Localized Defect States in Alumina Irradiated with Siliconions

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Abstract – Irradiation of dielectrics with ions is available for aims of optical, mechanical and other properties modification. Changes were caused by induced defects, its clusterization and new compounds formation. The defect localized states effect on alumina optical absorption and other properties depends on ability of incorporated elements to substitute lattice cations. Defect localized states characteristics of single alumina crystal irradiated with silicon ions ($\Phi=10^{17}$ cm^{-2}, $E_i=100$ keV) until and after annealing in vacuum ($P=1–0^5$ Pa, $T_{an}=300–1800$ K) were investigated. Nature and thermal stability of defects complexes, silicon nanocrystalls and their effects on properties were established. Single vacancy defects, interstitial aluminium and silicon ions, complexes on these base and nanoparticles nc-Si are create continuous localized levels spectra exponentially distributed on energy in the alumina band gap and determine the optical absorption and photoconductivity parameters changes.

1. Introduction

Irradiation of oxide dielectrics with ions is perspective for aims of elaboration the new technologies of small-lot production elements of the solid-state electronics [1–5]. Implantation of alumina with the silicon ions changes its luminescent and electronic properties owing to introduction of the induced defects (ID) and forming the silicon nanoparticles nc-Si [2, 4]. The ID states localized in band gap sharply appear in the sapphire single crystals as they are subjected to a minimal influence from impurity elements [4–7]. Nanostructure compositional materials are applied for manufacture of the waveguides, optical switchers and lazers emission limiters [1–3].

Silicon nanocrystall nc-Si is one available material for nanoelectronic aims. Ion implantation allows to provide the control and properties modification of dielectric due to doping by impurities. The luminescent properties of the created system nc-Si in dielectric are determined by factors: crystalline structure of matrix, sizes of nanoparticles, presence of boundaries between the structure fragments, kind and concentration of introduced impuruties, the content of existing until irradiation the defects and the broken bonds [8–10].

Formation of the silicon ions clusters precedes the generation nanoparticles. Besides, high concentration of the ID lighten this process by thermal treatment [7, 8, 11]. Introduction of nc-Si in the oxides increases the luminescent ability inherent to impurity ions by means of interaction between the nanoparticles electronic levels localized in forbidden band and the intrinsic defects levels. The defects influence on optical properties depend on ability of the incorporated elements to substitution of the lattice atoms [12]. Investigation of dielectrics photoelectrical and optical properties changes allows study the localized states (LS) of defects peculiar to ion implantation, interaction between the ID within complexes and their participation in the nanoparticles formation.

Purpose of this work is investigation the defects LS characteristics in single sapphire crystals irradiated with silicon ions; analysis the nature and thermal stability of the complexes on base defects and implanting Si^{n+} ions, study formation the silicon nanocryctalls and determination of partial contribution of the induced imperfection into properties changes.

2. Result and discussion

The ability of implanted silicon ions to substitution the cations of alumina lattice is close to zero [12]. Silicon introduction is sensitizes the optical activity of ID and growth defects – cations V_{Al} and anions V_O vacancies, changes the localized states population, defects charge state and power of their influence on the properties too [7]. Accumulation of the induced defects $V_{O,Al}$ and the Si^{n+} ions by irradiation stipulates formation the complexes on their base after thermal treatment [7].

Irradiation of sapphire plates with ions was realized in pulse-frequency regime ($E_i=50–150$ keV, $\Phi=10^{16}–10^{18}$ cm^{-2}, $j=10^{-3}$ A/cm^2). Annealing after implantation was fulfilled in vacuum ($P\leq10$ Pa, $T_{an}=300–2000$ K). The spectral dependence of absorption coefficient $\alpha(h\nu)$ was calculated from diffusive reflection spectrums [7]. Integral K and spectral photosensitivity $K_i(h\nu)$ was calculated in according to expression $K_i=(\sigma_{h\nu}–\sigma)/\sigma$, where σ and $\sigma_{h\nu}$–dark conduction and photoconduction. The charge carriers type and defects charge state were estimated from photothermostimulated currents in the interval T=300–700 K.

Ion clusters $Si^{n+}…Si^{n+}$ may be to play a role as the nucleus in processes of formation nc-Si in the oxides. The imperfection induced by irradiation and annealing create in the forbidden band absorbing localized states. Density of this states is exponentially distributed on energy at $\varepsilon=1.5–3.7$, 1.5–2.7 and 1.9–4.9 eV (Fig. 1). The spectral photosensitivity K_i change after irradiation and annealing was stipulated by electron transitions between the ID levels which are closed on energy to optical LS. Spectral photosensitivity correlates with the overlapping degree between the localized defect states, which is proportional to Urbach energy E_u, calculated from approximation spectrums by expression $\alpha(h\nu)\sim\exp(h\nu/E_u)$ in the intervals $h\nu$=1.5–2.5, 2.6–3.4 and 1.9–4.2 eV (Fig. 1, 2). Parameters of localized at the ε>4.0 eV levels were stipulated by influence the interstitial ions $(Si^{n+})_i$ on population levels induced by radiation $F^{+(0)}$ – and interstitial $Al_i^{(0)}$-centers [7] (Fig. 1).

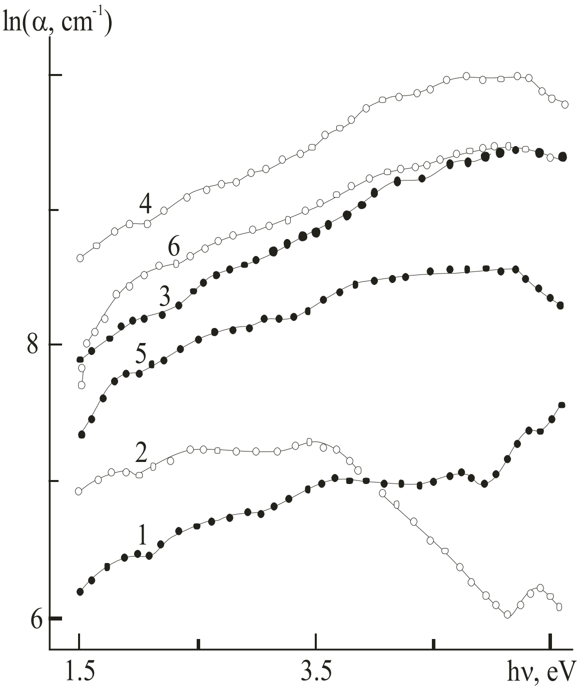

Fig. 1. Absorption spectrums of sapphire single crystals $\alpha(h\nu)$ after irradiation with silicon ions (1, 2) and annealing at T_{an}=1000 K (3, 4) and 1350 K (5, 6). Ions fluence $5\cdot10^{16}$ (1, 3, 5) and 10^{17} cm^{-2} (2, 4, 6)

Spectrums $\alpha(h\nu,\Phi)$ and parameters of the interband absorption, which is realized by the direct and indirect allowed transitions in the energy intervals ε=1.5–3.5, 3.0–5.0, 1.5–5.4 eV respectively, allows us to deduce that localized states owing to accumulation ID (concentration growth from $N_i=10^{18}$ to 10^{21} cm^{-3}) and formation complexes on its base are cooperated into subband [7]. Interband absorption changes are determined by compensating effect from interstitial ions $(Si^{n+})_i$ on charge state of the defects $V_{O,Al}$ and Al_i within the clusters $F_{2,3}^{0}\ldots F_2^{n+}$ and $Al_i^{+(0)}\ldots F_{2,3}^{0\ldots n+}$ [7]. Parameters of absorption and photoconduction were subjected to recharge processes between the divacancies $F_2^0\rightarrow F_2^+\rightarrow F_2^{2+}$, having the localized states with energies ε=3.9–4.2, 3.5–3.8 and 2.6–3.0 eV (Fig. 1–3). The contribution into photosensitivity changes submits the exchange by electrons between the conduction band and donor levels with energies in range ε_σ=0.05–1.2 eV, which are determine the temperature dependencies of conduction $\sigma(T)$ and photoconduction $\Delta\sigma_{h\nu}(T)$ $(\Delta\sigma_{h\nu}=\sigma_{h\nu}-\sigma)$ (Fig. 4). These shallow donors states were caused, probably, by the clusters consisted from di – and trivacancies $F_{2,3}^{n+}$.

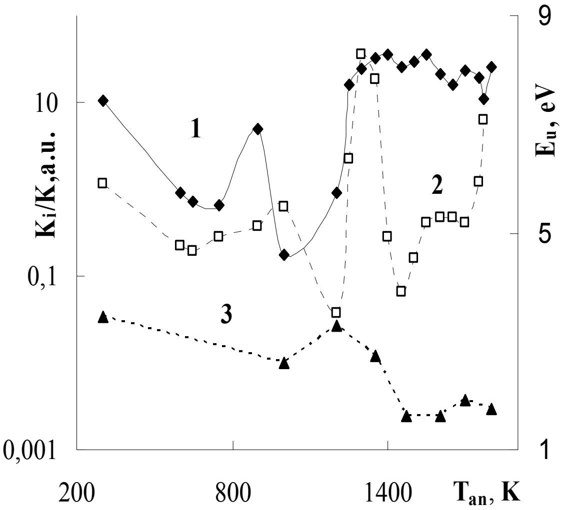

Fig. 2. Annealing effect on the relative spectral photosensitivity $K_i/K(h\nu)$ (1, 2) and Urbach energy E_u (3) in sapphire irradiated with silicon ions at fluence 10^{16}–10^{17} cm^{-2}: $h\nu$=3.3–4.0 (1), 3.0–3.2 (2) and 1.5–4.0 eV (3)

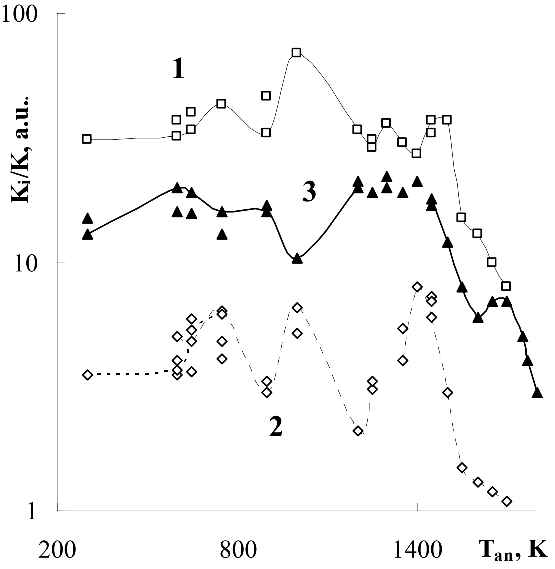

Fig. 3. Annealing effect on the relative spectral photosensitivity $K_i/K(h\nu)$ in sapphire irradiated with silicon ions at fluence 10^{16}–10^{17} cm^{-2}: $h\nu$=1.6–2.0 (1), 2.1–2.4 (2) and 2.8–3.0 eV (3)

Annealing effect on the absorption and photoconduction parameters was caused by transformation of the induced defects into clusters $F_{2,3}^{0}\ldots F_2^{+n}$ and $Al_i^{+(0)}\ldots F_{2,3}^{0\ldots+n}$. Besides impurity-vacancy complexes (IVC) on base interstitial ions $(Si^{+n})_i$ and induced defects $V_{O,Al}$ are form in material. The clusters and IVC level parameters changes take place during three stages T_{an}=300–1000, 1000–1500 and 1500–1800 K

(Fig. 1–3). The primary contribution into property changes give the excitation energy transfer between the defects $V_{O,Al}$ and levels, identified with nc-Si, which located in the forbidden band of alumina [7, 11]. Annealing effect on the spectral photosensitivity $K_i/K(\Phi, h\nu)$ most clearly was proved at hν=1.6–2.4, 2.8–3.0 and 3.0–3.2 eV (Fig. 2, 3). An correlation during annealing between the values K_i/K and α in the interval hν=1.5–3.2 eV and Urbach energy in ranges hν=1.5–2.5, 2.6–3.4, 1.9–4.2 eV testifies about predominant contribution in properties from the complexes on base the intrinsic induced defects $V_{O,Al}$ Al_i (Fig. 1–3).

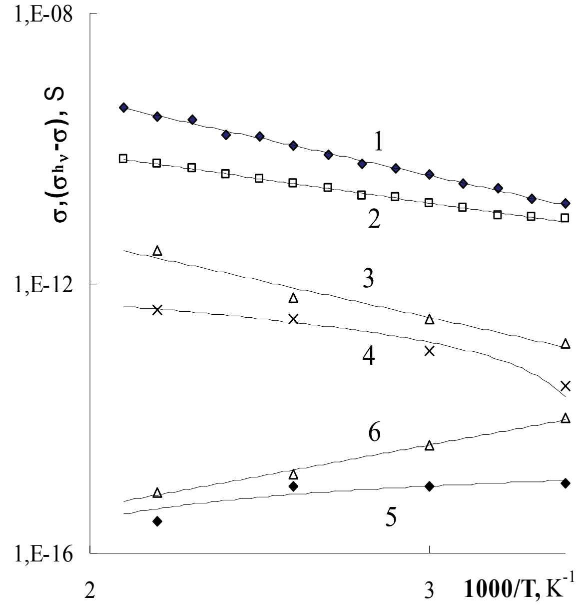

Fig. 4. Temperature dependency of the dark σ (1) and the photoconduction $\Delta\sigma_{h\nu}=\sigma_{h\nu}-\sigma$ (2–6) in sapphire irradiated with the silicon ions at the $\Phi=10^{16}$ cm^{-2} and annealing at T_{an}=760 K: hν=1.6–4.0 (2), 1.8–2.0 (3), 2.1–2.4 (4), 3.0–3.2 (5) and 3.8–4.0 eV (6)

The changes of the parameters α, E_u, K_i (Φ), which were provided by levels with the energy 1.5–4.2 eV, was achieved the maximum after annealing at T_{an}=300–1000 K. This fact was conditioned by instability of alumina electronic structure distorted by defects having high concentrations $N_i=5\cdot10^{19}–10^{21}$ cm^{-3} (Fig. 1–3) [7]. Additionally formation of the clusters $F_{2,3}^{0}…F_2^{n+}$ and $Al_i^{+(0)}…F_{2,3}^{0…n+}$ is correlates at annealing with accumulation impurity-vacancy complexes. The photosensitivity decrease, conduction growth (from $\sigma=10^{-15}$ to 10^{-6} S) and the activation energy lowering (from ε_σ=0.2–0.4 to 0.05–0.15 eV) are coincide with redistribution spectral photosensitivity K_i/K between intervals with hν=3.0–3.2, 3.3–4.0 and 1.6–2.0, 2.1–2.4, 2.8–3.0 eV. These relations between the states parameters deduce to prevail influence on properties from the acceptor levels with energy ε>2.3 eV (Fig. 2–4). These levels according to [7] are induced by complexes $V_{Al}^{0(-)}…(Si^{n+})_i$ and $V_O^{+(2+)}…(Si^{n+})_i$.

Peaks appeared on the curves $K_i/K(T_{an})$ at T_{an}=800–1000 K in the energy interval 1.6–2.4 eV were stipulated by divacancies accumulation and its recharge $F_2^{+,2+}\to F_2^0$ (Fig. 3). Instability of the population states 1.6–2.8 eV by clusters $Al_i^{+(0)}…F_{2,3}^{0…n+}$ gives the definite input too. Activation of the defects Al_i levels 3.8–4.2 eV determines the peak K_i/K at hν=3.4–4.0 eV (Fig. 2, curve 1). The dependencies $K_i/K(\sigma,\Phi,T_{an})$ are confirm this assumption (Fig. 2,3; Fig. 5, curves 1,3). Lack of the coincidence behavior of curves $K_i/K(T_{an})$ and α, $E_u(T_{an})$ determined by LS with energy ε>3.4 eV (Al_i, $F^{(0)+}$-centres with concentrations $N_i=5\cdot10^{19}–7\cdot10^{20}$ cm^{-3}) take place in consequence of suppression population of its states by trapping the optical electrons on the levels of ions Si^{n+} [11].

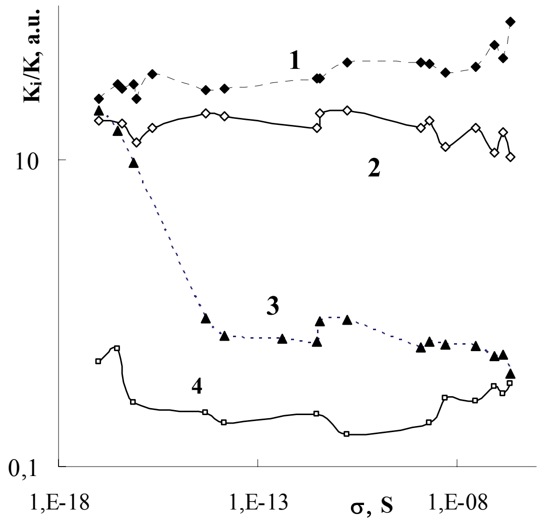

Fig. 5. Dependency of the relative spectral photosensitivity $K_i/K(h\nu)$ from conduction σ in sapphire irradiated with silicon ions at $\Phi=5\cdot10^{16}–10^{17}$ cm^{-2} and annealing at T_{an}=300–1500 K: hν=1.6–2.0 (1), 2.8–3.0 (2), 3.8–4.0 (3) and 3.0–3.2 eV (4)

Maximums of relative spectral photosensitivity after annealing at T_{an}=600–900 K, temperature dependencies of dark and photoconduction and dependencies $K_i/K(\sigma)$ in interval 1.6–3.0 eV were caused by electrons exchange between ID levels and the states which belong to silicon nanoparticles (Fig. 3, 4; Fig. 5, curves 1,2). The electronic structure models of Al_2O_3 contained the nc-Si having the different sizes and calculations of ions cluster on foundation of properties changes alow us to connect the strong sensitive band at hν=2.8–3.0 eV with electronic transitions between nc-Si levels situated in the alumina band gap [8–11] (Fig. 3, curve 3). Definite contribution into photoconduction parameters at hν=1.6–2.4 eV gives the excitation of levels belonging to clusters of interstitial ions $(Si^{n+})_i…(Si^{n+})_i$. These clusters are as nucleus by nc-Si formation. Expansion of localization regions of donor levels correlates with growth of overlapping degree between LS (Fig. 1, 2). Besides changes of parameters K_i/K, α and E_u in intervals 1.6–2.4 and 2.8–3.0 eV correlate by annealing (Fig. 1–3). These facts are confirm that LS induced by inclusions of the nc-Si has the strongly influence on photoelectrical parameters stipulated by clusters of induced defects.

After annealing at the temperature interval T_{an}=1000–1500 K the absorption parameters and the photosensitive levels were stipulated by lowering of concentration ID in the unstable clusters owing to its dissociation and activation of single defects V_{Al}, Al_i, V_O levels (ε=3.0–3.2, 3.8–4.2 eV [7, 11]) (Fig. 1–3). At the same time clusters on base ID, having levels with ε=1.5–3.6 eV, are more stable than impurity-vacancy complexes with levels $\varepsilon \geq 4.0$ eV (Fig. 1, 3). Association the interstitial silicon ions and cation vacancy into IVC is observed too. The spectral, dose and annealing dependencies $K_i/K(h\nu,\Phi,T_{an})$ indicate to redistribution of population the photoelectrical states from shallow LS to more deep levels in forbidden band (Fig. 2, 3, 5).

Bands within the interval 3.4–3.8 eV induced by di- and trivacancies $F_{2,3}^{n+}$ are disappear. That is correlates with change of dominate type of charge carriers from holes to electrons. This change of the type $\sigma_{h\nu}$ **(p→n)** is stipulated by recharge of defects $Al_i^{+} \to Al_i^{0(-)}$ and $F_2^{+(2+)} \to F_2^{0}$ (Fig. 2, curve 1; Fig. 5, curve 3). Annealing dependencies of photosensitivity and absorption coefficient in energy interval 3.3–4.0 eV are confirm that predominant input in photoconduction give the localized states of the complexes $Al_i \ldots V_O$ than clusters $(Si^{+n})_i \ldots (Si^{+n})_i$.

The strong peak of the p-type of photoconduction in the narrow energy interval ε=3.0–3.2 eV is appear after annealing at 1300–1400 K (Fig. 2, curve 2). The connection between dark conduction and photosensitivity in band $h\nu$=3.0–3.2 eV is weak in compare with dependency $K_i/K(\sigma)$ in interval $h\nu$=1.6–2.0 and 2.8–3.0 eV (clusters of ID) (Fig. 5). However photosensitivity in band 3.0–3.2 eV well correlates with value K_i/K at $h\nu$=2.8–3.0 eV, stipulated electronic transitions in the nc-Si (Fig. 2, 3). In spite of absence of connection between absorption coefficient α at $h\nu$=2.9–3.3 eV and K_i/K at $h\nu$=3.0–3.2 eV, growth the overlapping degree levels localized at 1.5–3.3 eV (Fig. 2, curve 3) indicates to formation IVC [7]. Identification of the bands conditioned the V_{Al} and ability the silicon ions to influence on optical activity of vacancies allows us to suppose that IVC are form on the base V_{Al} and interstitials $(Si^{n+})_i$. The photosensitivity growth at $T_{an} \geq 1500$ K owing to contribution from states in band 3.0–3.2 eV is carried out by carriers exchange between cation vacancies acceptor levels and interstitial ions $(Si^{+n})_i$ (Fig. 2).

The photosensitivity growth after thermal annealing 1500–1800 K is stipulated by contribution electrons transitions between localized induced defects Al_i^{+} states and levels belong to complexes $V_O^{+,0} \ldots (Si^{n+})_i$ and $V_{Al}^{0,-} \ldots (Si^{n+})_i$ (Fig. 1–3). These imperfections play role the trapping centres for inequilibrium charge carriers and change the dark conduction and photoconduction type from **n** to **p** and lower values of conduction and photosensitivity**.** Complexes on the base interstitial defects Al_i have the higher stability to temperature (Fig. 2, curve 1). The photosensitivity induced by nc-Si levels, intrinsic ID clusters and interstitial clusters $(Si^{+n})_i \ldots (Si^{+n})_i$ states is lower.

3. Conclusions

Defects, their complexes and nanoparticles nc-Si, induced in the sapphire single crystals after irradiations with the silicon ions, create in the alumina band gap the continuous spectra of the localized levels. This levels exponentially distributed on energy determine the optical absorption and photoconductivity parameters changes. The induced irregularities levels effect on characteristics depend on interaction by electron exchange between the single defects and the defects complexes. The stability of electronic structure changes is determined by ions fluence and varied after annealing during three stages.

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