fig. 3. Absorption spectrums of polycor (1–3, 5) and single alumina (4) after irradiation Co^{n+} and its approximation by (2). $\Phi = 10^{16}$ (1, 5), $5 \cdot 10^{16}$ (2); 10^{17} cm^{-2} (3, 4); $\alpha_0'' = 2800$ cm^{-1}, $E_{g0} = 5.4$ eV, $\sigma = 1.6$ eV (1); 3900 cm^{-1}, 5.4 eV, 1.8 eV (2); 6500 cm^{-1}, 5.4 eV, 1.9 eV (3); 7700 cm^{-1}, 5.4 eV, 2.3 eV (4); 16000 cm^{-1}, 4.7 eV, 0.3 eV (5)

Value $E_{g0} = 5.4$ eV is coincide with focal point $h\nu_0 = 5.37$ eV of spectrums $\alpha(h\nu, \Phi)$ and it dispersion σ, stipulated by induced disorder in materials, is close to values E_U. In $\Delta''(h\nu) = 4.0–5.0$ eV spectrums $\alpha(h\nu)$ of polycor obey to (2) at $E_{g0} = 4.6–4.7$ eV (E_{g0} correspond to $A \rightarrow B$ transitions at $\varepsilon \sim 4.8$ eV in F$^+$-centre), $\alpha_0'' = 10000–16000$ cm^{-1} and $\sigma = 0.32–0.45$ eV (Figs. 2 and 3). Same relations between interband and exponential absorption are peculiar to materials with static and dynamic disorder [11, 12].

Transitions with local ID levels are introduce the contribution into absorption (Figs. 1, 2). Decomposition of $\alpha(h\nu)$ was showed that transitions in Co$_{Al}^{2+,3+}$ ($\varepsilon_i = 1.80–1.85$ and 2.75–2.85 eV) give considerable contribution. Divacancies F$_2^{0(+)}$ ($\varepsilon = 3.5–3.6$ eV [8])

and interstitials $Al_i^{0(+)}$ (ε = 4.10–4.20 eV) are become stronger with Φ growth. Recharge of defects $F_2^+ \to F_2^0$ and $Co_{Al}^{3+} \to Co_{Al}^{2+}$ is dominated. Most intensive bands at ε_i = 5.10 eV taking into account [8, 16] is identified with complexes between V_O and Co^{n+}.

Annealing effect on properties is determined by redistribution Co^{n+}, its precipitation, formation of cobalt NP and association Co with matrix atoms [2–6]. Specific effect Co on properties Al_2O_3 appears in higher stability compare with implantation of other ions (Figs. 4, 5).
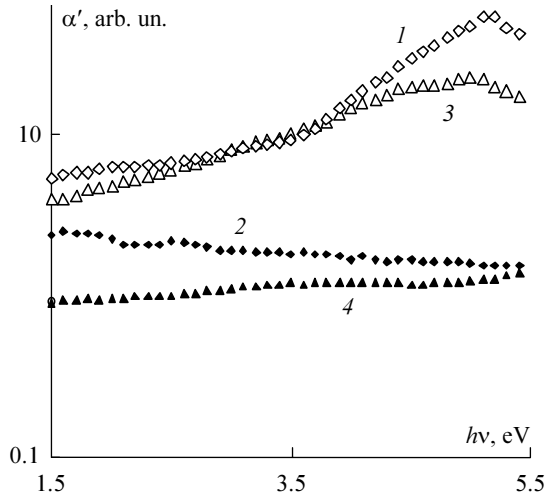

Fig. 4. Spectral dependency of relation α induced by irradiation of alumina ($\Phi = 10^{17}$ cm^{-2}) and subsequent annealing at 1000 K to α induced by only irradiation: ions Si^{n+} (1); Fe^{n+} (2); Cr^{n+} (3); Co^{n+} (4)
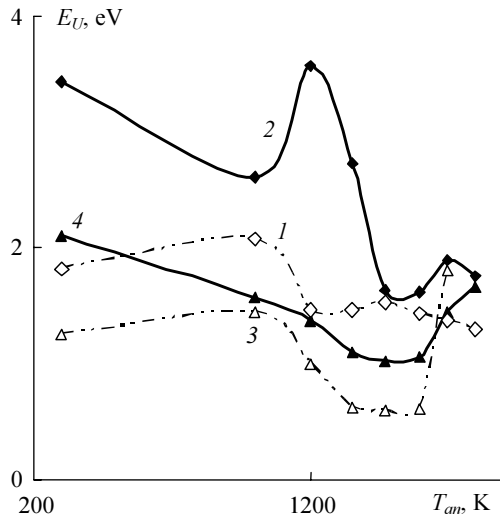

Fig. 5. Annealing effect on Urbach energy in alumina, irradiated ($\Phi = 10^{17}$ cm^{-2}) with Fe^{n+} (1), Si^{n+} (2), Al^{n+} (3) and Co^{n+} ions (4); $\Delta(h\nu)$ = 4.0–4.5 (1), 1.5–3.3 (2), 1.5–4.4 eV (3, 4)

Annealing at 300–1200 K cases maximum growth density LS as in [2–5, 8]. Degree of LS overlapping ($\sim E_U$) is depends on ions kind (Fig. 5). Stability of E_U is stipulates by effect on defects LS population from

cobalt NP. Identification of metals NP optical bands in alumina (Co^{n+} at $\varepsilon \sim$ 4.1 eV [4]; Zn^{n+} at $\varepsilon \sim$ 4.4 eV [18]), in quartz (Co^{n+} at $\varepsilon \sim$ 3.7, 4.7 eV [4]) and in MgO (Zn^{n+} at ε = 4.20 eV [18]) allow to connect the optical parameters change at $h\nu$ = 4.1–4.3 eV with cobalt NP accumulation at T_{an} = 300–1400 K (Figs. 5, 6). Correlation between parameters of F_2-centres ($\varepsilon \sim$ 3.4 eV) and cobalt-vacancy complexes (ε = 5.0–5.1 eV) may be stipulated by NP "quasifree" electrons effect on divacancy LS population (Fig. 6).
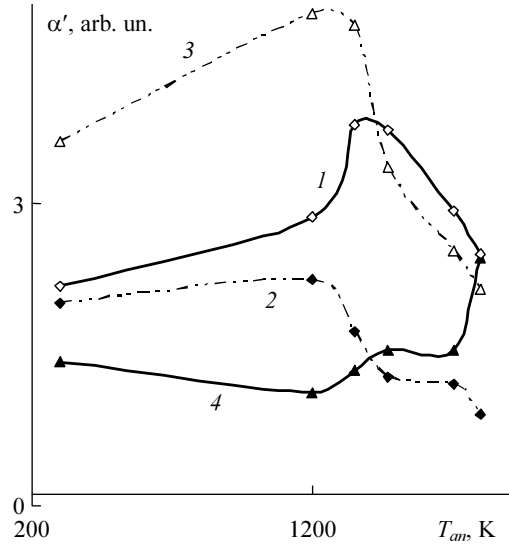

Fig. 6. Annealing effect on relation α_0' obtained by decomposition of the spectrums $\alpha(h\nu)$ of single alumina irradiated with Co^{n+} ions. There are relation value α_0' at ε_i = 4.2 eV to value α_0' at 2.75–2.80 eV (1), 2.75–2.80 to 4.65 eV (2), 4.2 to 4.65 eV (3), 5.1 to 3.55 eV (4)

Analysis relations between intensities of elementary gauss components α_0' received by decomposition of spectrums deduce that $Co_{Al}^{2,3+}$ until 1300–1400 K render the stabilized action on others ID levels (Fig. 6). Decrease the E_U is caused by ID recharging $Co_{Al}^{2+} \to Co_{Al}^{3+}$ and redistribution Co^{n+} from tetrahedral to octahedral coordination in lattice (Fig. 5, curve 4; Fig. 6, curve 1) [13–16]. Behavior of $E_U(T_{an})$ is stipulated by F_2-, $Al_i^{0(+)}$–centers with concentration $N = (2–6) \cdot 10^{20}$ cm^{-3} (Figs. 5, 6). Decrease the concentration of Co_{Al}^{n+} is realized faster than intrinsic ID and cobalt NP ones. Annealing of divacancies and Co-vacancy complexes occurs (Fig. 6). Divacancies (ε = 3.5–3.6 eV) possess lesser stability compare with Co-vacancy complex (ε = 5.0–5.1 eV) (Fig. 6, curve 4). The same difference in stability of complexes was fixed in cases of implantation in Al_2O_3 other kind of ions [8]. The change relations between α_0' at $h\nu$ = 2.75–2.85, 4.6–4.7 eV and 5.0–5.1 eV may be caused by redistribution of electrons between the levels of Co_{Al}^{n+} and V_O in complex (Fig. 6, curves 2, 4). Fast decrease α stipulated by NP ($h\nu$ = 4.1–4.3 eV) compare with F^+-centers and complexes may be result of segregation the ID generated at complexes dissociation on boundaries

between the NP and Al_2O_3 matrix and trapping the "quasifree" electrons on LS of these defects (Fig. 6, curves *3*, *4*). The concentrations of Co_{Al}^{n+} and V_O decrease and overlapping degree its LS ($\sim E_U$) differ in dependence of its thermal stability (Figs. 5, 6). These processes are stipulate low probability of interband absorption compare with exponential ones. Optical gap growth from $E_g = 2.6$ to 3.2 eV indicates about recovery the electronic structure of material owing to ordering the crystalline lattice atoms in modified surface layer. That is occurring to similarly of E_g change at transition from the amorphous Al_2O_3 to ordered state [19]. Values $E_g = 3.1$–3.3 eV for direct allowed transitions is close to width BG at $E_g = 3.2$ eV of amorphous Al_2O_3 that is stipulated by stable ID effect on the interband absorption [19].

Annealing at $T_{an} \geq 1700$ K causes the partial restoration the parameters of the electronic building of Al_2O_3. That is confirmed by different kind of absorption characteristics (Figs. 4–6). The enlarge Urbach energy in intervals 1.5–3.4, 3.3–4.2 eV in alumina single crystals and 2.3–3.2, 3.2–4.0 eV in polycrystalls is stipulated by formation the complexes on base of ID and replacement defects (Fig. 5, curve *4*).

The same contribution in E_U growth in single alumina and polycor carry in the recharge of defects $Co_{Al}^{3+} \rightarrow Co_{Al}^{2+}$. That is confirmed by changes in the ratio the values α_0' in band with energy $\varepsilon_i = 1.85$ eV (identified as defects Co_{Al}^{2+}) to values α_0' at $\varepsilon_i = 2.75$–2.80 eV (Co_{Al}^{3+}). Interband absorption stipulated by ID complexes levels is realizes with low intensity by indirect and direct transition in energetic ranges $h\nu = 2.1$–4.8 eV and 3.4–5.0 eV into allowed bands of alumina through optical gaps $E_g = 0.9$–1.2 eV and 2.9–3.1 eV, correspondingly. That is occurring likewise [8]. Effect to absorption from the replacement defects Co_{Al}^{n+} possessed the concentration $N_i = (1–5) \cdot 10^{19}$ cm^{-3} is negligible (Fig. 6).

The divacancies and cobalt-vacancy complexes annealing occur (Figs. 5, 6). The optical activity of cobalt nanoparticles ($\varepsilon_i = 4.1$–4.3 eV) compare with other defects, probably, is connected with formation stable chemical bonds between ID and cobalt atoms on the surface of nanoparticles.

3. Conclusions

Defects and its complexes, cobalt nanoparticles create continuous localized state spectrums in alumina band gap. Substitution defects effect on absorption is lesser compare with divacancies and nanoparticles. Focal point formed at 5.40 eV is a result of defect formation and ability of cobalt ions to precipitation in Al_2O_3. Interband and exponential absorption parameters indicate about formation in Al_2O_3 a strongly defective material with maximum band gap 5.4 eV.

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