Formation of metallic nanostructures on the surface of ion-exchange glass by focused electron beam

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Abstract. This paper presents a new method for formation of metallic nanostructures on the surface of ion-exchange glass. The method is based on the interaction of a focused electron beam with ions in ion-exchange glass. In experiments nanostructures with different shapes were obtained, depending on the electrons irradiation conditions.

1. Introduction

Currently, metal nanostructures of different configurations are widely used in photonics and of interest for optical measurements, detection of molecules and device fabrication. Nanoparticles and thin films of silver or gold show plasmon resonances in the visible spectral range [1] and they are used in different photonic devices such as plasmon waveguides, concentrators of surface plasmon waves, microresonators and others. Metal nanoparticles and films produced on the glass substrate amplify the light signal of the studied objects [2] and could be used in sensors, based on surface enhanced Raman spectroscopy [3]. Existing methods of obtaining nanoparticles include chemical synthesis [4], laser ablation [5], vacuum deposition [6] and thermal processing of metal-ion-containing glass in hydrogen atmosphere. [3,7]. Also, formation of metal nanoparticles in a subsurface layer of metal-ion-containing glass could be carried out by exposing them with an electron beam [8,9].

2. Experiment

This paper presents a method for creating metal structures with nanoscale sizes on the surface of ion-exchange glasses. The method is based on the interaction of a focused electron beam with ions in glass and gives opportunity to produce metal structures of various shapes. In the experiments we used Soda-lime glass with the composition of SiO$_2$-Na$_2$O-MgO-Al$_2$O$_3$, where Ag$^+$ ions were introduced in subsurface layer by ion-exchange mechanism by partly replacement of sodium ions with silver ions. Aluminum film with thickness of 90 nm was deposited on the surface of prepared glass for charges drain when glass is irradiated by electrons. Deposition of aluminum film was performed by electron beam evaporator Edwards Auto 500. Focused electron beam exposure was carried out with using a scanning electron microscope (SEM) Carl Zeiss CrossBeam Neon 40 with Raith Elphy Plus
lithography attachment. On the sample surface pattern with an array of disks with a diameter of 200 nm and period of 600 nm was exposed. In experiments we used different exposure parameters: beam current and dose. Acceleration voltage in all experiments was 25 kV. After irradiation, the aluminum layer was removed with a ten percent solution of KOH. Next, the surface of glass was studied with a scanning electron microscope and with an atomic force microscope (AFM) NT-MDT Ntegra Aura. Metal structures were formed in the irradiated areas on the glass surface, and shapes of these structures were circles (figure 1), triangles (figure 2), rectangles or polygons (figure 3) depending on the exposure regime. In our experiments we used three different beam currents: 12, 215, 707 pA and four irradiation doses: 20, 40, 60 and 80 mC/cm². Triangle structures appeared in case of 12 pA beam current and 20 mC/cm² irradiation dose. Expositions with higher doses and 12 pA beam current led to formation of circle structures with diameter of 400 nanometers. Using beam current with 215 pA caused the emergence of polygon structures regardless of irradiation dose. In case of beam current with 707 pA any structures appearance was not detected.

![Figure 1. SEM images of array of circle structures (a) and single circle with wrapped edge (b).](image_url)

![Figure 2. SEM (a) and AFM (b, c) images of array of triangles structures, image (c) presents area of image (b).](image_url)
The study of nanostructures carried out by AFM showed that the height of structures was in a range of 30-40 nm (figure 4). It was also found that obtained nanostructures were inhomogeneous and formed from the multiple clusters. In addition, it was found that formed structures in all cases are surrounded by separated metal clusters with smaller diameters laying in the range of 25-60 nm. Creation of metallic structures with proposed method is reproducible.

Figure 3. SEM (a) and AFM (b) images of array of polygon structures.

Figure 4. AFM image of single triangle structure (a) and its cross section (b).

3. Discussion
Interaction between electron beam and glass with metal film was considered with the use of Monte-Carlo method. In case of 25 kV acceleration voltage of electron beam and 90 nm aluminum film on the glass substrate electrons could penetrate into the glass on distance exceeded 6 microns (figure 5).
Formation of metallic structures on the glass surface is explained as follows. Under electron beam irradiation negatively charged region is formed near the glass surface due to the accumulation of thermalized electrons. Positively charged silver and sodium ions migrate to that area (figure 6), reduce to neutral atoms after interaction with electrons and emerge on the glass surface, forming clusters, and combining in structures at locations where the current density of the electron beam was maximized [10]. In addition, electrons from incident electron beam could ionize neural atoms of silver and sodium, preventing formation of clusters. However, appearance of metal structures and separated clusters between them indicates that process of field migration and combining into clusters more efficient than process of neural atoms ionization by electron beam. Because of ion-exchange, concentration of silver ions exceeds concentration of sodium ions in subsurface layer, so appeared structures composed mainly from silver. Also, formed structures may consists aluminum ions, due to dissolution of the upper metal film under incident electron beam and following field migration of aluminum ions to the negatively charged region.

4. Summary
A new method of the formation of metallic nanostructures on the surface of ion-exchange glasses was presented. Structure formation occurs due to the interaction of a focused electron beam and free metal ions in glass. Shape of the structures can be modified with exposure parameters. This method of metallic nanostructures producing can be used in the fabrication of plasmon devices on glass, because it has the advantages of electron beam lithography (high resolution) while being productive due to small number of process steps.

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