2022

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Funder: Irish Research Council

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Abstract.

Thermal dewetting of silver thin film can lead to SERS-active Ag nanoparticles. Here, we report our progress towards using scanning probe energy loss spectroscopy (SPELS) to map the plasmonic behaviour of SERS-active Ag nanoparticles (NP) by investigating NPs produced through the dewetting study of Ag thin films on SiO_2/Si and Ti/SiO_2/Si substrates. The nanoparticles size and spatial distribution were controlled by the deposition and thermal annealing parameters. The results of preliminary SPELS measurements of these structures, alongside SERS data show that there is a correlation between the Raman enhancement and the nanoparticle size and interparticle spacing.

1. Introduction

Raman spectroscopy is a widely used tool for the detection of target molecules in forensic, environmental, pharmaceutical and diagnostic applications. Surface-enhanced Raman (SERS) overcomes the low sensitivity of conventional Raman by enhancing optical fields through resonant coupling with localised surface plasmon resonances (LSPR) in metal nanostructures. Molecules adsorbed on such structures experience significantly enhanced Raman scattering [1], improving sensitivity to the point of single-molecule detection. In our previous communication [2], we have proposed that scanning probe energy loss spectroscopy (SPELS), which utilises field emission of electrons from an STM tip followed by detection of backscattered electrons from the surface to produce highly localised electron energy loss spectra, may be used to map the plasmonic behaviour of SERS-active nanostructures. In this paper, we present our current progress towards plasmon mapping of SERS-active nanostructures using SPELS. NP have been produced on silicon substrates by dewetting of thin silver films. The morphology of these films has been characterised by atomic force microscopy (AFM), preliminary SPELS measurements have been performed and their SERS enhancement factor has been assessed using Raman measurements of μM solutions of the Rhodamine 6G (R6G) molecule.

2. Experiment

For SPELS measurements a 30 nm-thick Ag film was deposited onto Si(111) in ultrahigh vacuum using electron beam evaporation. The native oxide was retained on the silicon to inhibit alloying and was assumed to be 2 nm thick. The film was deposited at room temperature and annealed at 700 °C for 30 min in vacuum. SPELS measurements were performed using a modified STM setup that is described elsewhere [3, 4]. In SPELS, the STM tip is biased at voltages up to -400 V with respect to the sample. Electrons are field emitted from the tip towards the sample and backscattered electrons (BSE) are collected by a retarding field analyser placed at an oblique angle to the surface. The field emission current measured at the sample is used to produce constant-current topographic images, while the energy loss spectrum of BSE can be used to produce spectroscopic maps of loss features such as plasmons.

For SERS measurements, 10 nm-thick Ag films were deposited onto Si(100) substrates by magnetron sputtering in a Lesker PVD75 deposition system. The substrates were cleaned with a RCA-1 etch to remove organic contaminants before loading into the deposition system. The native oxide, assumed to be 2 nm thick, was left in place on the surface of the silicon. Half of the Ag films were deposited onto the bare SiO_2 surface, while the other half were deposited onto a 2 nm-thick Ti adhesion layer. Films were annealed under an inert N_2 atmosphere in a three-stack furnace at temperatures of 300, 500 and 700 °C for periods of 15, 30 and 60 min, respectively. The dewetted NP were imaged using an Agilent 5500 AFM in tapping mode. SERS measurements were performed using the Horiba Jobin Yvon LabRAM HR 800 system, using a 660 nm solid state diode laser (100 mW) and a 50x objective. A 1 μM solution of R6G was drop cast onto the surface of each sample and Raman measurements were performed while the sample was still wet.

3. Results

3.1. SPELS measurements

Figure 1 shows a series of topographic and BSE images of Ag islands on SiO_2/Si(111). As previously reported, the resolution of the topographic images decreases with increasing field-emission voltage as the tip-sample separation and spot size of the electron beam on the sample increase. However, increasing the field-emission parameters increases the BSE count rate. The BSE images show evidence of a contrast change between the Ag and SiO_2 as the field-emission voltage is increased from 80 V to 100 V. The use of primary electrons in this energy range on image contrast have been discussed in detail with respect to very low-voltage scanning electron microscopy [5]. At low energies, the atomic number-dependent material contrast decreases and the angular emission distributions of electrons become important. The BSE yield will be dependent on crystal orientation and diffraction of electrons can occur. Differences in the angular distributions of the electrons emitted from different materials affect their relative alignment with the detector entrance aperture and will vary as a function of beam energy. This can lead to contrast reversals being observed between elements such as carbon and gold in this energy range.

3.2. Ag film dewetting

To investigate the effect of temperature and anneal time on NP size and spacing, a dewetting study was performed using 10 nm-thick Ag films deposited onto SiO_2/Si(100) with and without a Ti adhesion layer. Particle size distributions were measured in Gwyddion [6] using watershed analysis, while average interparticle gap was determined from line profile measurements. The results of annealing films for 30 min at 300, 500 and 700 °C, respectively, are shown in Figure 2. This shows a series of AFM images of NP formed on the native oxide-coated Si surface with and without the Ti adhesion layer along with the corresponding particle size distributions. Increasing the anneal temperature for films deposited without an adhesion layer was found to increase the mean particle size from 33 nm at 300 °C to 36 nm at 500 °C and 39 nm at 700 °C, while the

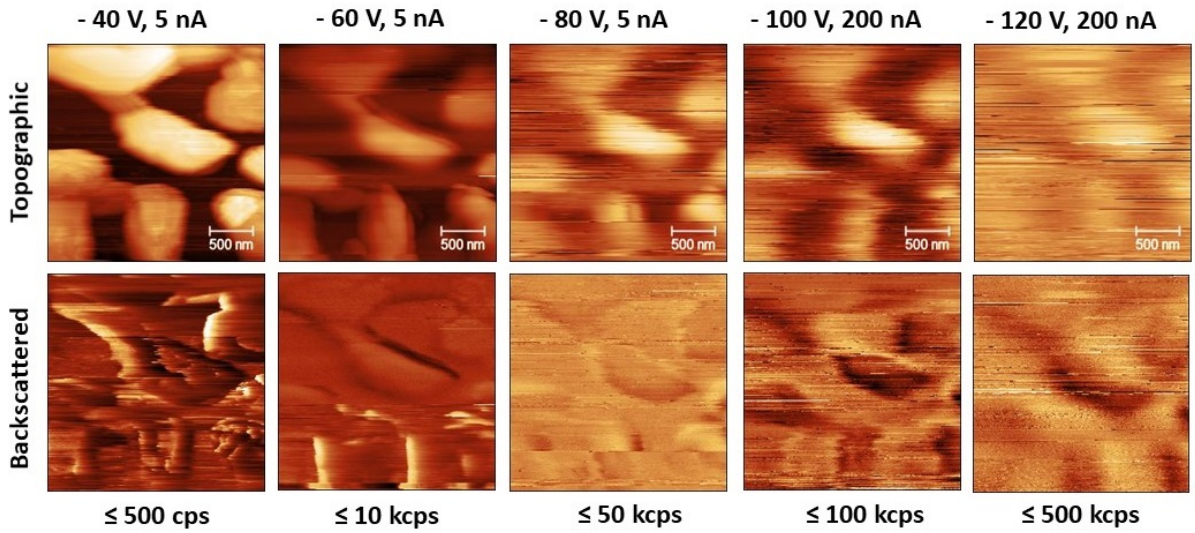

Figure 1. SPELS images of Ag NP on SiO_2/Si(111). (top row) Topographic images obtained in constant field-emission current mode. The field emission parameters used to acquire the data are shown above each image. (b) Backscattered electron images measured by the retarding-field analyser. The approximate count rate for each image is indicated below.

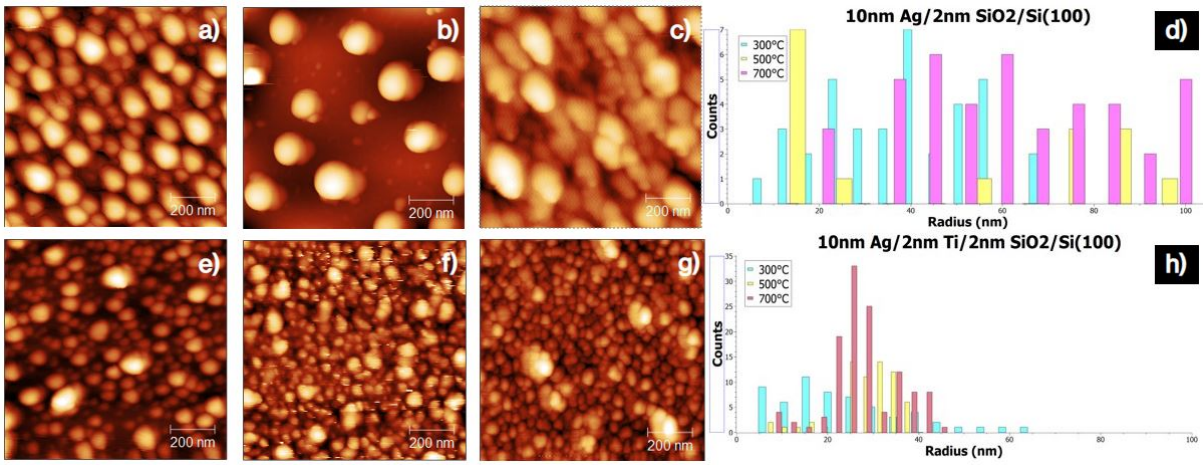

Figure 2. (a-c) AFM images of NP on SiO_2/Si(111) formed by dewetting of a 10 nm thick film annealed for 30 min at (a) 300 °C, (b) 500 °C and (c) 700 °C. (d) Corresponding particle size distributions measured for each sample. (e-g) AFM images of NP formed by dewetting of 10 nm film on a Ti adhesion layer on SiO_2/Si(111) by annealing for 30 min at (e) 300 °C, (f) 500 °C and (g) 700 °C, along with (h) particle size distributions for each sample.

interparticle gap varied from 2.4 nm at 300 °C to 6.2 nm at 500 °C and 1.5 nm at 700 °C. The addition of the Ti adhesion layer resulted in a significant decrease in mean particle size, ranging from 24 nm at 300 °C to 27 nm at 700 °C. The interparticle gap measured between NP on the adhesion layer also decreased. Increasing the anneal time from 15 min to 60 min was generally found to increase the mean particle size slightly and decrease the interparticle gap.

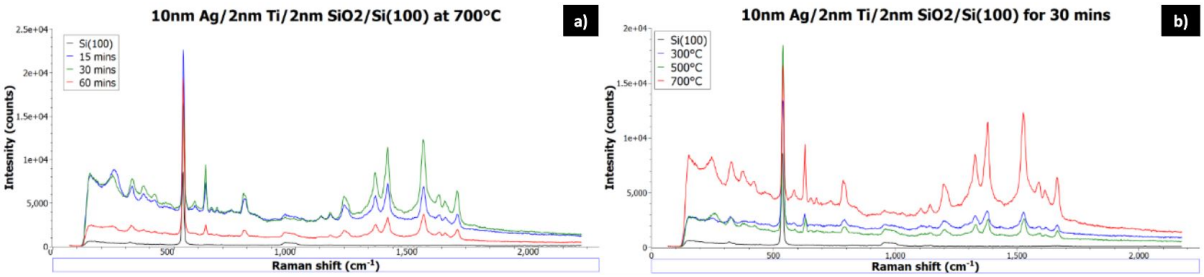

Figure 3. Raman spectra of 1 μM R6G on dewetted Ag/Ti/SiO_2/Si(100). Effect on Raman signal of dye molecule of (a) annealing time at 700 °C, and (b) annealing temperature for 30 min anneal time. The dye signal measured on bare SiO_2/Si(100) is shown for comparison.

3.3. SERS measurements

To investigate the SERS enhancement of the samples as a function of anneal parameters, Raman measurements were performed on the substrates with the Ti adhesion layer using 1 μM R6G. The optimum anneal time and temperature at which the dye signal was maximised were found to be 30 min at 700 °C as shown in Figure 3. This appears to correlate with the fact that the average interparticle gap was found to be smallest for these anneal parameters in the AFM data. A stronger LSPR coupling between the particles due to the smaller interparticle gap could be the reason for the larger enhancement.

4. Conclusion

A dewetting study of 10 nm-thick Ag films deposited on SiO_2/Si(100) showed that increasing the anneal temperature from 300 °C to 700 °C resulted in an increased mean particle size from 33 nm at 300 °C to 39 nm at 700 °C on SiO_2/Si(100). Addition of a Ti adhesion layer resulted in a smaller mean particle size under the same anneal conditions, ranging from 24 nm at 300 °C to 27 nm at 700 °C. The interparticle gap varied considerably in both cases, but was generally smaller in the case of Ag NP formed on the Ti adhesion layer. SERS measurements of 1 μM R6G dye solution showed a maximum enhancement was obtained for films on the Ti adhesion layer that had been annealed for 30 min at 700 °C. This is attributed to the small interparticle gap (0.8 nm) obtained for this sample, leading to a stronger LSPR coupling between the NP. Preliminary SPELS measurements of dewetted Ag NP on SiO_2/Si(100) have shown energy-dependent contrast changes between the Ag and SiO_2 in BSE images that are attributed to the different electron emission angular distributions of the two materials at low primary electron energies.

4.1. Acknowledgments

This work was supported by the Irish Research Council through a Government of Ireland postgraduate scholarship (GOIPG/2020/1572). SM acknowledges support from the University of Birmingham, UK through the provision of equipment.

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