

Control of surface plasmon resonance in out-diffused silver nanoislands for surface-enhanced Raman scattering

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Abstract. We present the studies of self-assembled silver nanoislands on the surface of silver ion-exchanged glasses. The nanoislands were formed by out-diffusion of reduced silver atoms from the bulk of the glass to its surface. Control of silver ions distribution in the glass by thermal poling after the ion exchange allowed formation of relatively big, up to 250 nm, isolated silver nanoislands while without the poling an ensemble of silver nanoislands with average size from several to tens of nanometers with random size distribution was formed. The nanoislands were characterized using atomic force microscopy and spectral measurements. We used optical absorption spectroscopy for “random” nanoislands and dark field scattering spectroscopy for isolated ones, corresponding spectra showed peaks in the vicinity of 450 nm and 600 nm, respectively. The “random” nanoislands significantly enhanced Raman scattering from Rhodamine 6G, also the modification of Raman signal from deposited on the surface of the samples bacteriorhodopsin in purple membranes was registered.

1. Introduction

Nowadays, the development of ultrasensitive biosensors is one of the priority scientific and engineering problems, and sensors based on surface-enhanced Raman scattering (SERS) are of particular interest [1]. Recently the ensembles of self-assembled nanoislands that are metal island films (MIF) have attracted attention as SERS-active substrates [2,3]. MIF provide the excitation of surface plasmon resonance (SPR) which increases local electric field of incident light-wave. This E-field enhances Raman scattering from biomolecules or other analytes [4,5]. The spectral position of the SPR can be tuned via varying of MIF formation conditions, which influence size distribution, concentration and shape of the nanoislands [6], and the substrate and cover materials used [7]. These also influence the Raman scattering enhancement which can be as high as $\sim 10^{10} - 10^{11}$ [8].



MIF are conventionally fabricated via depositing metals onto dielectric substrates using thermal and e-beam evaporation, sputtering, and chemical or plasma-chemical metal deposition [9]. Here we use the formation of silver nanoparticles on the surface of a silver ion-exchanged soda-lime glass in the course of out-diffusion during annealing the glass in hydrogen [2]. Recently developed technique employing thermal poling treatment of silver-enriched glass with profiled anodic electrode followed by the annealing of the glass in hydrogen [10] has also allowed us to form single nanoparticles. Such 2D-structuring modifies electrodynamic properties of the MIF that expands their applicability as SERS substrates.

2. Sample fabrication

2.1. Self-assembled silver nanoisland MIF fabrication

For SERS experiments we use self-assembled silver nanoisland films. The fabrication process starts from 20 minutes ion exchange step, for which a soda-lime glass slide [11] is placed in $\text{Ag}_{0.05}\text{Na}_{0.95}\text{NO}_3$ melt heated up to 325°C . As the result of thermally-activated silver-sodium ion exchange, the subsurface layer of the glass is enriched with silver ions.

After the ion exchange step the glass substrate is treated for 10 minutes in hydrogen atmosphere at the temperature of 250°C . Hydrogen diffused into the subsurface glass layer reduces silver ions. Due to the low solubility of neutral silver in the glass matrix silver atoms coagulate and form an ensemble of randomly distributed nanoislands on the glass surface [2].

2.2. Single silver nanoisland fabrication

To grow isolated systematically placed silver nanoislands we use modified technique [10]. In the fabrication procedure described in subsection 2.1, after the ion exchange step we include thermal poling of the glass with profiled anodic electrode (square net of $300 \times 300 \text{ nm}^2$ deepenings with the periodicity of $5 \mu\text{m}$) to alter silver ions distribution in the glass under the electrode. In the poling, the ion-exchanged glass is heated up to 300°C while applied voltage is 500 V. After the poling for 4 minutes 30 seconds the sample is treated for 30 minutes in hydrogen atmosphere at the temperature of 250°C . As the result silver reduction is prevented in poled regions as schematically shown in Figure 1. To avoid degradation of the sample in the air, the surface with patterned nanoislands is coated with 5 nm titanium dioxide layer using atomic layer deposition (ALD) technique [3,12].

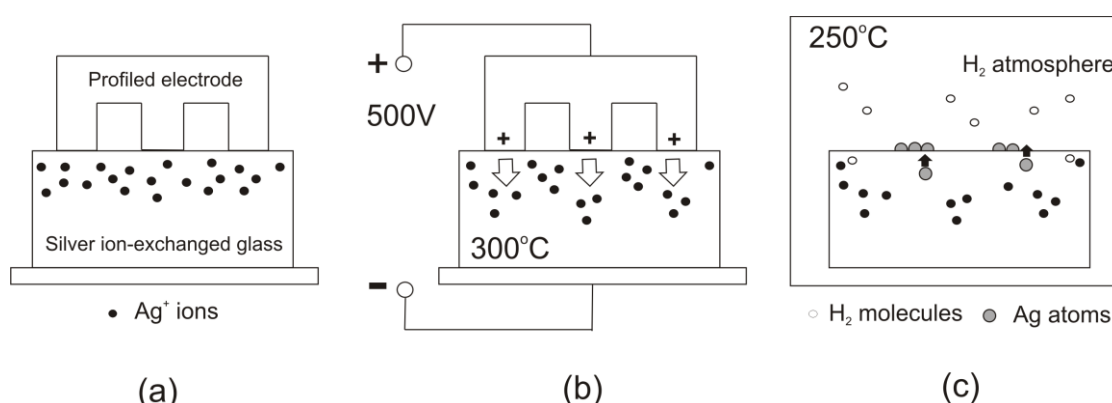


Figure 1. Single silver nanoislands fabrication: (a, b) poling treatment; (c) formation of patterned silver nanoisland film under thermal annealing in hydrogen atmosphere.

3. Studies of the samples

The silver nanoislands were characterized using an “Aist-NT” atomic force microscope (AFM); we also used an UV VIS spectrophotometer Specord 50 to measure optical absorption spectrum of self-

assembled silver nanoisland film and a dark field setup with spectrometer Horiba LabRAM HR UV-VIS-NIR to characterize the spectral properties of single (isolated) nanoislands. In the dark field setup we used s-polarized light from a halogen lamp focused at the sample surface with M Plan Apo 10x/0.26 objective lens. Scattered light was collected with 100x/0.7 objective lens.

AFM images of the samples are shown in Figure 2. It is seen that the glass poling after the ion exchange allowed formation of isolated, relatively big, up to 200–250 nm, silver nanoislands on the surface while without the poling stage randomly distributed silver nanoislands up to tens of nanometers in size were formed.

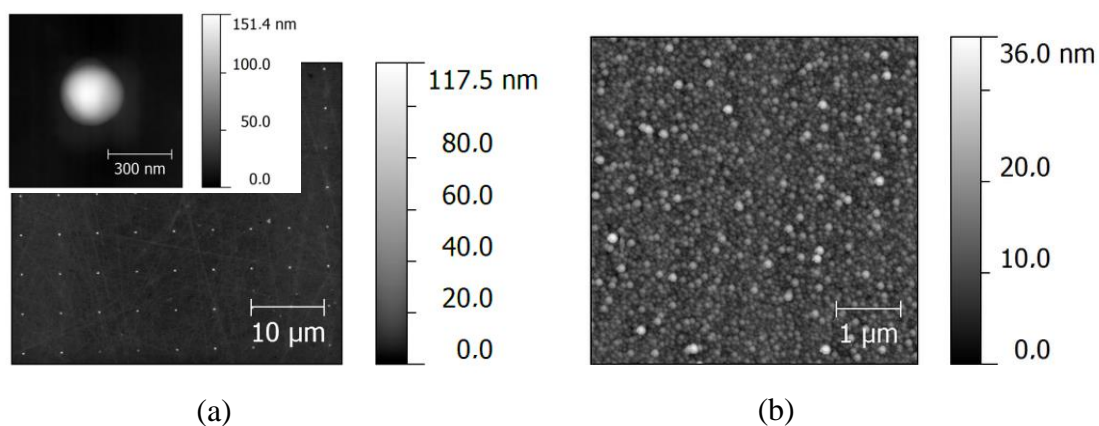


Figure 2. Typical AFM images of the fabricated samples: (a) patterned silver nanoisland film with isolated nanoislands on the glass surface; (b) self-assembled silver nanoisland film with random distribution of silver nanoislands.

The optical absorption spectrum of “random” nanoisland film is presented in Figure 3a, the absorption peak at 430 nm corresponds to the SPR in the MIF [12]. Being used as a substrate for Raman spectroscopy this sample is capable to provide a signal enhancement for laser excitation wavelength in the vicinity of 430 nm [13]. It is worth to note that one can move the SPR peak within the range of 420–470 nm via varying the mode of the nanoislands growth, as it was shown in Ref. 10 (see Fig. 3b).

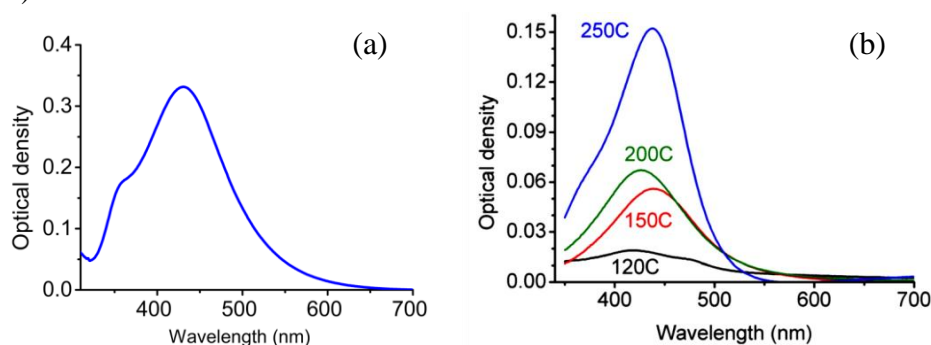


Figure 3. Absorption spectra of the “random” silver nanoisland film under study (a) and of MIF prepared under different annealing temperature (b) [10] (adopted from S. Chervinskii, V. Sevriuk, I. Reduto, A. Lipovskii *Journal of Applied Physics* **114**, 224301 (2013). Copyright 2013, American Institute of Physics).

The dark field spectra and corresponding AFM images of several single nanoislands are shown in Figure 4. All chosen nanoislands have approximately the same round shape in the plane, but vary in

height. One can see that the height difference of a few nanometers results in a shift of the SPR peak by about 10 nm. In comparison with “random” silver nanoislands film, the system of single nanoislands is more flexible to control the SPR position and change spectral properties of samples. Detailed studies and modeling of the SPR in single nanoisland structures are presently in progress.

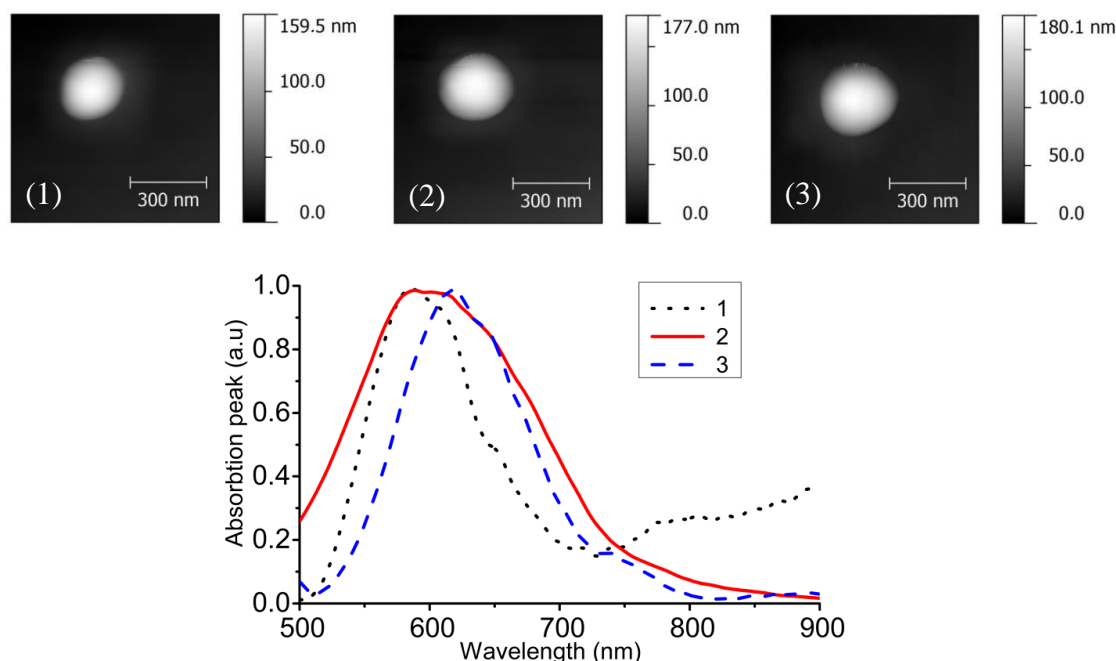


Figure 4. AFM images and corresponding dark field spectra of several single nanoislands.

4. Silver nanoisland films as SERS substrates

We tested the self-assembled silver nanoisland film as a substrate for surface enhanced Raman spectroscopy (SERS) using a dye Rhodamine 6G (R6G) and a protein Bacteriorhodopsin embedded in purple membranes (BR in PM) [14]. For the measurements we used a confocal Raman spectrometer Horiba LabRAM HR UV-VIS-NIR and a frequency-doubled (532 nm) continuous-wave Nd:YAG laser. The laser beam was focused at the sample surface with a 50x/0.55 objective lens. The beam waist was approximately 1.5 μm .

The Raman spectrum shown in corresponds to the monomolecular layer of R6G prepared via drying a drop of 10 μl 10^{-6} M R6G aqueous solution with ~ 7 mm diameter of the spot remained on the substrate. The registered R6G spectrum is in a good agreement with literature [15]. The Raman spectrum from the R6G monolayer deposited on a virgin glass could not be measured because of extra low level. The absence of the reference spectrum did not allow the evaluation of the signal enhancement using standard procedure [16]. Nevertheless, achieved sensitivity is comparable with the reported one for a similar plasmonic structure and measurements conditions [17].

Figure 6 presents BR in PM Raman spectra obtained after drying of 5 μl droplets of water with the membrane concentration of 0.48 and 0.048 mg/ml deposited on both the prepared substrate with “random” nanoislands and a virgin glass. The droplets were dried in the dark at room temperature to form spots of diameter ~ 3 mm. For the concentration of 0.48 mg/ml characteristic Raman spectra corresponding to known purple membranes spectra [18] were registered using both pure glass and silver nanoisland film. One can see more pronounced Raman peaks in the SERS spectrum, for example at ~ 858 cm^{-1} , ~ 1375 cm^{-1} , and ~ 1610 cm^{-1} , in contrast to Raman signal obtained from BR deposited onto the virgin glass. This difference may be because of the influence of silver

nanoparticle plasmonic field on retinal photoisomerization process in BR [19, 20] and the dependence of electromagnetic enhancement factor on the distance between chemical bonds of the analyte and the metal surface [21]. The reduction of the BR in PM concentration by an order of magnitude resulted in resolved Raman signal only from the substrate with nanoislands.

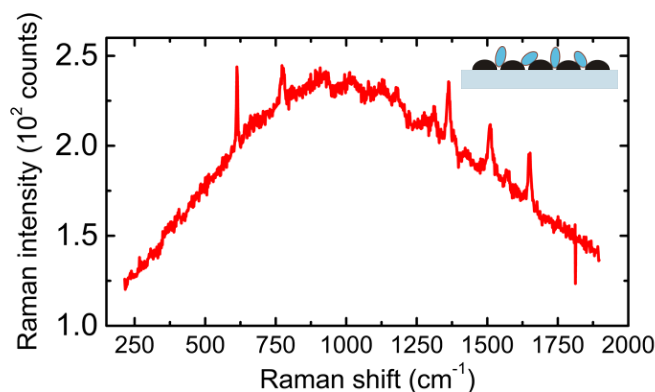


Figure 5 R6G SERS spectrum acquired at laser power of 20 nW, 30 s exposition, 1.5 μm beam waist. Adopted from [14]. Inset: positioning of R6G between the nanoislands.

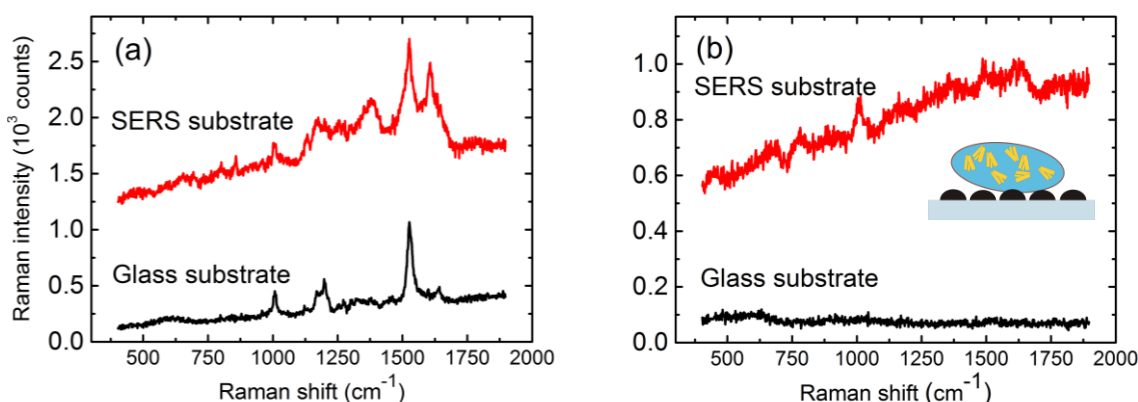


Figure 6. Raman spectra of BR in PM in the concentrations of (a) 0.48 and (b) 0.048 mg/ml. The black and red curves correspond to reference Raman spectra of BR on pure glass substrate and SERS spectra of BR deposited on the nanoisland film respectively. The spectra were acquired at laser power of 200 μW , 50 s exposition, 1.5 μm beam waist. Adopted from [14]. Inset: positioning of BR in PM relatively to nanoislands.

It is also worth to note that a purple membrane thickness is about 5 nm and typical lateral size is of the order of several hundreds of nanometers [22]. Therefore, contrary to R6G, BR in PM is unable to penetrate between the nanoislands where the local enhancement of the electric field of the light wave is maximal as illustrated with the insets in Figure 5 and Figure 6. These results in an essentially weaker Raman signal from BR in PM compared to one obtained from R6G molecules despite the fact that semispherical form of the silver nanoislands provides the highest enhancement in comparison with other design of silver nanostructure [23]. This feature of analytes containing bigger structural units should be taken into account for optimal choice or design of SERS substrates [24].

5. Conclusions

We fabricated the self-assembled silver nanoisland film by means of diffusion during silver-sodium ion-exchange and following hydrogen annealing and isolated single silver nanoislands using thermal poling with profiled electrode as the intermediate step. The samples demonstrated different surface distribution of nanoislands, with size up to 50 nm for nanoislands in MIF and of 250 nm for the isolated nanoislands. This resulted in differing optical characteristics: the SPR peak position and the position dependence on nanoislands size.

Performed SERS measurements of the R6G dye and a protein allowed us to verify the capability of the fabricated silver nanoisland films to enhance Raman signal from different type of analytes. The obtained results properly correspond to known Raman spectra of these analytes.

Acknowledgements

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