Optical and Photoelectrical Properties of Single Sapphire Crystal After Irradiation with Silicon Ions

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Abstract – Irradiation of oxide dielectrics with ions change within the large-scale limits the mechanical, electrical, catalytic and optical properties of materials – absorption, luminescence, photoconduction. Properties change was caused by the defects accumulation, its association into complexes and new conductive phase formation. In this work characteristics of the sapphire optical absorption and the time, temperature and spectral dependencies of conduction and photoconduction after irradiation with the silicon ions ($\Phi=10^{17}$ cm^{-2}, E_i=100 keV) and after annealing in the vacuum (P=1–10^5 Pa, T_{an}=300–1800 K) were investigated. The stability of the optical absorption parameters, the energetic and kinetic characteristics of photoconduction was established. Effects on the optical and photoelectrical property parameters from implanted silicon ions, concentration of the nanoparticles and induced defects complexes were determined. Characteristics of the photoconduction and conduction correlate with the optical parameters changes. The thermal stability of photoconduction parameters and character of interconnections between the optical and photoconduction properties are determine by the ions fluence and are depend on the thermal treatment conditions.

1. Introduction

Irradiation of the dielectrics with ions is perspective for aims of modification the mechanical, electrical, catalytic and optical properties too: absorption [1–5], luminescence [6–9], photoconduction. Ion implantation as a method of the synthesis of nanoparticles allowes to devise the nonlinear elements of optoelectronic obtained the unique optical properties [1–4, 7]. Ion implantation is one of the perspective methods of synthesis the silicon nanocrystals nc-Si in the dielectric matrix.

Optical properties of the system nc-Si in dielectrics are determined by the factors having the structured-chemical character. Electroluminescent structures on the base Al_2O_3 contained the add-in nanoparticles component (system Al_2O_3: nc-Si) have the advantages compare with known technologies of nc-Si [9,10]. These facts stimulate the elaboration of analogous systems for aims of technology the silicon integral chips. The dielectrical properties of Al_2O_3 allow to form the more dense arrays of the non-interacting silicon quantum dots.

The accumulation the silicon ions clusters is precede the formation of the silicon nanoparticles in oxide dielectrics [2, 5, 6]. Introduction the nc-Si particles into oxides change the optical activity of the neighbour impurity atoms served as a radiative centers by means of the interaction between the nanoparticles electronic levels with the levels of impurities and defects [10]. Investigation the effect of implantation Si^{n+} ions on the photoelectrical properties of oxides connected with absorption and luminescent parameters changes allow to study the role of the silicon ions clusters and particles of the nc-Si in properties changes.

Purpose of this work is investigation the absorption of single sapphire crystals irradiated with silicon ions, the stability to temperature annealing of these changes; determination the time, temperature and spectral dependencies of the dark conduction $\sigma(t, T)$ and photoconduction $\sigma_{h\nu}(t, T, h\nu)$; estimation the stability of the energetic and kinetic characteristics of photoconduction, effect on the optical and photoelectrical properties from the implanted silicon ions, the nanoparticles nc-Si and the complexes on base the induced defects.

2. Result and discussion

Irradiation of the 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 [11]. 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 $J_{PhTSC}(h\nu,T)$ in the interval T=300–700 K.

Electrical conduction of the near surface layer modified by irradiation with the silicon ions is determined by the fluence of ions and the subsequent postimplantation annealing temperature (fig. 1, curves 1, 2). The change of absorption coefficient α and integral photosensitivity K of irradiated material occurs during the three stages: T_{an}=300–1000 K, 1000–1500 K and 1500–1800 K (fig1, curves 3, 4; fig.2, 3).

Dependencies α, σ, $K(\Phi, T_{an})$ and $K(\sigma)$ testify about the instability behavior of the electronic structure of alumina forbidden band (FB), distorted by implantation with silicon ions (fig. 1–3). The properties stabilization comes after annealing in the temperature interval T_{an}=1000–1300 K (fig. 1, 3). The specific characteristic behavior for effect the silicon ions distinction from irradiation with other ions which good substitute the alumina lattice cations (for example for chromium ions degree of substitution is 0.6–0.95 [12]) is the irreversible character of the dependencies $K(\sigma, \Phi, T_{an})$ at annealing and fluence growth (fig. 2, 3). High photosensitivity occurs in case of the conduction growth after annealing in the optimal temperature interval T_{an}=300–1100 K (fig. 2, curve 1). Reduction photosensitivity is obtained with temperature growth in the interval T_{an}≥1200 K that correspond to conduction decrease from the values $\sigma=10^{-7}$ to 10^{-16} S (fig. 2, curve 2).

The conduction growth (from $\sigma=10^{-(16...10)}$ to $10^{-(8...6)}$ S) and absorption coefficient increase in energetic range $h\nu$=2.0–3.2 эВ and peculiarities of dependencies $K(\sigma, \Phi, T_{an})$ too are stipulated by silicon ions effect on properties. Besides, these facts indicate to strong influence of the ions clusters and the inclusion nc-Si on the optical and electrical parameters too. Photosensitivity changes are stipulated by the electron exchange between the allowed bands and shallow levels having energies ε_σ=0.05–0.3 and 0.5–1.2 eV too. These levels are determine the temperature dependencies $\sigma(T)$ and $\Delta\sigma_{h\nu}(T)$ ($\Delta\sigma_{h\nu}=\sigma_{h\nu}-\sigma$) (fig. 4, table). The fundamental contribution into the optical and photoelectrical properties change with consideration the annealing effect give the transfer the electronic excitation in the alumina FB between the defects levels and wide localized bands induced by the silicon nanoparticles [2, 5–10].

Ions fluence and the subsequent thermal treatment effect on the spectral photosensitivity $K_i(h\nu)$ is appeared sharply in the energetic interval h=1.6–3.2 eV where accumulation of the localized induced defects states is achieved the maximum values (fig. 1, 5). Absorption spectrums and parameters of the interband absorption realized by direct and indirect allowed transitions in intervals 1.5–3.5, 3.0–5.0, 1.5–5.4 eV respectively allow us to deduce that defect localized states owing to formation defects complexes are cooperated into subband [11]. Interconnection between the spectral photosensitivity and optical absorption coefficient α in intervals $h\nu$=1.6–2.2, 2.8–3.0 eV obtained at variation the fluence and annealing temperature testify to existing the correlation between optical and photoelectrical properties and indicates to similar nature of imperfection determined properties changes such as intrinsic defects complexes, interstitial silicon ion clusters and inclusion of nanoparticles too (fig. 1, 3, 5) [10, 11, 13].

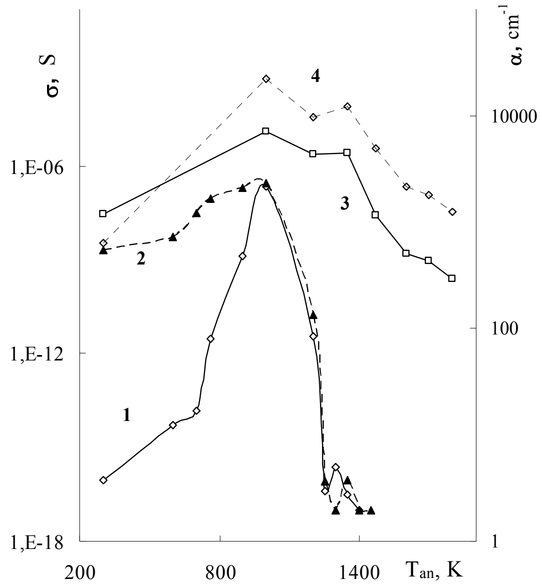

Fig. 1. Annealing effect on the conduction (1, 2) and optical absorption coefficient α (3, 4) in sapphire irradiated with silicon ions at fluence $\Phi=5\cdot10^{16}$ (1) и 10^{17} cm^{-2} (2–4): $h\nu$=2.0–3.2 (3) and 4.2–5.4 eV (4)

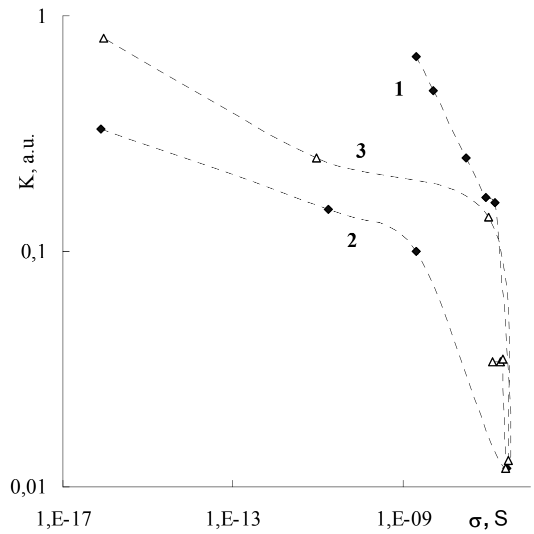

Fig. 2. Dependency of the integral photosensitivity K from conduction σ in the sapphire irradiated with Si^{n+} ions (1, 2) and Cr^{n+} ions (3) and annealing at 300–1500 K. Fluence $\Phi=10^{17}$ cm^{-2}

The time dependence of photoconduction $\sigma_{h\nu}(t)$ is determined mainly by velocity of trapping on the deep defect complexes levels with energies $\varepsilon_\sigma\geq1.0$ eV of the unequilibrium electrons excited by light irradiation from defect levels (ε=2.0–3.4 eV) into conduction band (table). The values of buildup photoconduction currents signal τ' and decay ones τ'' (τ' and τ'' were determined from the time dependencies of photoconduction $\sigma_{h\nu}(t)\sim(1-\exp(-t/\tau'))$ and $\sigma_{h\nu}(t)\sim\exp(-t/\tau'')$), τ' and τ'' growth with increase the energies transition, ions fluence and material conduction value are evidence of these supposition (table).

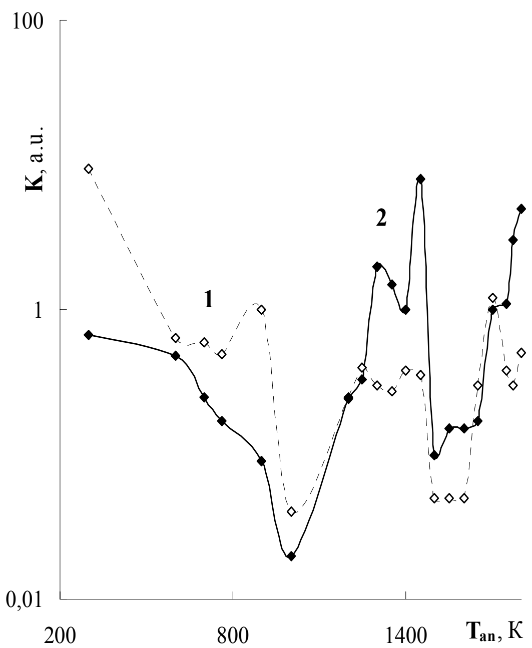

Fig. 3. Annealing effect on the photosensitivity K in the sapphire irradiated with Si^{n+} ions. Fluence $\Phi=5\cdot10^{16}$ (1) и 10^{17} cm^{-2} (2)

After annealing at temperature interval T_{an}=300–1000 K take place the growth of conduction from $\sigma=10^{-(14...10)}$ to $10^{-(6...8)}$ S simultaneously with enlargement density of optical absorbing states in the wide energy interval (fig. 1). However, the photosensitivity is lower strongly owing to accumulation of complexes on base the intrinsic defects [11] (fig. 3). Contribution into conduction and photoconduction from the holes transport increases, how were showed currents J_{PhTSC} (table). The relaxation constants of $\sigma_{h\nu}(t)$ are increase respectively (table). Negative photoconduction with T growth at excitation with energies $h\nu$>3.0 eV is observed due to growth of the concentration deep trapping levels with $h\nu$=3.2–5.4 eV (fig. 1, 4). Dependency of absorption coefficient on spectral photosensitivity is distinguished for intervals $h\nu$=1.6–3.0 and 3.3–4.0 eV (fig. 5). These facts and doses, annealing dependencies of ptotothermostimulated currents indicate about the dominant effects on sapphire photoconduction from the acceptor defects levels with energies ε>2.3 eV.

The peaks on curves $K(T_{an})$ in temperature interval 700–900 K ($\Phi\leq5\cdot10^{16}$ cm^{-2}) are deternine by the dianion vacancies recharge and activation of the single interstitial ions of aluminum and silicon. The photosensitivity maximums at T_{an}=1000–1500 K may be cased by electrons exchange between the wide bands induced of the silicon nanoparticles nc-Si and the narrow levels of defects V0 and Al_i (fig. 3). Interstitial ions clusters Si^{n+}...Si^{n+} are the nucleus at the nanoparticles nc-Si formation.

Behavior of optical and photoelectrical parameters after annealing in interval T_{an}=1000–1500 K testifies about unstability of the electronic structure of band gap peculiar to processes of the induced defects clusters dissociation, rebuilding defects structure of material and change nature of the dominant defects (fig. 1–3). Activation of the single defects levels identified as Al_i and F^+-centers [11] is occured too. Besides there are place association of implanted silicon ions into complexes with participation of the induced and biographical cation vacancies. This supposition is confirmed by the correlation existence between the integral and spectral photosensitivity change and values of photoconduction relaxation constants and absorption coefficient (fig. 1–5, table).

Table. Parameters of the photoconduction of single alumina crystal after irradiation with the silicon ions ($\Phi>10^{16}$ cm^{-2}) and thermal annealing (*–$\Phi=10^{16}$ cm^{-2})

$T_{отж}$, K	σ, S	ε_σ, eV	$h\nu$, eV	J_{PhTSC} 10^{14}, A	τ'', s
300	$2\cdot10^{-9}$	0.41	2.0 2.8 3.4	+3000	80 120 230
600	$2\cdot10^{-8}$	0.23	3.4	+33000	150
900	$2\cdot10^{-7}$	0.05	2.3 3.4	+55000	200 300
1000*	$3\cdot10^{-9}$*	0.13* 0.50	2.2* 3.4	+30*	250* 600*
1200	$2\cdot10^{-11}$	0.06	4.0	–15000	100
1400	$1\cdot10^{-16}$		3.4	+4	2
1800	$1\cdot10^{-16}$	0.15 0.62	3.4	+2	1–3

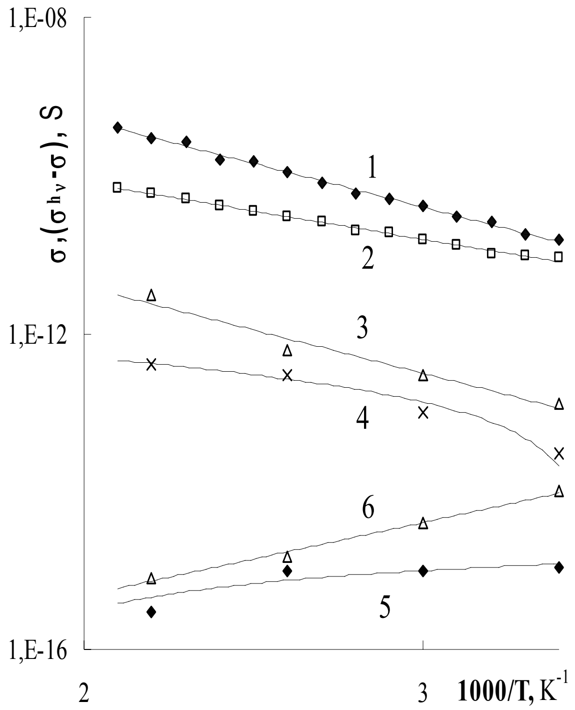

Fig. 4. Temperature dependency of the dark σ (1) and the photoconduction $\Delta\sigma_{h\nu}=\sigma_{h\nu}-\sigma$ (2–6) in sapphire irradiated with the silicon ions at the $\Phi=10^{16}$ cm^{-2} and annealing at T_{an}=760 K: $h\nu$=1.6–4.0 (2), 1.8–2.0 (3), 2.1–2.4 (4), 3.0–3.2 (5) and 3.8–4.0 eV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

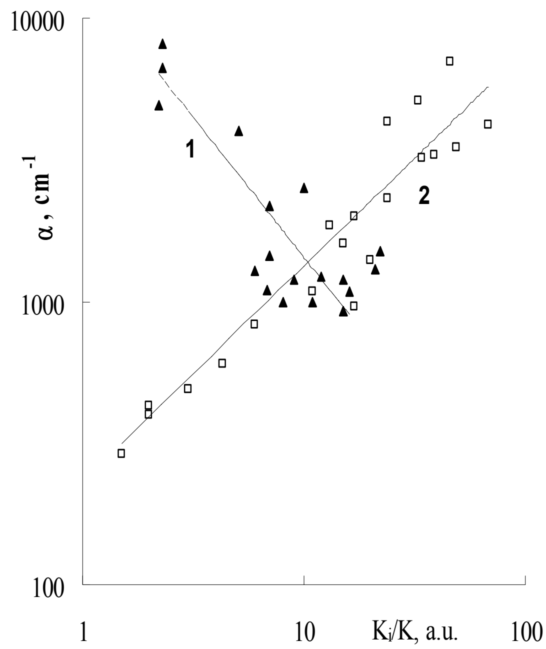

Fig. 5. Interconnection between the relative spectral photosensitivity K_i/K and the optical absorption coefficient α in sapphire irradiated with the silicon ions at $\Phi=10^{16}-10^{17}$ cm^{-2} and annealing at T_{an}=300–1800 K: hf=3.3–4.0 (1) and 1.6–2.2, 2.8–3.0eV (2)

Considerable contribution to the properties change gives the recharge processes occured between the induced defects. On that indicates the charge carrier type change $p \rightarrow n$ in according to measurement of photothermostimulated currents (table). The recharge of the anion vacancies $F^+ \rightarrow F^0$ and divacancies $F_2^+ \rightarrow F_2^0$ is dominates in the single sapphire crystals against from polycrystalline corundum [11]. This process is imaged on curves $K(\sigma, T_{an})$ and $\alpha(K_i/K, \Phi, T_{an})$ too (fig. 2–5).

Photosensitivity growth after annealing at 1500–1800 K is stipulated by contribution into photoconduction from the induced single defects and and impurity-vacancy complexes on base the cation vacancies and the interstitial silicon ions (fig. 3, 5). Besides the role of exchange processes by holes between the acceptor levels of cation vacancies and states belonging to interstitial silicon ions clusters $(Si^{n+})_i...(Si^{n+})_i$ is increases. These inperfections play role of the trapping centres for unequllibrium charge carriers and they lower conduction and change the photoconduction type $n \rightarrow p$ (fig. 1, table). The photosensitivity and optical absorption induced by nanoparticles inclusions of the nc-Si and the residual clusters of interstitial ions and vacancies defects are lowered (fig. 1, curve 3, 4; fig. 5, curve 2). In sapphire single crystals most resistant to annealing temperature has the complexes on base the induced interstitial aluminum ions.

3. Conclusions

The photoelectrical properties and conduction energetic and kinetic parameters changes are occur in correlation with the optical absorption parameters changes. The characteristics of the dark conduction and photoconduction, their thermal stability to annealing in the vacuum and the character of interconnection between the photoconduction and absorption parameters are determine by ions fluence and change after thermal treatment. These changes are stipulate by formation the interstitial silicon ions clusters, inclusion of the silicon nanocrystals and the interaction by electron exchange between these structure imperfections in irradiated alumina.

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