Evolution of Defective State of Aluminum Oxide Irradiated with Chromium Ions after Annealing in Oxygen Environment

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Abstract. The characteristics of interband and exponential optical absorption of leucosapphire and polycrystalline corundum (polycor) after irradiation with chromium ions and subsequent annealing in vacuum at 300–1800 K and in air at 300–800 K are studied. Contributions of defects with different thermal and chemical stability into optical parameters were established. The effect of intrinsic radiation defects, of substitutional defects and of complexes on base of oxygen and defects on formation the focal point in absorption spectra owing to fulfilment of the Urbach rule was determined. Heating in air of strongly defective material synthesized in surface layers of alumina by the ion–heat modification influences the characteristics of defects and the electronic structure of band gap negligibly.

1. Introduction

The application of irradiation with ions for the modification of properties of dielectric materials stimulates studying the radiation damage processes and the changes in their electronic structure [1–6]. Postimplantation thermal annealing of materials is a necessary stage of modification of their properties [2, 4, 5]. Thermal annealing in vacuum and in reducing atmosphere stabilizes the properties of material owing to coagulation of implanted elements into clusters and formation of new phases, having characteristics different from those for pristine matrix [2, 4]. Thermal annealing in oxygen–containing environment influences the electronic structure of material owing to realization oxidative and restoration reactions with participation of defects and oxygen and formation of oxygen–containing complexes (OCCs) [3, 4]. Localized states (LSs) induced by radiation defects (RDs) well manifest in leucosapphire and polycrystalline corundum (polycor), which contain a low concentration of impurities [1–3, 5]. The implantation of ions with different ability to substitute for lattice atoms of Al₂O₃ and to form the solid solutions allows evaluating of their role in changing of properties [1–6].

RDs and complexes on their base induce in the band gap (BG) of Al₂O₃ the complicated spectrum of LSs [1–3, 5]. The study of the produced nonequilibrium state in dielectrics requires approaches using generalized microscopic parameters characterizing structural disordering of the system of a whole [7, 8]. In the analysis of radiation–induced disorder is taken into account the principle of equivalence of static and dynamic components of its [7, 8]. That allows determining quantitatively the contribution of the atomic disordering into properties change. The parameters of induced disordering, calculated from absorption spectra with using of Urbach rule, depend on concentration of RDs [5–7] and stoichiometric and phase–composition of compounds [8].
The aim of this paper is to study the characteristics of the optical absorption of leucosapphire and polycor after irradiation with chromium ions Cr\textsuperscript{m+} and subsequent annealing in vacuum and in air, to determine the thermal and chemical stability of the defects of different nature and to determine the degree of their influence on the optical properties.

2. Experimental

Leucosapphire and polycor plates were irradiated with Cr\textsuperscript{m+} ions in the frequency pulse mode (the ion energy was 50–150 keV, the fluence Φ was 10^{16–2,10^{17}} cm\textsuperscript{-2}, and the current density in the pulse was 10\textsuperscript{2–3} A/cm\textsuperscript{2}). Annealing after irradiation was performed in the temperature range T\textsubscript{ann}\textsubscript{1}=300–1800 K at the residual pressure P\leq10 Pa and in air in the temperature range T\textsubscript{ann}\textsubscript{2}=300–800 K at atmospheric pressure P=10\textsuperscript{5} Pa. Choice of the Cr\textsuperscript{m+} ions for irradiation was caused by high probability for synthesis of hard solutions on base of these ions in the surface layers of alumina [2, 4–6]. The high concentration of RDs allows considering this solution as disordered.

The spectral dependence of absorption coefficient α(hν) calculated from the diffraction reflection spectra according to [2, 5, 6] was approximated by the Urbach rule of general form

\[ \alpha(h\nu,T) = \alpha_{00} \times e^{(h\nu-h\nu_0)/E_U(T)}, \]

where \( E_U \) is the Urbach energy which depend on the total dynamic and static disorder in the lattice [7, 8]. The pre–exponential factor \( \alpha_{00} \) and the characteristic energy \( h\nu_0 \) are the parameters of the Urbach focus [7, 8]. For the energy ranges \( \Delta(h\nu) \) in which the Urbach rule is satisfied we calculated \( E_U \) and the pre–exponential factor \( \alpha_0 \) from the simplified equation

\[ \alpha(h\nu) = \alpha_0 \times e^{(h\nu/E_g)}, \]

To evaluate the applicability of the concept of Urbach focus we calculated the dependence \( \alpha_0(E_U) \) taking into account (1) and (2) according to equation

\[ \alpha_0 = \alpha_{00} \times e^{(-h\nu_0/E_g)}, \]

where parameters \( \alpha_{00} \) and \( h\nu_0 \) were determined from the spectra \( \alpha(h\nu, \Phi, T\textsubscript{ann}1, \textsubscript{2}) \). Isoabsorption optical gap \( E_{\alpha_0} \) was calculated from spectra for a number fixed values of \( \alpha' \). Value \( E_{\alpha_0} \) corresponds to energy of transitions hv for execution of equality \( \alpha(h\nu)=\alpha' \) [6, 7, 8]. Values \( E_{\alpha_0} \) and \( E_U \) were compared with dependence \( E_{\alpha_0}(E_U) \), calculated with using of parameters \( h\nu_0 \) and \( \alpha_{00} \) according to equation [7, 8]

\[ E_{g_{\alpha'}} = h\nu_0 - [\ln(\alpha_{00}/\alpha')] \times E_U. \]

The interrelation between the absorption by the LSs produced by RDs and the interband absorption was verified using the approximation of the \( \alpha(h\nu) \) in the ranges \( \Delta'(h\nu) \) by the power–like law

\[ (\alpha \times h\nu) = (h\nu - E_{g_{\alpha'}}(E_{g_{\alpha'}}))^m, \]

where \( m=1/2 \) and 2 correspond to the direct and indirect interband allowed transitions across the optical gaps \( E_{g_{\alpha'}} \) and \( E_{g_{\alpha'}} \) [5]. We determined the contribution of local levels of RDs into the absorption by using the expansion of the \( \alpha(h\nu) \) in terms of elementary components in the Gaussian form.

3. Result and discussion

The charge state of the substitutional defects Cr\textsubscript{Al}\textsuperscript{n+} (n=2–4) and intrinsic RDs (anion and cation vacancies \( V_0 \) and \( V_{Al} \), as well as interstitial defect \( Al \)) is determined by \( \Phi \) of ions and vary after annealing in vacuum, that reflects on the absorption spectra (figures 1 and 2). The interband absorption in the ranges \( \Delta'(h\nu)=2.4–4.2 \) and 3.4–4.8 eV is caused by electronic transitions in clusters Cr\textsubscript{Al}\textsuperscript{m+}…Cr\textsubscript{Al}\textsuperscript{m+} which were formed after annealing at T\textsubscript{ann}1=300–1300 K. The complexes on the base Cr\textsubscript{Al}\textsuperscript{m+} and intrinsic RDs (T\textsubscript{ann}2=1300–1600 K) determine the exponential absorption with participation of their LSs in ranges \( \Delta(h\nu)=1.5–3.4 \) eV and 3.1–3.9 eV and the interband absorption in ranges

\[ \Delta(h\nu)=1.5–3.4 \text{ eV} \text{ and } 3.1–3.9 \text{ eV}. \]
irradiation of ions and annealing in vacuum. Relation $E_{\Delta}$ in influence of oxygen environment, occurs proportional to quantity of disorder, which is induced by $E_{\Phi}$. Optical parameters depend on building of materials and on concentration of RDs, which determined by $Smoothing and disappearance of the local bands with centers at energies $E_{\Phi}$ level localization in BG and it is achieved of maximal values at energy $h\nu=3.6$ eV (figures 1 and 2). The change of absorption parameters in range $4.0–5.4$ eV to levels with $1.5–3.0$ eV occurring after annealing at $T_{\text{an}2}=300–500$ K and accompanies by the expansion of ranges $\Delta(h\nu)$ and by growth of values $E_{\Phi}$ in single crystals and in polycrystals is subject to the general laws (figures 1 and 2). Two stages of annealing in air were obtained at $T_{\text{an}2}=300–500$ and $500–800$ K. The change of optical parameters depend on building of materials and on concentration of RDs, which determined by $\Phi$ and $T_{\text{an}1}$ (figures 1 and 2). The redistribution of LSs density from range $4.0–5.4$ eV and from LSs with $3.0–4.0$ eV to levels with $1.5–3.0$ eV occurring after annealing at $T_{\text{an}2}=300–500$ K and accompanies by the expansion of ranges $\Delta(h\nu)$ and by growth of values $E_{\Phi}$ in these ranges (figure 1, curve 3; figure 2, curves 4 and 5). Between the value of Urbach energy after annealing in vacuum $E_{\Phi}(T_{\text{an}1})$ and its value after annealing in air $E_{\Phi}(T_{\text{an}2})$ the relation in form of the equation $E_{\Phi}(T_{\text{an}1})=a\cdot E_{\Phi}(T_{\text{an}2})+b$ ($a=1.1–2.2$, $b=0.2–0.5$ eV) was obtained (figure 3). The increase in $E_{\Phi}$ occurs in $1.5–2.2$ times after irradiation of $\text{Al}_2\text{O}_3$ by fluences $\Phi$$\leq$$5\times10^{16}$ cm$^{-2}$ and increase in $E_{\Phi}$ occurs only in $1.1–1.5$ times after $\Phi$$>$$10^{17}$ cm$^{-2}$ (figure 3). The optical gap is narrowing on the value $0.2–0.4$ eV (figure 4). The growth in quantity of disorder in lattice of $\text{Al}_2\text{O}_3$, which is caused by influence of oxygen environment, occurs proportional to quantity of disorder, which is induced by irradiation of ions and annealing in vacuum. Relation $E_{\Phi}(T_{\text{an}2})/E_{\Phi}(T_{\text{an}1})$ is increased with depth of level localization in BG and it is achieved of maximal values at energy $h\nu=3.6$ eV (figures 1 and 2). Smoothing and disappearance of the local bands with centers at energies $\approx$$2.6$ eV and $3.2$ eV shows, that contribution of continuous component of spectrum of LSs is increased owing to absorption of oxygen on RDs and formation of OCCs (figures 1 and 2).

The change of absorption parameters in range $\Delta(h\nu)=1.5–4.0$ eV after annealing at $T_{\text{an}2}=500–800$ K is caused by exchanging by electrons between the energetic levels of substitutional defects, the levels of divacancies $F_{2n}^{\pm}$ (their LSs were identified in [1, 2, 9]) and acceptor levels created by OCCs ($\Phi$$\geq$$4.0$ eV). The recharge of divacancies $F_{2n}^{\pm}$$\rightarrow$$F^0$$\rightarrow$$F^+$, which stimulated by the sequential acts.

Figure 1. Absorption spectra $\alpha(h\nu)$ of leucosapphire before (1) and after irradiation with $\text{Cr}^{3+}$ ions and after annealing in vacuum at $T_{\text{an}1}=1800$ K (2) and in air at $T_{\text{an}2}=500$ K (3) and $800$ K (4). The fluence is $\Phi=10^{17}$ cm$^{-2}$.

Figure 2. Absorption spectra $\alpha(h\nu)$ of polycor before (1) and after irradiation with $\text{Cr}^{3+}$ ions and after annealing in vacuum at $T_{\text{an}1}=1470$ K (2, 3) and in air at $T_{\text{an}2}=500$ K (4, 5) and $800$ K (6). The fluences are $\Phi=10^{16}$ (2, 4) and $10^{17}$ cm$^{-2}$ (3, 5 and 6).
of adsorption and dissociation of molecules $O_2$ and formation of stable chemical bonds, influences on optical parameters also (figures 1 and 2). Shift of range of localization $\Delta(h\nu)$ to high energy region is manifested in leucosapphire in compare with polycor (figures 1 and 2). Values $E_U(T_{ann1})$ are distributed between the lines 1 and 2 in case of strong influence of adsorption on properties. Change in the structure of LSs causes the intersection of the linear sections of the spectra (figure 4). The change in the structure of LSs causes the intersection of the linear sections of the spectra $\alpha(h\nu)$, where relation (2) is valid in the high energy range. The convergence region (is denoted by a rectangle in figures 1, 2) is located at $h\nu_0=4.8 \pm 0.08$ eV ($\alpha_0=800 \pm 90$ cm$^{-1}$) in leucosapphire (figure 1) and at $h\nu_0=3.95 \pm 0.15$ eV ($\alpha_0=8500 \pm 500$ cm$^{-1}$) in polycor (figure 2) and can be interpreted as a focal point of generalized Urbach rule, just as in [6–8]. Annealing in air supplements the criteria of Urbach rule (1) for irradiated $Al_2O_3$ (similar points were fixed at $h\nu_0=4.4$ eV for $Cr^{3+}$ and $Ti^{3+}$ ions and at 4.2 eV for $Si^{2+}$ ions) [5, 6]. The similarity of focal points for ions with different ability to substitution of cation of lattice is caused by existence of interrelation between the kinetic of RDs accumulation and parameters of the exponential absorption [1–5, 6]. The fan–like character of curves $\alpha(h\nu, \Phi)$ persists after adsorption of oxygen in the surface layers of alumina (figures 1 and 2). The separation of focal points for single and polycrystals occurs (figures 1 and 2). At that, the low–energy shift of focal point on $\sim 0.3$ eV was fixed in polycor. The focal point in polycor at $h\nu_0=3.95$ eV is situated between the levels induced by the interstitials defect $Al_{\text{i}}^{3+}$ ($\epsilon=4.1$ eV [2, 9]) and divacancy $F_{2}^{0}$ ($\epsilon=3.6$ eV [2, 5, 9]). This point is connected with boundary of deep LSs in BG of irradiated alumina [2, 8]. Focal point in leucosapphire at $h\nu_0=4.8$ eV is neared to energies of $F^–$–center [9, 10] and of defect $Cr_{\text{Al}}^{3+}$ ($\epsilon=4.7–4.8$ eV [5, 6, 10]). Besides, value $h\nu_0=3.95$ eV is neared to value $E_g=4.3$ eV in films $Al_2O_3$ containing the amorphous and ordered phases [11–13]. Biographical defects have a stabilized effect on parameters of RDs (figure 2). Contribution of composition disorder into total disorder of alumina is 15–20 % according [6]. Influence of distortion of stoichiometry is negligible. The basic component of disorder in alumina lattice is the RDs formation, as show the optical parameters (figures 1–4).

Figure 3. Dependency of the Urbach energy after annealing in air $E_U(T_{ann2})$ from its value $E_U(T_{ann1})$ after prior irradiation of $Al_2O_3$ with $Cr^{3+}$ ions and subsequent annealing in vacuum.

Figure 4. $E_g^0$ vs. $E_U$ (1–3) and $E_{g^0}$ vs. $E_U$ (4–7) for indirect (1) and direct transitions (2 and 3) after irradiation and annealing in vacuum at $T_{ann1}$=1470 K and 1800 K and in air at $T_{ann2}$=500 K and 800 K.
Other criteria of this approach is accordance of dependence between parameters \( \alpha_0 \) and \( E_U \), which calculated from the spectra, with dependence \( \alpha_0=\text{f}(E_U) \), which calculated according equation (3) with using of focal point coordinates \( h\nu_0=3.95 \text{ eV}, \alpha_0=8500 \text{ cm}^{-1} \) (figure 5). The values \( E_U \) and \( \alpha_0 \) until and after impact of oxygen are united into common array for leucosapphire and polycor (figure 5). The values \( \alpha_0 \) situated lower the curve 2 correspond to spectra of alumina after \( \Phi \lesssim 5 \times 10^{16} \text{ cm}^{-2} \), and values \( \alpha_0 \) situated higher the curve 2 – to spectra of polycor after \( \Phi \geq 10^{17} \text{ cm}^{-2} \). The basic contribution to this dependency give the clusters \( \text{Cr}_3 \text{Al}^{3+} \ldots \text{Cr}_6 \text{Al}^{2+} \) and complexes on the base of RDs. Isosborsorption optical gap \( E_{g_0} \) and optical gaps \( E_{g_{\text{opt}}} \) for interband direct (ranges \( \Delta(h\nu)=3.3–4.0 \text{ and } 4.0–5.3 \text{ eV} \) and indirect transitions (\( \Delta(h\nu)=1.5–4.0 \) and \( 3.0–5.1 \text{ eV} \)) are changed in correlation with \( E_U \) changing (figure 4). This relationship has a general character for materials containing the high concentration of defects [6–8].

![Figure 5](image1.png)

**Figure 5.** \( \alpha_0 \) vs. \( E_U \) in Al\(_2\)O\(_3\) after irradiation at fluence \( \Phi=10^{16}–10^{17} \text{ cm}^{-2} \) and annealings in vacuum and in air. Parameter \( \alpha_0 \) (2) was calculated from Eq. (2) and Eq. (3) on array (1) at \( \alpha_{00}=8500 \text{ cm}^{-1}, h\nu_0=3.95 \text{ eV} \).

![Figure 6](image2.png)

**Figure 6.** Absorption spectrum \( \alpha(h\nu) \) of leucosapphire after irradiation with \( \text{Cr}^{3+} \) ions at fluence \( \Phi=10^{17} \text{ cm}^{-2} \) and subsequent annealings in vacuum at \( T_{\text{ann}}=1800 \text{ K} \) and in air at \( T_{\text{ann}}=800 \text{ K} \) and its decomposition.
Stability of centers to oxidation is increased as growth of ions fluence and temperature of vacuum annealing from $T_{\text{anneal}}=1470$ to 1800 K (figure 2). The weakening of bands induced by electronic transitions in the defects $\text{Cr}_{\text{i}}^{3+}$ was caused by recharging $\text{Cr}_{\text{Al}}^{3+} \rightarrow \text{Cr}_{\text{Al}}^{2+}$, as shows the relation between concentration $N_i$ of defects $\text{Cr}_{\text{Al}}^{n+}$ with different $n$. Divacancies $F_2^0$ and clusters of the intrinsic defects $\text{Al}_{i}^{0(3)}...F_{2,3}^{n+}$ ($n=2-4$) were identified in [2, 5, 9] and have influence on the recharging of defects also. The processes of recharging of defects are predominate according to scheme $F^{i} \rightarrow F^{0}$, $\text{Cr}_{\text{Al}}^{2+} \rightarrow \text{Cr}_{\text{Al}}^{3+}$ and $F_2 \rightarrow F_2^0$, as show the absorption spectra. The stability of the bands induced by RDs to oxidation is higher in polycor in compare with leucosapphire owing to influence on optical absorption of boundaries between the structural fragments in the polycrystals (figures 1, 2 and 6). The band at $\varepsilon=2.15$ eV induced by substitutional defects $\text{Cr}_{\text{i}}^{2+} \rightarrow \text{Cr}_{\text{i}}^{4+}$ and band at $\varepsilon=3.0$ eV connected with the cation vacancy $V_{\text{Al}}^{(0)-}$ in leucosapphire disappear after annealing in air. Annealing at $T_{\text{anneal}}=500-800$ K promotes the redistribution of absorption in polycor in the bands of $F^–$-centers from the band with center at $\varepsilon=4.8$ eV to $\varepsilon=5.3$ eV (figure 2). The new band with $\varepsilon=4.4$ eV appears in leucosapphire and this band is caused by forming of OCCs on the base of $V_{\text{O}}$, $Al_{i}$ and $O_2$ (figure 6). At that, bands induced by $F^–$ and $Al_{i}$-centers disappear. We cannot exclude the influence of the electronic transitions (at $\varepsilon=3.7-3.9$ eV) between the LSs of compounds $(\text{Cr}_2\text{O}_3)_x(\text{Al}_2\text{O}_3)_y$ [5] on the absorption processes in substitutional defects and divacancies.

4. Conclusion

Annealing in air of alumina after irradiation with chromium ions and subsequent annealing in vacuum changes characteristics of the energetic levels induced by the RDs and complexes on their base. This is reflected in parameters of the exponential and interband absorption and in their interconnection. The charge state of substitutional defects and intrinsic RDs and degree of their influence on properties are determined by fluence of ions and by annealing temperature in vacuum and in air. Annealing in air of irradiated alumina stabilizes the structure of defects and their energetic characteristics. Fulfillment of criteria of generalized Urbach rule is supplemented owing to realization of oxidation and reduction reactions between the defects and oxygen molecules. Accumulation of OCCs with participation of RDs changes negligibly the electronic structure of irradiated alumina with small decreasing of maximal optical gap from 4.5 to 4.0 eV.

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