Journal of Molecular Structure 1012 (2012) 56–61

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

# SERS study of molecules on Ag nanocluster films deposited on glass and silicon substrates by cluster deposition method

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ARTICLE INFO

*Article history:*
Received 26 September 2011
Received in revised form 10 December 2011
Accepted 24 December 2011
Available online 5 January 2012

*Keywords:*
SERS
Crystal Violet
Ag nanoclusters
Glass
p-type Si(100)

ABSTRACT

Ag nanoclusters were deposited on glass as well as p-type Si(100) wafers using a nanocluster deposition system and subsequently annealed at 300 °C for 2 h to achieve desirable cluster sizes which tune the surface plasmon resonance (SPR) for SERS studies. The surface morphology of these substrates was examined through FESEM images. The SERS studies were carried out on these substrates with 100 μM and 1 μM Crystal Violet (CV) as a test molecule using 514.5 and 632.8 nm as excitation wavelengths. The dependence of SERS enhancement on the nature of the substrate, shape, size and inter particle distance of Ag nanoclusters is briefly discussed. The experimental findings suggest that the SERS enhancement is higher on glass substrate compared to p-type Si(100) substrate. The substrates investigated in this study were highly reproducible, repeatable and stable.



## 1. Introduction

Soon after the discovery of Surface Enhanced Raman Scattering (SERS) as a tool for the detection of organic/bio molecules at the ultra low level concentration, it has been growing as one of the promising areas of research in nanoscience and technology due to its power as an analytical tool for sensitive and selective detection of molecules adsorbed on noble metal (Au, Ag, Cu etc.,) nanostructures [1–3]. The commonly used SERS-active substrates have been prepared by employing many chemical and physical routes. The chemical route is based on aggregated Ag and Au colloids and these metal colloid solutions of Ag or Au particles of nanometer size have shown high SERS enhancement factors [4–8]. The problem involved in this method is that the tendency for colloidal particles to aggregate spontaneously upon addition of analytes leads to poor stability of system and irreproducibility in the magnitude of SERS signals [9,10]. The substrates made of electrochemically roughened gold and silver surfaces, are relatively easy to produce and present good SERS enhancement, however, their reproducibility is poor [11]. But these problems were slightly overcome in the physical route. SERS effects of various nanostructures, for example, flowerlike Ag nanostructures [12], Ag nanowire bundles [13], Ag nanorod arrays [14], Ag nanoparticles [15], Ag nanowell and nanopore array [16,17] and bimetallic (Ag–Au) substrates [18] were reported in the literature. Among them, lithographic technique provides highly organized nanostructures that lead to high sensitivity and reproducibility [19,20]. However, this technique is quite expensive and requires elaborative preparation methods. Both the chemical and physical routes have their advantages and drawbacks and hence both of them are currently used for the preparation of highly efficient SERS substrates. In this context, there is a need to develop cheaper and reliable substrates for enhancing the sensitivity and reproducibility of the SERS signals.

The present work is carried out to fabricate a suitable SERS substrate using a physical route namely cluster deposition method with Ag as target. This method offers ease of fabrication and also provides nanoparticles with high purity. It also allows fabricating variety of nanoparticles using various target metals like Au, Cu, and Pd etc. From the literature it is well established that the SERS intensity depends on the excitation of the localized surface plasmon resonance (LSPR), which in turn depends upon many factors such as shape, size and inter particle spacing of the material. Based on these points we optimized the Ag nanoclusters (from hereafter it is referred to as Ag NC's) size and density through a cluster deposition system [21]. Our recent report [21] shows that this preparation method can generate SERS substrates suitable to detect ultra low concentrations of molecules. Following the research line of this work, we were motivated to take up the present work to study the suitability of an efficient substrate for SERS.

Very few studies have been published on the influence of the nature of the substrates of nanoparticles in SERS measurements [22,23]. Thus it seems dependency of the nature of the substrates has been ignored or given less priority in the field of SERS. There-

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doi:10.1016/j.molstruc.2011.12.044

fore, we kept the aforementioned aspect in the mind and carried out the present work to study the nature of the substrates (p-type Si (100) and glass) on SERS signal enhancement and compare their signal intensities generated by both the substrates. A special focus is also been given on the reproducibility and repeatability of these substrates. The SERS activity of the Ag NC's/p-type Si (100) and Ag NC's/glass substrates was evaluated with CV as the probe due to its high Raman scattering cross-section.

## 2. Experimental

### 2.1. Preparation and characterization of Ag nanocluster films/substrates

The microscope glass slides and p-type Si (100) wafers (hereafter it is referred to as Si) were used to prepare substrates for Ag nanocluster deposition. These were cut into $1 \times 2$ cm$^2$ pieces and surface contamination was removed by sonication for ten minutes, first in methanol, then in ethanol and finally in Milli-Q water. The slides/wafers were subsequently dried with $N_2$ gas at room temperature before placement in the vacuum chamber. Silver nanoclusters were deposited on these substrates at a base pressure of $2 \times 10^{-6}$ Torr using a cluster deposition system (NANODEP 60 from Oxford Applied Research, UK). The power of the magnetron was maintained at ~70 W (with a voltage of 350 V and a plasma current of 200 mA). The Ag atoms were grown in the form of clusters while they traversed towards the substrate placed at a distance of few centimeters from the exit of the magnetron chamber. Ag NC's were deposited on glass as well as Si substrates for different exposure times (6, 7 and 8 min) by maintaining all other deposition parameters such as Argon gas flow rate, power etc. at the same levels. This was done to achieve the variation in the cluster sizes. Further these substrates were annealed at 300 °C for 2 h under Ar environment to grow desired and homogeneous nano size clusters. Field Emission Scanning Electron Microscope (FESEM) images of as-deposited and annealed substrates were recorded using Carl-Zeiss Ultra 55 system. The UV–Vis spectra of the present substrates were measured at room temperature in the range of 200–800 nm using UV–Vis spectrophotometer (JASCO V-670).

### 2.2. Surface Enhanced Raman Scattering (SERS) studies

SERS spectra of CV adsorbed on these substrates were recorded using micro-Raman spectrometer (LABRAM-HR) using laser excitation lines of 514.5 nm ($Ar^+$), and 632.8 nm (He–Ne) at room temperature. The reason for recording SERS spectra with these excitation wavelengths was to confirm the resonance and non-resonance SERS effect of adsorbate on Ag nanoclusters. All measurements were made in a backscattering geometry, using a 50× microscope objective lens with a numerical aperture of 0.75. Typical laser power at the sample surface was 2.4 mW with a spot size of 2 μm diameter. CV of 100 and 1 μM concentration was prepared by dissolving the required amount of CV in water. For each test, 10 μl of the CV solution was dropped onto each of the SERS substrates ($1 \times 2$ cm$^2$) and dried at room temperature.

## 3. Results and discussion

Fig. 1A shows the FESEM image of Ag NC's on glass substrate (8 min deposited) that was annealed at 300 °C for 2 h. It is observed from the image that this substrate has irregular nanoclusters or aggregates with large size distribution (poly dispersive). Similarly, Fig. 1B shows the FESEM image of Ag NC's on Si substrate (8 min deposited) that was annealed at 300 °C for 2 h. We can observe less poly dispersity of Ag NC's on Si substrate compared to glass. The insets of Fig. 1A and B show the surface morphology of pristine glass and silicon substrates. It is seen that the surface roughness is more for glass substrate compared to silicon. From the obtained FESEM images, the histograms were plotted to represent the size distributions of the nanoclusters. One such histogram is shown in Fig. 2 for 8 min deposited on glass and its inset shows the histogram obtained for Si substrate (annealed) for the same time of deposition. The average size of the Ag NC on the glass was estimated to be approximately 157 nm with a standard deviation of 119 nm. Similarly, the same method was adopted for all other substrates and the estimated nanocluster sizes were approximately 95 ± 78 nm, 118 ± 77 nm for 6 and 7 min deposition respectively. For Si substrate the estimated average nanoclusters sizes were approximately 73 ± 65 nm, 94 ± 71 nm, 110 ± 67 nm for 6, 7 and 8 min deposition respectively.

Fig. 3 show the UV–Vis spectra of annealed Ag NC's/glass substrates for 6 and 8 min deposition. We found that the surface plasmon resonance (SPR) wavelengths for all Ag NC's/glass substrates lie in the range of 360–480 nm. The spectra have peaks at ~360 nm and ~470 nm, corresponding to small (<100 nm) and large Ag NC's (>100 nm) respectively [21]. From the literature it is known that SPR frequency is sensitive to the particle size as well as the dielectric behavior of the substrate [24]. The inset of Fig. 3 shows the reflectance spectra of annealed Ag NC's/Si substrates for 6 and 8 min deposition. Under the assumption that the measured reflectance ($R$) is equal to the total reflectance and the transmission through the Si substrate is zero (opaque material), the absorbance ($A$) can be estimated as $A = 1 - R$. Thus the absorption spectrum has a peak at ~400 nm corresponding to the SPR of Ag NC's on Si substrate. Due to the smaller size of Ag NC's (~73–110 nm) on Si and dielectric nature of Si (the dielectric constant is ~11–12), the SPR on Ag NC's/Si substrates is found to be at shorter wavelength as compared to the glass substrate with an average size of Ag NC's (~95–157 nm) and having a dielectric constant in the range of 3.7–10. In addition to this, the SPR tunability is found to be broad on glass substrate as compared to silicon. The wide size distribution of Ag NC's on glass than that of silicon is thought to be responsible for SPR broadening.

The laser excitation (514.5 nm) was chosen in such a way that the excitation wavelength falls within the SPR absorption band of Ag NC's on the glass and Si substrate but is away from the CV absorption as its absorption band maximum is located at ~590 nm. Besides this, the excitation wavelength of 632.8 nm was also chosen for recording SERS spectra as it matches well with the electronic absorption band of CV (~590 nm) but it matches at the tail end of the SPR peak resulting in Resonant Raman Scattering (RRS). In accordance with the literature it is known that electromagnetic contribution to Raman signal is dominant (5 or 6 orders higher) always over the chemical contribution (due to the molecule electronic resonance and charge transfer state). Therefore the excitation wavelengths of 514.5 and 632.8 nm produces SERS enhancement, RRS enhancement respectively.

The SERS spectra were recorded with the excitation wavelengths of 514.5 nm and 632.8 nm for CV with concentration of 100 and 1 μM adsorbed on both Ag NC's/glass and Ag NC's/Si substrates. We observed from the results that the maximum SERS signal enhancement occurs for the average size of 157 ± 119 nm on glass substrate and 110 ± 67 nm on Si substrate. The literature also suggests that the Ag nanoclusters in the size range of 100–150 nm are expected to be most efficient for surface Raman enhancement when the excitation wavelength is around 500 nm [25–27]. The wavelength dependence on SERS enhancement effects for Ag nanoparticles is described elsewhere [10,28–30]. Therefore we have compared the SERS signal enhancements on the two substrates of glass and silicon that has Ag NC's of the size 157 and 110 nm respectively.