Long-Term Stable Structures Formed by Ion-Beam Modification of Silver Film for SERS Applications

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Abstract. Ensembles of silver nanoparticles (NPs) with size ~45 nm formed from the silver film using an ion beam modification are studied. The optical spectroscopy demonstrated that the fabricated ensembles of silver NPs keep stable their plasmonic properties in an ambient atmosphere for at least 39 days due to their monocrystalline nature. We use the scanning Raman microscope to map the SERS from Crystal Violet homogeneously adsorbed on these ensembles. It was found that the manufactured ensembles have a strong amplification factor, and this factor is preserved for these ensembles even after more than one month of storage in the surrounding atmosphere. Hereby, by ion beam modification of silver film, it is possible to fabricate the NPs with stable plasmonic properties and form nanostructured surfaces to be applied in sensor technologies and SERS.

1. Introduction

Controlled and reliable field enhancement (FE) effects associated with the excitation of plasmons in resonant metal nanostructures [1,2] is an essential aspect for the development of new sensors, especially for applications in surface-enhanced Raman spectroscopy (SERS) [3-5]. Noble metals nanoparticles (NPs) providing localized surface plasmon resonance (LSPR) are of increasing interest for application in optics, catalysis, electronics, sensing, for the development of ultra-bright and stable single-photon sources. The practically important issue is the stability of plasmonic properties, which often limits the use of some metals due to their chemical reactivity.

Silver is one of the metals exhibiting excellent plasmonic properties [6,7] that can be used in the above mentioned applications. There are many strategies for the fabrication of plasmonic nanostructures using silver. Different approaches such as particle formation by evaporation or sputtering, high-fluency ion implantation, chemical and photoreduction, production from colloids, etc. were suggested. Many of them allow the formation of nanomaterials with attractive efficiency. However, rapid oxidation or sulfidization of silver in the ambient atmosphere dramatically decreases all bonuses of this metal and cause complications in terms of practical applications [8, 9]. Recently, it has been shown that silver NPs formed by a cluster beam depositional technic exhibiting great stability of plasmonic properties and strong resistance to oxidation due to the monocrystalline nature [10-12]. In this work, we have
demonstrated the possibility to fabricate monocrystalline silver NPs with stable plasmonic properties using a combination of dual magnetron sputtering system and ion beam modification technique [13-15]. This method allows us to control the size and surface coverage of NPs, and we anticipate that the obtained results are very promising for further sensing applications.

2. Samples Fabrication

The coating process is carried out in a high-vacuum chamber with preliminary pumping up to 10^{-5} Torr, followed by the synthesis in an argon atmosphere at a residual pressure of about 10^{-4} Torr. The cover glass and Si are used as substrates. Before applying the coating, the surface of the substrates is preliminarily etched by the ion beam 1 keV energy for 5 min. A thin coating is deposited by RF magnetron with a silver target with a purity of 99.99% are used. The discharge power is approximately 30 W. The obtained coating consists of the film with a thickness of ~20 nm. The quoted “thickness” of the silver films is the average nominal coverage values measure by the quartz oscillator. After the deposition, the argon-ion irradiation of 150 eV energy and 20 mA current is applied to the deposited films to form the NPs. The ion beam is produced by Hall-effect ion source with cold hollow cathode Klan 53-M (Platar Corp.). Figure 1(a) shows schematically the sample fabrication process. Here we use electron-beam lithography (EBM) to make silver discs of about 500 nm diameter. The introduction of ion irradiation leads to the formation of discs consisting of nanoparticles, in which an average size is near 45 nm (Figure 1(b)). Thus, we show that the method allows not only to create an extended surface covered with nanoparticles, but also the ability to nanostructured the surface.

![Diagram](image1.png)

**FIGURE 1.** (a) The schematic illustration of fabrication of sample with Ag NPs, (b) SEM images of Ag film with a thickness of ~20 nm deposited by RF magnetron on Si substrate (left-up). Formed Ag NPs after the argon-ion irradiation (left-bottom) and final structures with Ag NPs.

3. Samples Characterization

After the formation of NPs, the samples are characterized by UV-Vis-NIR spectrophotometer Agilent Technologies Cary 5000 (175-3300 nm). Optical spectra of the samples with ensembles of silver NPs are presented in Figure 2(a) and show the LSPR band with a maximum at near 418 nm. The intensity and spectral position of the plasmon band was monitored for 39 days. After 7 days, the resonance band becomes slightly red-shifted and its intensity was insignificantly decreased. In the period between 7 and 23 days, the intensity was slowly decreasing and the band became even more redshifted. After 39 days, the band intensity decreased to less than 10% from the origin intensity, thus demonstrating the excellent stability of the optical properties. The possible reason for the observed insignificant redshift and decrease in intensity can be the beginning of the formation of an oxide shell due to interaction with an ambient atmosphere. Additionally, we made the X-ray photoelectron spectroscopy (XPS) analysis. The spectra taken 0 and 14 days after NPs formations do not show any measurable difference in the peak positions or intensities (Figure 2a insert).
The Raman measurements were performed in order to estimate the applicability of the fabricated samples for SERS. We used a confocal Raman microscope Horiba LabRAM HR Evolution. The measurements were conducted with a laser wavelength of 633 nm, 600 lines/mm diffraction grating, integration time 0.5 sec., 100× objective (N.A.=0.9) and with the incident power ~0.3 mW. All samples were covered by 10⁻⁶ M water solution of Crystal Violet (CV) and dried under ambient conditions. The measurements were carried out on the sample kept in an ambient atmosphere for 39 days after the fabrication. The typical SERS spectra obtained from the sample with ensembles of Ag NPs (0, 14 and 39 days after the fabrication) are shown in Figure 2b. Spectra demonstrate relatively similar intensities for the samples with are kept in an ambient atmosphere for 0 and 14 days. The SERS intensity recorded for the sample after 39 days in the ambient atmosphere is a little bit less ~ 10-15% (Figure 2(b)), demonstrating high stability silver NPs even after prolonged exposure to the laboratory environment.

![Figure 2](image)

**FIGURE 2.** (a) Evolution of the relative absorption of a sample with Ag NPs as a function of time. Insert XPS spectra obtained from the sample at the day of formation NPs and after 14 days. (b) SERS spectra of CV with concentration 10⁻⁶ M adsorbed on ensembles of silver NPs and obtained after 0, 14 and 39 days after the formation NPs on the glass substrate.

Finally, the analytical enhancement factor (EF) was used to compare a signal increase in SERS, with that in ordinary Raman under the same experimental parameters [16]. The average EF is estimated to be ~0.82×10⁵ for the ensembles of NPs after 0 days and ~0.67×10⁵, after 39 days, respectively. Thus, it is possible to create samples using all the advantages of silver and with the ability to use a long time.

4. Conclusion
We demonstrate the possibility of fabrication of the silver NPs with the great stability of plasmonic properties by the ion beam modification technique. The SERS characterization demonstrated that the manufactured ensembles have a strong amplification factor. The average EF is estimated to be ~0.82×10⁵ for the ensembles of NPs after 0 days and ~0.67×10⁵, after 39 days, respectively. Thus, it is possible to create samples using all the advantages of silver and the ability to use them for a long time. Considering the high stability of the plasmonic properties of our silver NPs, the presented technic can be interesting for the sensor technologies and SERS applications.

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