Modification of silver-containing glass under the action of the electron beam

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Introguction

Metal nanocrystals and nanostructures are widely used in plasmonic devices: plasmonic waveguides and switches, biosensors, luminescent devices, etc. In the glasses, containing metal ions (Ag^+, Au^+, Pt^+, or Cu^+), the classical method of creation of metal nanoparticles is the UV-irradiation with the following thermal treatment. In this work we describe the new method of initialization of silver nanocrystal and film growth near and on the surface in usual and silver-containing glasses – electron-beam irradiation. This process has its own particularities which change kinetics of nanocrystal and film growth in comparison with classical techniques.

Experimental

In our experiments we used two types of glasses:

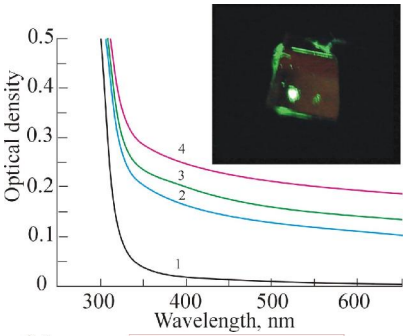
1. Optical glass with the composition SiO_2 - B_2O_3 – Al_2O_3 – BaO – K_2O – Na_2O. Silver film (100 nm) on the glass surface was deposited in vacuum

2. Soda-lime glass with the composition SiO_2-Na_2O-MgO-Al_2O_3-CaO. Silver ions were inserted to the near-surface layer of the glass by the ion exchange method ($Ag^+ \rightarrow Na^+$) in the melt of the mixture of $AgNO_3$ (5 mol.%) + $NaNO_3$ (95 mol.%) at t = 350 °C during 15 min.

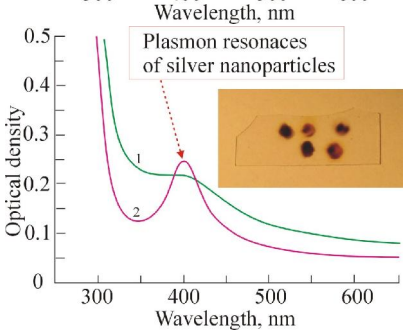
The samples were exposed at RT using SEM JEBD-2 with electron energies 5-20 keV and current density about 20-50 μAcm^{-2}. The dose of irradiation varied between 5 - 50 mCcm^{-2}. The spectra of optical density were measured with Carry 500 UV-VIS-NIR spectrophotometer.

1. Electron energies 20-50 kev

Glasses with the silver film on the surface

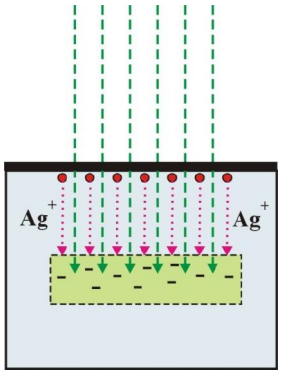


Optical density after deleting of silver film:
1 – without irradiation
2 – E = 30 keV
3 – 40 keV
4 – 50 keV
Q = 20 mC/cm^2



Optical density after deleting of silver film and thermal treatment (500 °C, 1 h):
1 – 40 keV
2 – 50 keV

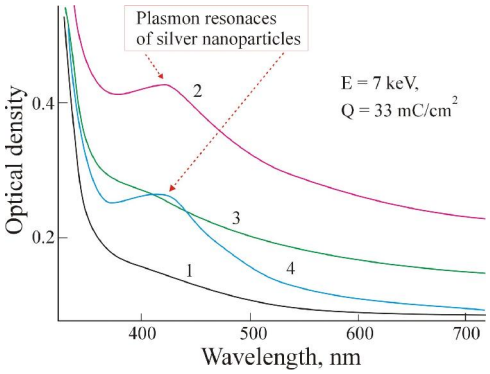
Mechanism of silver film dissolving



Main effect – the dissolving of silver film and the formation of silver nanoparticles under the glass surface

2. Electron energies 5-10 kev

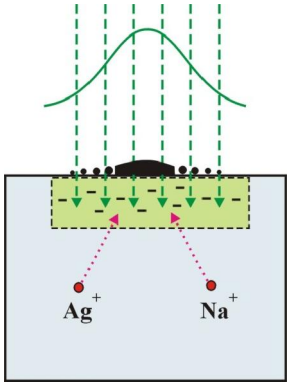
Glasses with the silver ions in volume

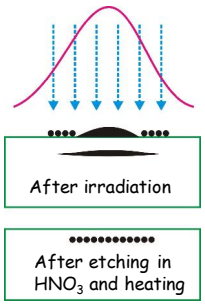


1 – before irradiation
2 – after irradiation
3 – after etching in HNO_3
4 – after heat treatment (350 °C, 3 h)

E = 7 keV

Mechanism of silver films formation





Main effect – the formation of silver films and nanoparticles on and under the glass surface

Summary

- Electron beam action with E = 20-50 keV on a glass with silver film on a surface led to the dissolving of the film in glass volume. During the following thermal treatment silver nanoparticles are formed in a glass volume.
- Electron beam action with E = 5-10 keV on a glass with silver ions in glass volume led to the formation of silver films and nanoparticles on and under the glass surface.
- The main mechanism of both effects – field migration of silver ions to the negatively charged region located under the glass surface.