

Modes of silver nanoisland film growth on the surface of ion-exchanged glass

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Abstract. The behavior of silver nanoisland film growth on the surface of ion-exchanged glasses processed in the air and in hydrogen atmosphere is compared. The films grown in air degrade with the increase of processing time because of oxidizing. The growth of the film in hydrogen atmosphere tends to saturate with time due to the decrease in the flow of atomic silver towards the glass surface. This is because of the formation and growth of silver nanoparticles in the bulk of the glass, these nanoparticles being the preferable sink for silver atoms.

1. Introduction

Last decades metal island films (MIF) are of interest for photonics and plasmonics because of high local electric field formed in the vicinity of metal nanoislands irradiated with a light capable of excitation of surface plasmon resonance (SPR) [1]. This enhancement of the electric field provides high efficiency of Raman scattering in the agent deposited onto MIF [2], their good catalytic abilities [3] as well as high optical nonlinearity of transparent media embedded with metal nanoparticles [4]. Recently a technique to grow MIF, which is based on out-diffusion of metal from glass containing reducible ions under thermal processing of the glass in hydrogen, has been proposed [5]. This paper is aimed at the study of MIF growth dynamics on the surface of silver ion-exchanged glass under their thermal processing in the air and in hydrogen.

2. Experimental

In the experiments we grow silver nanoisland film (SNF) on the surface of ion-exchanged glass in the course of out-diffusion of neutral silver from the glass matrix enriched with silver ions in silver-sodium ion exchange processing as described elsewhere [6,7]. Soda-lime glass slides were ion-exchanged in the bath containing 5 wt.% of AgNO₃ and 95 wt.% of NaNO₃ at 325°C for 20 min. We annealed the ion-exchanged slides in the air and in hydrogen at temperatures varied in the range of 78-300°C during 10-320 min. The behaviour of SPR in the grown films was characterized using optical absorption spectroscopy, for this we used differential optical spectra obtained via subtraction of the spectra measured after removal of the grown film from the glass surface from the spectra measured after preparing the samples. This allowed us obtaining optical absorption spectra (optical density, OD) of the film itself without the influence of silver nanoparticles which grow in the bulk of the glass [8]. Topography of the silver nanoislands and their concentration were studied with atomic force microscopy (AFM). We also characterized the SNF grown on the surface of the ion-exchanged glasses stored at room temperature in air for a long time.

3. Results and discussion



Thermal processing of the glasses in the air resulted in the growth of SNF, which was evidenced by the formation of optical absorption peak corresponding to the SPR in the silver nanoislands, which is definitely because of water vapors in-diffusion [9], silver reduction and out diffusion. One can see that the increase in the SPR absorption is followed by its degradation at higher temperatures, see Figure 1, where the height of the SPR peak is plotted as the function of the annealing temperature.

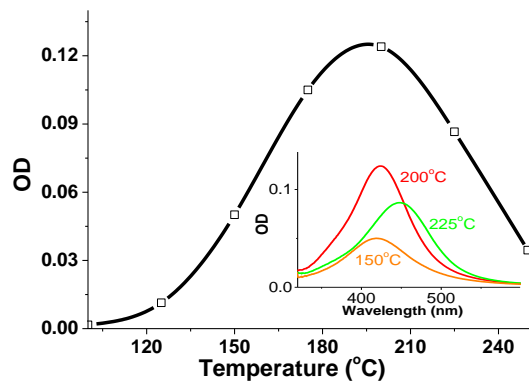


Figure 1. The height of the SPR absorption peak vs processing temperature. The samples are annealed for 10 min in the air. Inset: typical absorption spectra of the grown SNF.

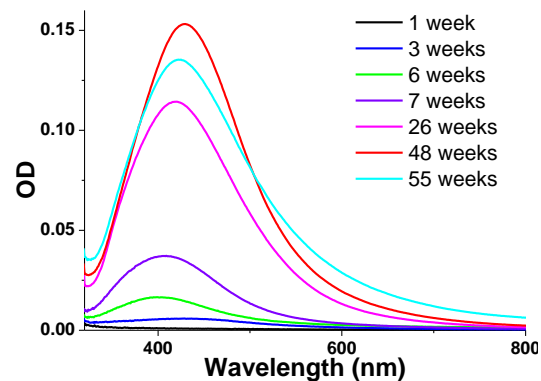
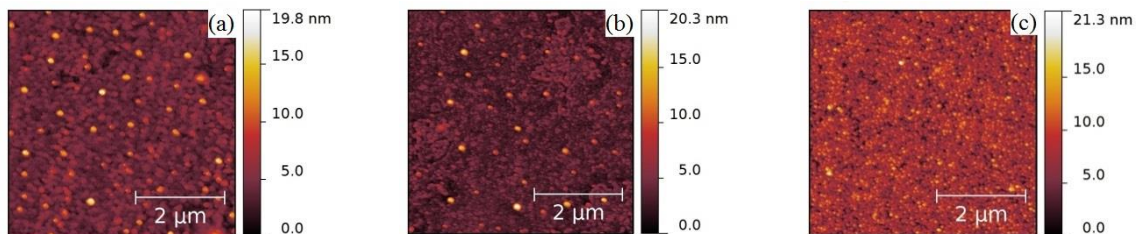


Figure 2. The absorption spectra of the ion-exchanged glass stored in the air at room temperature for 3-55 weeks.

AFM image of silver nanoislands grown in such anneal (Figure 3) show that longer processing in the air results in decreasing of both surface concentration of the nanoislands and their average size. This allows concluding that the most probable reason of the degradation is the oxidation/sulfidation of silver nanoparticles and back diffusion of silver into the glass matrix.

It is essential that the ion-exchanged glasses stored in the air at room temperature have also demonstrated the growth of SNF (Figure 2). In this case, optical absorption peak is wider comparatively to thermally-processed samples. Also the dispersion in the SPR peaks height is much wider, most probably this is because of defects of the glass surface. Despite this, the peak magnitude saturates with time. This allows concluding that only silver ions reduced in a very thin subsurface layer of the ion-exchanged glass make input in the film growth. AFM image of a SNF formed after storage in air of the ion-exchanged glass slide is presented in Figure 4.



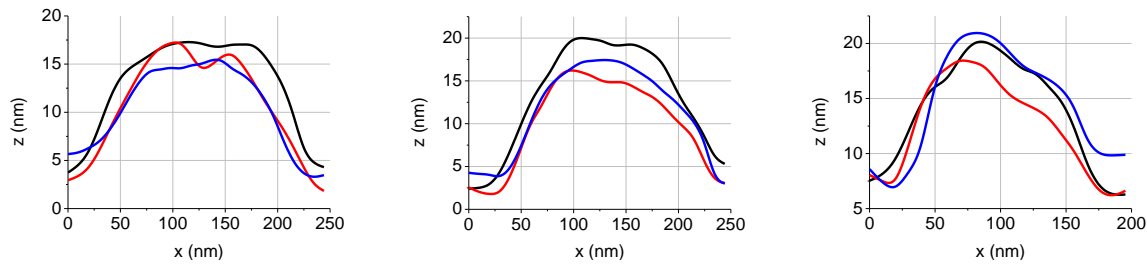


Figure 3. AFM images [3] and corresponding profiles for three nanoislands of MIF formed after 10 min processing of ion-exchanged glass in the air at 150°C (a), 200°C (b) and 250°C (c).

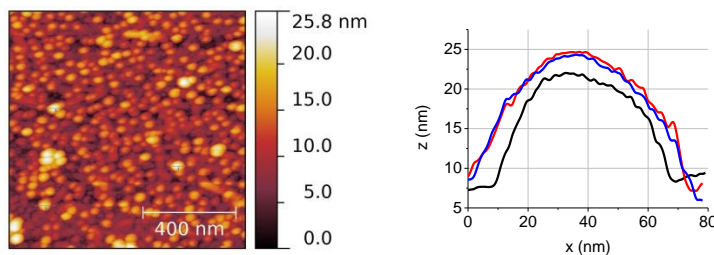


Figure 4. AFM image and corresponding profiles for three nanoislands of MIF formed after storing of ion-exchanged glass in air atmosphere at room temperature for 55 weeks.

Contrary, SNF formed under thermal processing of the glass slides in hydrogen are highly stable at room temperature and do not demonstrate any change after long storage in air. This allows concluding about the absence of silver ions and atoms in a subsurface layer of the glasses processed in hydrogen. Annealing of the glass samples in hydrogen

resulted in a monotonous growth of the SPR absorption peak with the increase of the processing temperature (Figure 5). However at higher temperatures temporal dependence of the peak magnitude shows saturation (Figure 6) because of the nanoparticles growing in the bulk of the glass, which behave as powerful sink for silver atoms. Measured with AFM lateral size of silver nanoislands grown in hydrogen varies from 20 to 400 nm depending on the mode of hydrogen anneal.

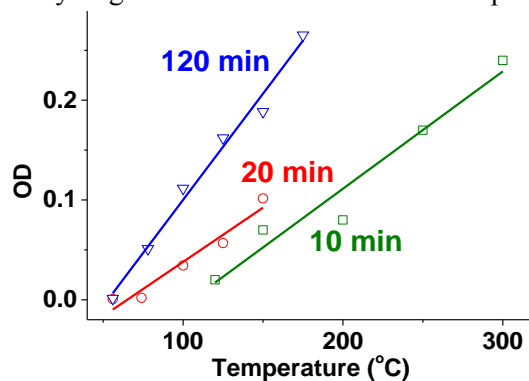


Figure 5. The dependence of the height of the SPR absorption peak on the temperature of annealing the samples in hydrogen for different durations of the annealing.

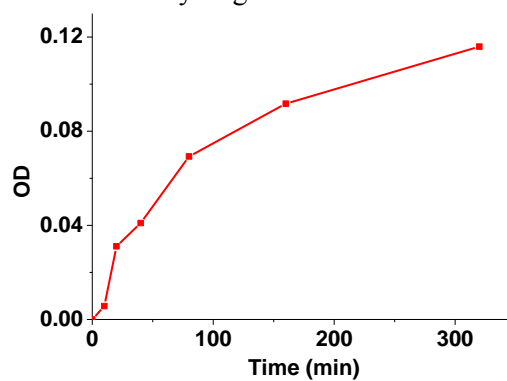


Figure 6. The dependence of the height of the SPR absorption peak on the duration of annealing the samples in hydrogen at 100°C.

Annealing of ion-exchanged glass slides in hydrogen at lower temperatures has also allowed us precise formation of SNF, AFM images of which are presented in Figure 7. Here one can see that formed nanoislands are only slightly less in size than the nanoislands formed at higher temperature, however

their concentration is essentially less. This evidences the preference of surface diffusion over the diffusion from the bulk of the nanoparticles in the nanoislands growth [10].

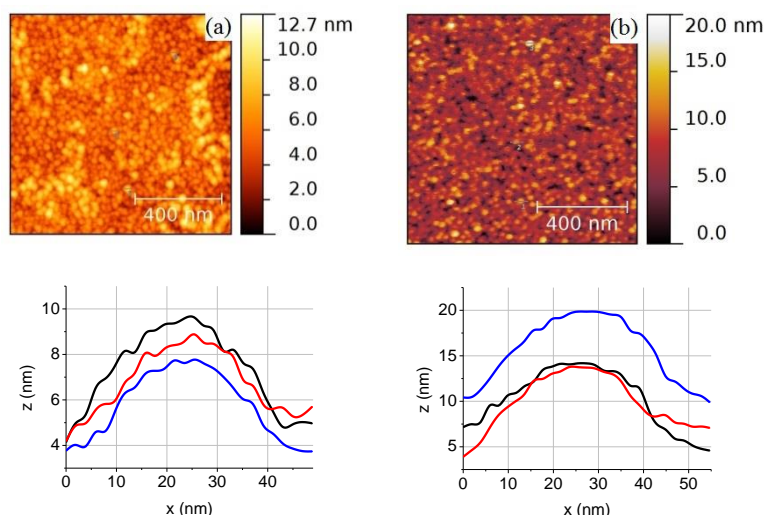


Figure 7. AFM images and corresponding profiles for three nanoislands of MIF formed after 120 minute processing of ion-exchanged glass in hydrogen atmosphere at 78°C (a) and 175°C (b).

4. Conclusion

The behavior of silver nanoisland film growth on the surface of ion-exchanged glasses processed in the air and in hydrogen atmosphere is compared. The SNF grown in hydrogen demonstrate linear growth of the SPR absorption peak amplitude with the temperature increase. This indicates the augmentation of silver concentration on the glass surface during the process. In contrast, the films grown in air degrade with the increase of processing

temperature that is most probably because of oxidizing of the film. Films grown in H_2 atmosphere are highly stable in the air because of the absence of silver ions and atoms in the subsurface layer of the processed glasses.

Acknowledgments

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