Structural and Optical properties of HNO$_3$ etched Ag thin films

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Abstract. Structural and optical properties, elemental analysis of Ag thin films before and after etching were investigate by using XRD, UV-Vis spectrophotometer, Raman spectroscopy and FESEM. These films were found to exhibit a strong SERS effect and excellent thermal stability. The HNO$_3$ roughened silver film seems to be a more routinely preparable substrate system for SERS study. The HNO$_3$ roughened Ag thin films exhibits excellent stability for enhancement, because the acid roughened Ag films features a strong enhancement factor better stability than pure Ag thin films. Hence, the method will be useful in the development of plasmon-based analytical devices, specifically SERS-based biosensors.

1. Introduction
Surface-enhanced Raman scattering (SERS) is a sensitive tool for exploring metal/adsorbate interactions and reactivity of adsorbed species [1-10]. Since Fleischmann et al.’s initial study [1], SERS has been subjected to extensively theoretical and experimental investigations. Surface Plasmon resonance, which is associated with collective electron resonance induced by incident light on a rough metal surface, is one of the electromagnetic effects contributing largely to the SERS phenomenon. In addition to their easy preparation and chemical stability, this kind of monolayer can find practical applications such as in the area of highly resistant surface modifications. It also provides insight into the structure and molecular packing of monolayer and multilayer organic films that is now a growing area of technique and materials sciences [11]. Knowledge of the structure of the thin films is the key to understanding the relationships between microscopic structure and macroscopic physical and chemical properties. Surface-enhanced Raman scattering (SERS), is a important analytical tool which allows the study of molecules adsorbed on a nanostructured rough surface or nanoparticles of noble (Ag, Cu, Au) metals [12,13] SERS is widely used for obtaining information about the vibrational spectrum of different chemical and biological substances. Development of the SERS technique provides the possibility to obtain Raman spectra from a very low amount of substance, even from a single molecule [14–18]. The SERS effect leads to a large enhancement factor relative to normal Raman scattering. The enhancement factor depends not only on the particular noble metal and excitation wavelength, but also on the size and shape of the nanostructures and their spatial locations. The method of metal nanostructure synthesis is crucial for these parameters. The SERS effect relates to the localized surface plasmon resonance (SPR) of metal nanoparticles, which is manifested in the absorption spectrum as an intensive and broad band. The SERS-active substrates for broad applications in the field of molecular detection and characterization. Surface enhancement depends critically on the creation of surface roughness, the HNO$_3$ etched roughened silver on which the remarkable phenomena. Herein we aim to
report a study and optical properties on the etching rate dependence of the surface-induced morphology of silver thin films.

2. Experimental part

Series of Ag thin films have been obtained by thermal evaporation in a high-vacuum chamber with base pressure $10^{-6}$ mbar. The silver wire used for evaporation was purchased from Aldrich Chemical (99.9% pure) and used as such. The substrates were borosilicate glass for structural, optical studies. All thin films were grown at room temperature ($25^\circ$C) and low deposition rates (<0.01 nm/Sec). The studied Ag thin films samples were 60nm thick on the average. The Ag films etched with diluted HNO$_3$ at different etched times. Silver films of 60nm thickness were immersed into diluted HNO$_3$ and distilled water (1:10) at room temperature, for about 20sec. This procedure creates a roughness future on a 2 or 3nm scale, as shown by the FESEM graphs. After etching, the silver films was thoroughly rinsed with distilled water and dried in air. This procedure is similar to the etching method for formation mechanism of $\gamma$-AgI thin films by sunandana and senthil kumar [19]. The pure, etched Ag films structural properties studied by X-Ray diffraction (XRD) and Field emission scanning electron microscopy (FESEM) techniques were used to evaluate the microstructure of the samples. The optical absorption of Ag thin films was determined by JASCO optical Spectrophotometer. The optical absorption was measured in the UV-Visible range 300nm to 800nm.

3. Results & Discussion

3.1 XRD

From fig1 x-ray diffraction, it was observed that the no crystal phases present in Ag thermal evaporated films but a broad huge peak observed at 30 degrees. Thus 60nm thick Ag films appear by and large quasi amorphous and it is observed no crystalline phases are present. The quasi-amorphous XRD pattern reflects the nanocrystalline nature of the Ag Nanoparticles. The Ag film was etched with diluted HNO$_3$ for 20 sec; upon which a high intensity broader peak with a larger FWHM was observed. These results indicate increase in the particle size and a decrease in density of particles which are in agreement with FESEM results.

3.2 Optical properties

UV-VIS absorption spectra have been proved to be quite sensitive to the formation of silver because silver nanoparticles exhibit an intense absorption peak due to the surface plasmon excitation. Fig. 2
shows that the intensity of SPR band and its full width at half maxima (FWHM) increases with etching time. There was no obvious change in peak position for etching, except for the increase of absorbance. These signatures of absorption spectrum are in accordance with the increase size of Ag nanoparticles. It is obvious that with the progress of etching reaction more and more Ag+ are reduced and this results in the increase size of silver nanocrystals through diffusion controlled mechanism. This tremendous increment in absorption spectrum useful to chemical sensors, detectors as well as some sensitive spectroscopic measurements. With the increasing size of Ag nanoparticles, multiple transitions of surface plasmon become more prominent and this is reflected on the increase in absorption intensity of etched Ag thin films. These broad (FWHM) SPR peaks mainly depend on the etching rate, thickness of the film, dielectric constant and preparation of the sample. One major reason for SPR broadening is electron surface scattering, which may be enhanced for very small clusters. For smaller particles, electrons reach the surface faster and scatter quickly, losing the coherence of collective oscillation. In this case thickness, etching rate is playing important role, based on this we are tuning the optical, structural properties.

![Absorbance spectrum of Ag films](image)

3.3 FESEM
The morphology of Ag thin films was examined by FESEM. Figure 3a shows the FESEM image of as deposited Ag thin film have uniform distribution with small nano agglomeration particles. In the case of etched Ag thin films were completely isolated after etching due to their agglomeration; the occurrence of separation, agglomeration on chemically etched silver films in atmosphere can be explained on consideration of the surface diffusion of Ag atoms. The etching rate is quick using strong acid solution because the consumed etchant can be resupplied rapidly in the strong acid. From FESEM results the average Ag nanoclusters sizes for unetched, etched Ag thin films are estimated as 15±5, 60±10nm respectively.

![FESEM image of 60nm Ag film etched for 20sec etched with diluted HNO₃ in atmosphere](image)
3.4 Raman
A shape and well-resolved Raman line was observed at 1548 cm\(^{-1}\) in unetched film which upon HNO\(_3\) etching became sharper and more intense and also shifted to 1587 cm\(^{-1}\), characteristics of Ag [20]. An excellent SERS spectrum was obtained from HNO\(_3\) – roughened Ag films as shown in the fig 4. The HNO3 roughened Ag thin films exhibits excellent stability for enhancement, because the acid roughened Ag films features a strong enhancement factor better stability than pure Ag thin films. This preliminary result shows that a careful optimization of film thickness and etching time would lead to SERS quality films. Studies in that direction are in progress. In summary, we found that very stable and optically tunable; SERS-active Ag films can be reproducibly fabricated simply by Ag film etched with diluted HNO\(_3\). Hence, the method will be useful in the development of plasmon-based analytical devices, specifically SERS-based biosensors [21].

4. Conclusion
Structural and optical properties, elemental analysis of Ag thin films before and after etching were investigate by using XRD, UV-Vis spectrophotometer and FESEM, Raman. UV-Vis spectra exhibited Surface Plasmon absorption characteristic of thin films and nano particle ensembles, respectively. Based on the etching mechanism, the etching rate should be change the morphology of the silver thin films was observed by using FESM. Thermal evaporated Ag films were found to exhibit a strong SERS effect and excellent thermal stability. The HNO\(_3\) roughened silver film seems to be a more routinely preparable substrate system for SERS study. The HNO\(_3\) roughened Ag thin films exhibits excellent stability for enhancement, because the acid roughened Ag films features a strong enhancement factor better stability than pure Ag thin films.

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