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Effect of the Ion Beam Current Density on the Formation of Implanted Metal Nanoparticles in a Dielectric Matrix

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Abstract—The effect of the ion beam current density, varied within 4–15 $\mu\text{A}/\text{cm}^2$, on the formation of metal nanoparticles in a subsurface layer of SiO_2 substrates implanted with 30-keV Ag^+ ions to a dose of $5 \times 10^{16} \text{ cm}^{-2}$ was studied by optical spectroscopy and atomic force microscopy techniques. An increase in the ion beam current density leads to the formation of nanoparticles of a greater size as a result of the glass substrate heating and due to an increase in the diffusion mobility of implanted silver atoms. These results suggest the possibility of controlling the dimensions of implanted nanoparticles in dielectrics by means of variation of the ion beam current density during the process. © 2003 MAIK “Nauka/Interperiodica”.

Ion implantation is a technologically convenient and effective method for introducing impurities into solids, in particular, for the obtaining of composite materials based on dielectrics containing dispersed metal nanoparticles [1]. Such composites are promising materials for ultrafast-response nonlinear optical devices dealing, for example, with pico- and femtosecond laser pulses [2, 3]. The synthesis of nanoparticles in dielectrics by ion implantation is a complicated process depending on a large number of factors, including ion energy, dose, type, and the dielectric matrix [4]. Recently, we have demonstrated that substrate temperature is an important factor influencing the size and distribution of nanoparticles [5–8].

This study was aimed at determining the influence of another implantation parameter—the ion beam current density—on the formation of nanoparticles.

The substrates for the obtaining of composites were made of a silicate glass (SiO_2 , Heraeus). The glass substrates were implanted with 30-keV Ag^+ ions to a dose of $5 \times 10^{16} \text{ cm}^{-2}$, at an ion beam current density variable from 4 to 15 $\mu\text{A}/\text{cm}^2$. The process was conducted in a vacuum of 10^{-5} Torr using an ILU-3 implanter system. At the beginning of ion bombardment, the substrates occurred at room temperature.

The optical properties of the metal-implanted composite material ($\text{Ag}:\text{SiO}_2$) were studied by absorption spectroscopy. The measurements were performed on a Perkin-Elmer Lambda 19 spectrophotometer. The surface morphology of ion-implanted glasses was studied on a Dimension 3000 scanning probe microscope (National Instruments) operating in the atomic force microscopy (AFM) regime in the tapping mode.

Figure 1 shows the optical transmission spectra of synthesized $\text{Ag}:\text{SiO}_2$ composite layers. As can be seen from these spectra, the samples exhibit selective absorption in the visible spectral range, which is indicative of the formation of silver nanoparticles in the glass matrix and is explained by the plasma polariton resonance of these nanoparticles [9]. The spectra are typical of the silver nanoparticles in a SiO_2 matrix, while a shift of the resonance absorption band toward long-wavelength spectral region with increasing ion beam current density can be related to an increase in the nanoparticle size and in the efficiency of aggregation of the implanted silver atoms [9].

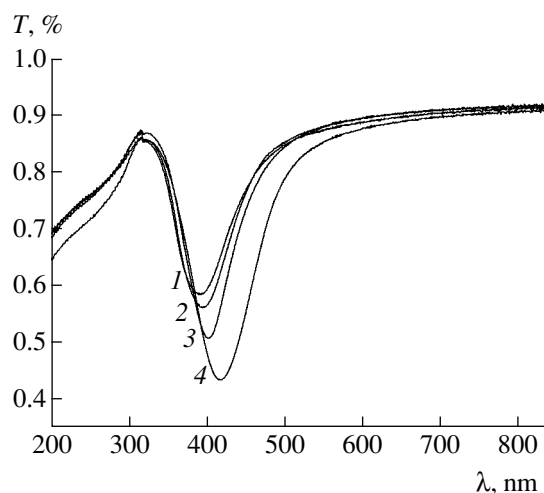


Fig. 1. The optical absorption spectra of SiO_2 implanted with 30-keV Ag^+ ions at various ion beam current densities ($\mu\text{A}/\text{cm}^2$): (1) 4; (2) 8; (3) 12; (4) 15.

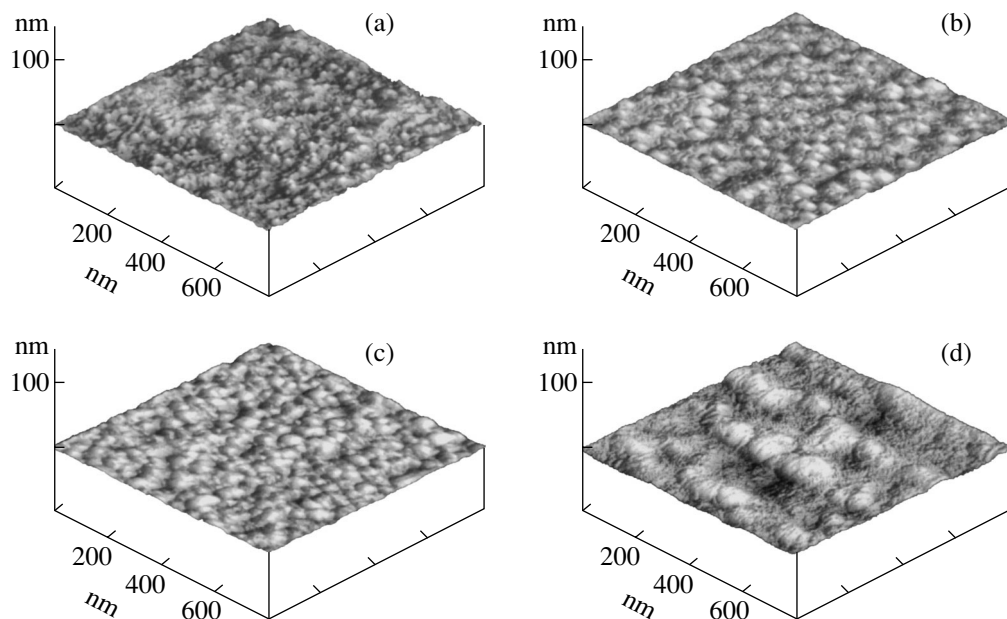


Fig. 2. AFM images of the surface of SiO_2 substrates implanted with 30-keV Ag^+ ions at various ion beam current densities ($\mu\text{A}/\text{cm}^2$): (a) 4; (b) 8; (c) 12; (d) 15.

Previously [10], the depth–concentration profiles of implanted silver were computer-simulated using a DYNA algorithm. The results showed that prolonged ion irradiation (to a dose of $\geq 10^{16} \text{ cm}^{-2}$) leads to a shift of the maximum in the implanted silver concentration profile toward the SiO_2 surface (to a depth of $\sim 10 \text{ nm}$), with a monotonic decrease of the metal concentration in depth of the sample. The effective accumulation of silver atoms to a level exceeding the solubility limit for this metal favors intensive nucleation and growth of nanoparticles immediately at the glass surface. It should be also noted that an important factor in the case of high-dose implantation is the effect of surface sputtering. Estimates show that, in the ion bombardment regime employed, the thickness of a sputtered glass layer amounts to several tens of nanometers [1]. Under these conditions, we may expect that metal nanoparticles can be exposed on the dielectric surface. Indeed, it was demonstrated that, during the high-dose implantation of low-energy ($< 60 \text{ keV}$) Fe^+ ions into SiO_2 [11], Ag^+ ions into Ta_2O_5 , SiO_2 , Si_3N_4 [12, 13], and soda-lime silicate glass [14], and Cu^{2+} ions into Al_2O_3 [15], the formation of metal nanoparticles is accompanied by the appearance of hemispherical protrusions on the dielectric surface.

Figure 2 presents the AFM images of the SiO_2 surface after implantation with Ag^+ ions at various ion beam currents. In contrast to a smooth surface of the initial glass, the morphology of ion-implanted samples is characterized by the presence of hemispherical protrusions reflecting the “emergence” of spherical nanoparticles to the surface as a result of glass sputtering.

This phenomenon provides for a methodological possibility of qualitatively estimating the dimensions of largest nanoparticles synthesized in the subsurface layer. As can be seen from Fig. 2, there is a clear tendency of the size of hemispheres to increase in the glasses implanted at a higher ion beam current density. A comparison of the results presented in Figs. 1 and 2 shows that an increase in the ion beam current density is accompanied by a correlated variation of the optical absorption spectrum (growth of the absorption intensity and shift of the peak toward long-wavelength region) and the AFM images (increase in the size of protrusions indicative of coarsening of the nanoparticles).

The most probable factor responsible for the growth of silver nanoparticles in the samples studied is the increase in the glass substrate temperature during ion implantation. Previously [6], we experimentally demonstrated that the implantation of 60-keV Ag^+ ions to a dose of $4 \times 10^{16} \text{ cm}^{-2}$ at a relatively low ion beam current density ($3 \mu\text{A}/\text{cm}^2$) into silicate glasses maintained at 20 or 60°C leads to the formation of greater particles in the substrates heated to the higher temperature. The results of theoretical modeling [8] indicate that, as the temperature of an ion-irradiated glass matrix increases from 20 to 100°C , the coefficient of silver diffusion in the glass grows by at least three orders in magnitude.

The whole process of nanoparticle synthesis by ion implantation can be divided into several stages, including incorporation of accelerated ions, diffusion, nucleation, and growth. In our experiments, all samples prior to the implantation occurred under equal conditions at room temperature. Different values of the ion beam

current density imply a difference in the number of ions supplied to the target and in the energy flux that is converted into heat. Thus, both the rate of substrate heating (i.e., the temperature gradient) and the temperature of glass are obviously higher under the conditions of greater ion current density. According to our estimates, an increase in the ion beam current density from 4 to 15 $\mu\text{A}/\text{cm}^2$ may increase the temperature of the sample surface layer up to 80–100°C. Comparing these estimates to the results obtained in [6, 8], we may ascertain that temperature-enhanced (thermostimulated) diffusion of metal in the glass takes place under the conditions of implantation at elevated ion beam current densities.

According to this, the higher temperature of the glass matrix and the greater temperature gradient in this matrix increase the diffusion mobility of silver atoms, thus leading to their effective sink to the nuclei and, hence, to coarsening of the nanoparticles (diffusion growth). As a result, a smaller proportion of implanted silver atoms in the “hot” matrix (in comparison to that in the “cold” samples) remain unattached to nanoparticles and stay dispersed in the implanted layer. In addition, heating creates conditions for the coarsening of nanoparticles due to the Ostwald maturation mechanism, whereby smaller nuclei (possessing lower melting temperatures) dissociate into atoms and this material is spent for the growth of other nanoparticles, this also resulting in a decrease in their total number. Apparently, under the implantation conditions studied in our experiments, the substrate temperature not yet reaches a level at which there arises an effective diffusion flow of incorporated atoms from the implanted subsurface layer to deeper layers.

In conclusion, we have established that using higher ion beam current densities during Ag^+ ion implantation into glass leads to the formation of metal nanoparticles of greater dimensions and even to their aggregation, probably as a result of the substrate heating and an increase in the diffusion mobility of incorporated silver atoms. This effect suggests the possibility of obtaining composite materials with the metal nanoparticle size in the subsurface layer controlled by variation of the ion beam current density during implantation.

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