

Electron beam modification of glasses containing Ag and Au nanoparticles

M A Prosnikov¹, A I Sidorov², O A Podsvirov³

¹Ioffe Physical Technical Institute of RAS, Polytekhnicheskaya 26, St.Petersburg 194021, Russian Federation

²ITMO University, Kronverskiy 49, St.Petersburg 197101, Russian Federation

³St.Petersburg Polytechnic University, Polytekhnicheskaya 29, St.Petersburg 195251, Russian Federation

E-mail: yotungh@gmail.com

Abstract. The goal of our work was the investigation of the processes of interaction electrons (5-30 keV) with metal nanoparticles in glasses. The objects of our research were the silicate glasses containing Au and Ag nanoparticles. The experiments have shown that electron irradiation with electron energy 5-10 keV of glass containing Au nanoparticles results in the formation of high reflective gold film about 50 nm thick on a glass surface. Electron irradiation (5-30 keV) of glass containing Ag nanoparticles results in the increase of optical density in the irradiated areas and formation of silver clusters (Ag_x , $x < 5$) in a form of a ring at periphery. Thus, electron beam can be used to produce photonic and plasmonic devices without etching mask.

1. Introduction

The limitation of modern electronics is huge ohmic losses at high frequencies caused by skin-effect. In 1969, Mayer proposed to use light to transmit signals in planar waveguides [1] at optical frequencies, but that imposes restrictions on the minimum size of devices, due to the diffraction limit. An alternative to integrated optics and dielectric photonics proposes the use of nanoplasmonics, with the collective electron oscillations at optical frequencies exciting at nanoscale metal/dielectric interface [2]. The traditional methods of such devices creation, which are mainly the complex shape thin metal films on dielectric substrate, are the optical or electron beam lithography, are multistage and laborious that restrains the development of nanoplasmonics.

In our previous works we demonstrate the possibility of the creation of Cu [3] and Ag [4] nanoparticles in glasses, V nanorods at glass surface [5], and the dissolving of Ag thin film in silica glass [6], under the effect of electron beam irradiation. Thus, electron beam is the powerful and

¹ To whom any correspondence should be addressed.

precision instrument for glass surface or subsurface volume modification, depending of electron energies.

2. Experimental

In the experiments we used: gold-ruby optical glass containing Au nanoparticles (10-50 nm) based on the $\text{SiO}_2\text{-B}_2\text{O}_3\text{-CaO-Na}_2\text{O-SnO}_3\text{-As}_2\text{O}_3\text{-K}_2\text{O}$ system with 0.025 mol% Au; and the glass containing silver nanoparticles based on $\text{Na}_2\text{O-ZnO-Al}_2\text{O}_3\text{-SiO}_2\text{-NaF-NaCl}$, where Ag was introduced by ion exchange from $\text{AgNO}_3\text{:NaNO}_3$ (5:95) melt at 360 °C within 30 minutes. After thermal treatment at 500 °C during 1 hour Ag nanoparticles were formed in ~30 μm subsurface layer. These samples are intense dark-red. It should be noted, that thermal treatment was not carried out in the reducing atmosphere (e.g. hydrogen), thus not all silver ions were reduced. Therefore the glass contains Ag nanoparticles, ions, atoms, neutral and charged small molecular clusters. Both samples were synthesised and prepared in ITMO University and represent the plane-parallel polished plates 2 mm thick. To remove the surface charge that appear on glass during electron irradiation, samples were coated with an Al layer 100 nm thick, which was removed after the irradiation by chemical etching in 10% KOH.

Electron irradiation was performed in high-current JEED-2 scanning electron microscope at electron energy 3-35 keV with the electron current density 40 $\mu\text{A}/\text{cm}^2$. The electron irradiation dose was varied in a range 20-500 mC/cm^2 . The irradiation was carried out at room temperature and according to our calculation, the surface of the samples was heated at less than 250 °C during irradiation at the chosen current and energies.

Heat treatment was performed in computer-assisted muffle furnace (Nabertherm). The optical density spectra were measured by Cary 500 (Varian) spectrophotometer at 300-800 nm spectral region. Luminescence spectra and images were obtained using luminescence microscope MSFU-K (LOMO) with excitation at 400-440 nm. The morphology and thickness of the formed films were studied with ASM Solver-Pro (NT-MDT).

3. Results and Discussion

3.1. Glass containing Ag nanoparticles

After the irradiation of the Ag nanoparticles containing samples by electrons ($E = 5\text{-}30\text{ keV}$, $Q = 20$ and $50\text{ mC}/\text{cm}^2$) one can observe the increase of optical density at irradiated areas. Microphotograph of one of this areas is shown at figure 1. Cross section of absorption through the spot is shown at figure 2. It can be seen the increased absorption at irradiated spot center and, more significantly, on its periphery.

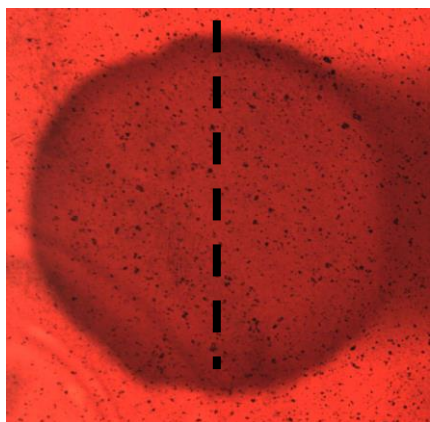


Figure 1. Microphotograph by transmitted light of irradiated zone after electron irradiation with energy 30 keV and dose 50 mC/cm^2 . Diameter of spot is 2 mm.

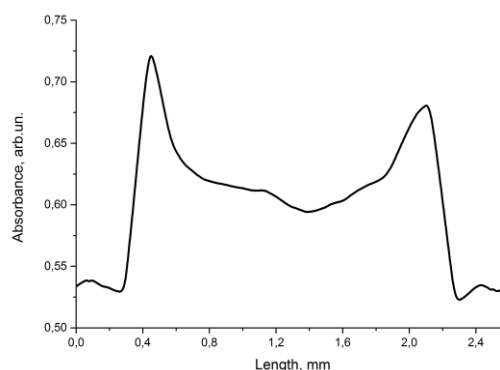


Figure 2. Cross section of absorption through dashed line across the spot at Fig. 1.

The absorption spectra of the irradiated areas for electron energies 5, 10, 20 and 30 keV with the same dose 50 mC/cm² are shown at figure 3. The decrease of optical density at 300 nm region can be caused by the reduction of Ag ions and charged molecular clusters [7] by thermalized electrons. The increase of optical density at 350 nm is due to the formation Ag atoms [7], and the deformed band at 440-480 nm results from the formation of Ag nanoparticles. It should be noted, that the high concentration of nanoparticles leads to their dipole interaction, which causes the offset and deformation of plasmon band [8].

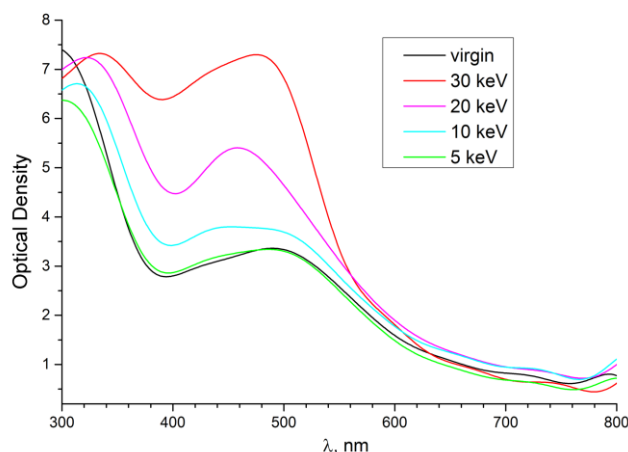


Figure 3. Absorption spectra of the irradiated zones after irradiation with various electron energies (shown at inset) with the same dose - 50 mC/cm².

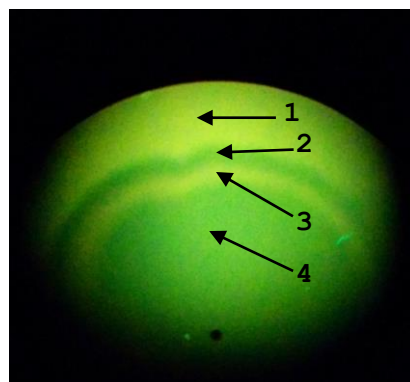


Figure 4. Photo of luminescence of irradiated zone shown at figure 1. Arrows and numbers indicate areas where luminescence spectra at figure 5 were obtained.

Luminescence photograph of one of the spots is shown at figure 4. One can see four zones: 1 – not irradiated zone, 2 – dark ring at periphery, 3 – bright ring, 4 – dark centre of spot. For each of these zones luminescence spectra were obtained (figure 5). For the excitation wavelengths 400-440 nm the contribution to the luminescence makes the neutral silver molecular clusters Ag₂, Ag₃, Ag₄ [9,10]. That way, figure 4 gives the information on the concentration of neutral molecular clusters in the irradiated spot.

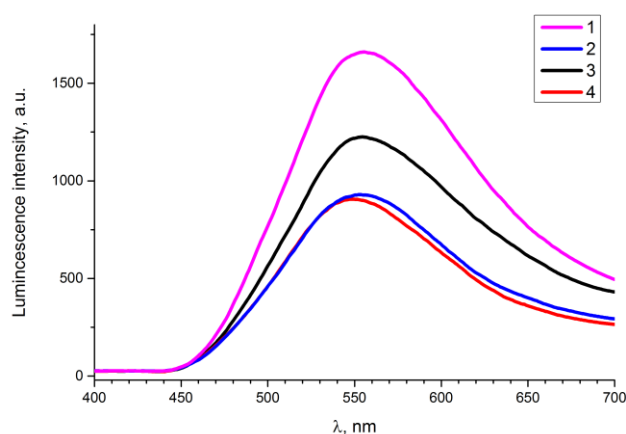


Figure 5. Luminescence spectra of the four zones at figure 4. Excitation wavelength is 400-440 nm.

Electric field strength in glasses due electron irradiation can reach 100 kV/cm [11]. Electric field can cause the decomposition of nanoparticles with metal ion formation, which effect was demonstrated in

[12]. Further, the positive Ag ions can migrate into the region of negative volume charge due to the bell-shaped current distribution in an electron beam cross-section, as is described in [13]. Then the Ag ions are reduced by thermalized electrons and can form nanoparticles of molecular clusters.

3.2. Glass containing Au nanoparticles

After the irradiation of the ruby-glass samples by electrons ($E = 5, 10 \text{ keV}$, $Q = 500 \text{ mC/cm}^2$), one can observe highly reflective gold films at the irradiated areas, which are shown at figure 6.

AFM showed that the created films are about 50 nm thick.

The effect of solid film appearance at the glass surface due electron irradiation can be described as in previous part, except for periodically volume charge depth, $\sim 200 \text{ nm}$ for $E = 5 \text{ keV}$ vs. $\sim 10 \mu\text{m}$ for $E = 35 \text{ keV}$. The periodically volume charge causes the high electrical field strength [11] wherein gold nanoparticles can decompose [12] becoming ions and which migrate to the negative charge area close to the glass surface, where ions can be reduced by thermalized electrons. Then, Au atoms come out to the surface, creating solid gold film. The higher the energy, the deeper the charge and the lower gold atoms leaves to surface, as is shown at figure 6.

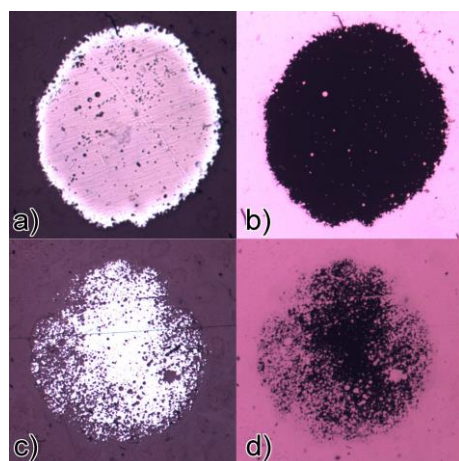


Figure 6. Microphotographs by reflected (a, c) and transmitted (b, d) light of irradiated zones after electron irradiation with a, b – 5 keV, c, d – 10 keV, dose 500 mC/cm^2 . Spots diameter are 2 mm.

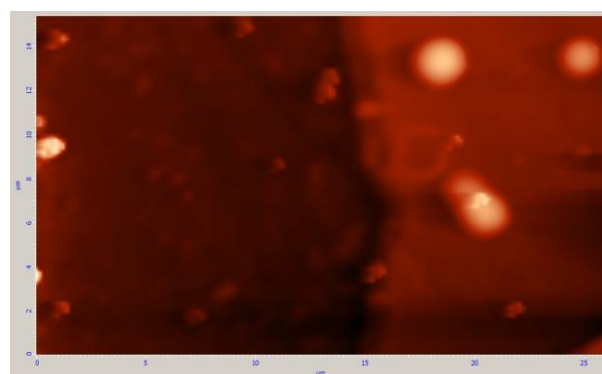


Figure 7. AFM image of periphery of created gold film (right) on ruby-gold glass (left). The film is $\sim 50 \text{ nm}$ thick.

4. Conclusion

It is shown experimentally that the action of electron beam irradiation ($E > 10 \text{ keV}$) on the Ag nanoparticle containing glasses results in the formation of high concentration molecular clusters and nanoparticles in a ring at the periphery of the irradiated area. The higher the energy, the more clearly the evident effect.

The action of electron beam irradiation ($E = 5, 10 \text{ keV}$) on the Au nanoparticle containing glasses results in the formation highly reflective $\sim 50 \text{ nm}$ (island-like for $E = 10 \text{ keV}$, and continuous for $E = 5 \text{ keV}$) gold film at the glass surface.

Both effects are caused by the creation of periodically volume charges due the electron irradiation, the decompose of metal nanoparticles in high strength electrical field, by the ion field migration and by their reduction by thermalized electrons.

The observed effects may be used for the creation of photonic and plasmonic devices without the need of etching masks, at any modern electron lithography setup.

Acknowledgments

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