Electronic Excitations and Optical Response of Metal Nanocomposites under Heavy Ion Implantation

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Abstract—The optical transmission and ion-induced luminescence under implantation of copper ions into quartz glass (a-SiO₂) have been measured to study the processes of formation of copper nanoparticles. It is shown that in situ measurements are more informative in comparison with the ordinary approach—investigation of the properties of ion-implanted nanocomposites only after implantation. A series of experiments was performed to prove that the ion-induced luminescence band at 545–550 nm is due to Cu⁺ ions dissolved in a-SiO₂. The combined use of in situ optical techniques makes it possible to monitor the states of implanted copper (metal nanoparticles and dissolved atoms) by the change in the optical absorption near the surface plasmon resonance of nanoparticles and by the intensity of ion-induced luminescence of Cu⁺ states in solid solution. It is shown that the optical bands of defects, dissolved copper, and nanoparticles can be separated within a simple linear approximation. Near the surface plasmon resonance and defect bands, ion-induced transient optical absorption has been revealed. The transient optical absorption near the surface plasmon resonance is explained by the temperature effect. The relationship between the electronic excitation, radiation-induced optical response, and the kinetics of nanoparticle formation is analyzed. Several stages of nanoparticle formation have been established: accumulation of implanted copper in solid solution, nucleation of nanoparticles, coalescence, growth of nanoparticles, and saturation of nanocomposites.

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INTRODUCTION

Optical nanocomposites based on quartz glass (a-SiO₂) with incorporated metal nanoparticles are promising for nonlinear optical devices operating in the femtosecond range in view of the effects related to the surface plasmon resonance (SPR) in nanoparticles [1]. Ion implantation makes it possible to introduce elements that do not mix with the substrate material, obtain supersaturation of an implanted impurity, and initiate clusterization in a-SiO₂. A simple criterion according to which gradients of chemical potential lead to the formation of nanoparticles during ion implantation was formulated in [2]. In reality, formation of nanoparticles involves competing processes induced by ion implantation, i.e., atomic collisions and electronic excitations. Ion implantation forms specific nonequilibrium conditions in solids, under which large portions of energy are statistically transferred to nanoscopic regions. Mobility of atoms—a necessary condition for clusterization and further evolution of the new phase (Ostwald ripening [3])—is stimulated by random energy transfer to the atomic network of a glass. Heavy ions “plough up” the surface and sputter the glass. These processes may impede the formation of nanoparticles in the case of shallow ion penetration. For fast (i.e., with kinetic energies of several megaelectron-volts) heavy ions, the effect of surface sputtering on nanocomposites is much weaker than for ions with energies of several kiloelectronvolts [4]. However, low energy density and shallow (several tens of nanometers) penetration are advantages of kiloelectronvolt ions, which make it possible to fabricate quasi-two-dimensional nanostructures using high fluxes during ion implantation [5, 6].

To understand the complex processes induced by intense ion implantation, it is necessary to use the advantages of in situ methods in order to control the states of implanted atoms. Recently, it has been shown that optical measurements performed during implantation of copper ions into a-SiO₂ are most informative: they have provided data on copper nanoparticles, copper in solid solution, and sputtered copper atoms. To study the external mass transfer during the implantation of 60-keV Cu⁺ ions into a-SiO₂, ion-induced luminescence spectroscopy was used [7]. Information on the amount of copper in nanoparticles can be obtained by optical transmission spectroscopy near the SPR [8]. It has also been found that the states of Cu⁺ in solid solution in a-SiO₂ can be monitored by studying the strong ion-induced luminescence band in the visible range [9].

It was shown in [10] that electronic excitations in ion tracks initiate the formation of copper nanoparticles
in $\alpha$-SiO$_2$. The amount of energy transferred in the form of electronic excitations depends strongly on the ion kinetic energy. For heavy kiloelectronvolt ions, a large part of the energy is transferred directly in the form of phonons or as a result of atomic collisions, whereas the contribution of electronic excitations is relatively small in comparison with megaelectronvolt ions. An additional electronic excitation can be induced by a laser beam. Recently, it was proposed to increase the efficiency of the formation of copper nanoparticles in $\alpha$-SiO$_2$ by simultaneous irradiation with 3-MeV Cu$^{2+}$ ions and a laser beam with a wavelength of 532 nm [11]. Simultaneous irradiation also improved the optical quality of implanted $\alpha$-SiO$_2$ by decreasing the optical absorption due to intrinsic centers [12]. In situ optical measurements are also useful for understanding the mechanisms of the effects of simultaneous irradiation.

In this study, we used a combination of optical transmission measurements and ion-induced luminescence during implantation of copper ions with different energies and fluxes into $\alpha$-SiO$_2$ to study the formation of copper nanoparticles. After a review of our previous results, we report some new data and discuss them in more detail. We will begin the analysis with the estimation of electronic effects, which, in our opinion, can be important for radiation-induced optical properties and the formation of nanoparticles.

**THEORY**

**Overlap of Tracks**

Deceleration of 3-MeV heavy (for example, Cu$^{2+}$) ions induces a high electron density in the substrate material. Since the energy transferred by the incident ions is localized in the ion tracks, electronic excitations of the medium are statistical. However, at ion fluxes that are sufficiently large for dynamic overlap of tracks, the energy transferred may cease to be a random variable. In [10], it was shown that an electronic excitation leads to neutralization and clustering of a copper atom in regions with a radius of about 15 nm. It was also noted in [10] that the characteristic radius of copper atom capture during clustering is approximately equal to the radius of the thermal peak calculated in [13] for amorphous semiconductors. Undeniably, generation of phonons, which leads to the occurrence of thermal peaks, is not the only process induced by electronic excitation. Radiation-induced charge carriers recombine with each other and are also localized separately. In particular, on recombination or trapping of charge carriers, the charge state of optical centers changes and electrically charged microscopic (or nanoscopic) regions are formed [14, 15]. In this section, we will consider the diffusion length and lifetime of the charge carriers formed in ion tracks. The dependence of the volume fraction $V_f$ of ion tracks in the steady state on the ion flux $F_{ion}$ is calculated on the assumption of cylindrical symmetry of tracks.

Since holes are self-localized (i.e., are immobile) in $\alpha$-SiO$_2$ [16], the charge transfer is only due to the migration of electrons from the center to the periphery of tracks. The diffusion length $L_e$ of radiation-induced free electrons determines the characteristic diameter of tracks [17] according to the expression

$$L_e = \sqrt{\frac{k E_{e,h} k_B T}{e^2 \rho}},$$

(1)

where $k$ is the coefficient of radiation-induced electrical conductivity ($3 \times 10^{-12}$ S/cm Gy$^{-1}$), $E_{e,h} \approx 18$ eV is the energy of generation of electron–hole pairs, $\rho$ is the density of $\alpha$-SiO$_2$ (2.23 g/cm$^3$), $e$ is the elementary charge, $k_B$ is the Boltzmann constant, and $T$ is temperature. According to expression (1), an increase in temperature from 300 to 1200 K doubles the value of $L_e$. $L_e$ is about 160 nm at room temperature [17]. Thus, neutralization of copper in solid solution may occur at distances many times larger than 15 nm (the value discussed in [10]). Free electrons arising in ion tracks can also be involved in the charge exchange between neighboring nanoparticles.

The lifetime of free electrons is related to the electron mobility $\mu_e$ by the expression

$$\tau_e = e L_e^2 / \mu_e k_B T,$$

(2)

which was derived using the Einstein formula. The electron mobility (21 cm$^2$ V$^{-1}$ s$^{-1}$) was measured in [18]. Accordingly, the lifetime of free electrons is about $6 \times 10^{-10}$ s at room temperature.

The probability $P$ of dynamic overlap of tracks, according to the Poisson distribution, depends on the ion flux as

$$P = 1 - e^{-V_f},$$

(3)

$$V_f = L_e^2 \tau_e F_{ion}.$$  

(4)

For 3-MeV Cu$^{2+}$ ions, overlap is significant at ion fluxes exceeding $10^{13}$ ions/(cm$^2$ s). At fluxes of $10^{13}$ ions/(cm$^2$ s) (3 $\mu$A/cm$^2$), which are typical of the formation of copper nanoparticles, the track overlap does not exceed $10^{-6}$. However, some part of charge carriers can be captured by traps during times greatly exceeding $\tau_e$ and then recombine with free charge carriers in new ion tracks. These processes may stimulate the formation of nanoparticles at distances of about $L_e$.

**Space Charge at Nanoparticles**

Since copper in solid solution in $\alpha$-SiO$_2$ is mobile only in the Cu$^0$ state [19], neutralization of other states (mainly, Cu$^+$ [20]) facilitates nucleation of nanoparticles. In particular, it was shown for $\alpha$-SiO$_2$ with the Cu$^+$ impurity [10] that ion irradiation initiates clustering if the local energy density transferred to an electronic excitation exceeds some threshold value, which turned