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Study of thickness dependent sputtering in gold thin films by swift heavy ion irradiation

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ABSTRACT

Gold thin films of varying thickness (10–100 nm) grown on silica substrates by e-beam evaporation method were irradiated by 120 MeV Au ions at 3×10^{12} and 1×10^{13} ions cm^{-2} fluences. Irradiation induced modifications of these films were probed by glancing angle X-ray diffraction (GAXRD), atomic force microscopy (AFM), Rutherford backscattering spectrometry (RBS) and surface enhanced Raman scattering (SERS). Irradiation didn't affect the structure, the lattice parameter or the crystallite size, but modified the texturing of grains from [1 1 1] to [2 2 0]. RBS indicated thickness dependent sputtering on irradiation. The sputtering yield was found to decrease with increasing thickness. AFM indicated increase of roughness with increasing irradiation fluence for films of all thickness. In agreement with the AFM observation, the gold nanostructures on the surface of 20 nm thick film were found to increase the SERS signal of acridine orange dye attached to these structures. The SERS peaks were amplified by many fold with increasing ion fluence. The effect of 120 MeV Au ion irradiation on the grain texture, surface morphology and SERS activity in addition to the thickness dependent sputtering in gold thin films are explained by the thermal spike model of ion-matter interaction.

1. Introduction

The bombardment of an energetic particle on to a solid induces several processes such as recoil and sputtering of constituent atoms, defect formation, excitation and emission of electrons and photons. The sputtering process i.e. removal of surface atoms or molecules of a solid under energetic ion bombardment has been widely studied for various target projectile combinations [1]. This phenomenon has found extensive applications in material modification and characterization. Depending on the energy of the projectile ion, different type of sputtering processes such as material ejection due to elastic collisions between atoms (nuclear sputtering) at keV energies [2], electronic sputtering [3] governed by electronic energy loss at higher energies (>1 MeV/u), and potential sputtering [4] by slow highly charged ions can occur in a solid. Nuclear sputtering is well described by Sigmund's theory [2]. Electronic sputtering has been mostly explained based on the different models of ion-matter interaction such as Coulomb explosion [5], thermal spike [6], shock wave model of sputtering [7], and a combination of Coulomb explosion and thermal spike [8].

Except a few metals like Ti and Zr, most of the metals do not exhibit sputtering under electronic energy loss [9]. This is mostly due to the high mobility of the conduction electrons effectively screening the ionized atoms, and quickly smearing out the deposited energy. This also is the reason, why ions do not create amorphized latent tracks in highly conducting metals like gold, silver and copper. This correlation of ion beam induced surface and bulk effects has also been seen in case of insulators like a-SiO_2 [10]. As compared to bulk systems, sputtering process in thin films due to irradiation is affected by several parameters such as substrate, grain size and thickness of the film, mass and energy of the incident ion, and irradiation temperature [11]. In case of the film, scattering at the surface and interface reduces effective mean free path of the excited electrons under irradiation. This additional consideration brings in yet another new phenomenon of thickness dependent electronic sputtering [11–13]. In spite of a large number of studies, a complete understanding of the sputtering mechanism in the electronic energy loss regime is still lacking.

To study the different aspects of sputtering induced by energetic ions, a noble metal like gold has been a material of choice

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of many investigators [11,14–18] due to the two fundamental reasons; (i) Oxide layer easily forms on a metallic surface even under ordinary vacuum conditions, which completely dominates the electronic sputtering process. A noble metal like gold does not easily convert to insulating oxide state and hence provides the opportunity to study the electronic sputtering process in metals. (ii) Bulk gold does not exhibit sputtering due to electronic energy loss of ions. Whatever sputtering has been seen in gold by energetic ions of any energy and mass, is solely due to nuclear energy loss of the ions [14,19,20]. Thus, gold has been used as a reference material for study of nuclear sputtering since it is insensitive to high electronic excitations [10]. Electronic sputtering of gold has been seen only in reduced dimensions like thin films and in nanoparticles [11,17,21]. Gupta et al. [11] observed a dramatic effect of film thickness on the electronic sputter yield of gold thin films under swift heavy ion (SHI) irradiation and explained this phenomenon based on reduced mobility of the electrons due to scattering from the surface and the grain boundaries. Since then a few other studies have been undertaken on the thickness dependence of the electronic sputtering yield of different materials.

From application point of view, gold thin films have aroused intense research interest due to the unique optical properties introduced by localized surface plasmon resonances (LSPRs). LSPRs are exciting optical phenomena that arise from the collective oscillation of conduction electrons in noble metal nanoparticles when the electrons are excited by an incident light radiation. This leads to enormous optical local-field enhancement on the surface of the nanoparticles, which have found potential applications in many fields such as chemical or biosensors [22], solar cell designs [23], and surface-enhanced Raman scattering (SERS) [24–26]. These applications rely particularly on the morphology of gold surfaces, especially their roughness that influences their functional properties. The SERS, in particular depends on the roughness of the surface of noble metals, which act as hotspots for enhancement of electric field due to localized surface plasmon resonance [27] and surface roughness. Irradiation by energetic ions is an ideal tool to control the surface roughness by sputtering as well as mass flow.

The present study examines the effect of 120 MeV Au ion irradiation on the structure, microstructure, surface morphology, sputtering yield and SERS in gold films of thickness in the range 10–100 nm. We show that, irradiation leaves the structure unaffected, but strongly affects the grain texture of the film. In addition, we show that the sputtering yield decreases with increasing film thickness. This result correlates with the surface roughening of the films observed by AFM. The roughness of the surface is also shown to increase the SERS signal of acridine orange (AO) dye molecules adsorbed on the surface nanostructures. The results are explained based on the thermal spike model of ion matter interaction.

2. Experimental

Gold thin films with varying thicknesses (~10, 20, 50 and 100 nm) were deposited on 1×1 cm^2 fused silica (SiO_2) substrates in high vacuum (8.0×10^{-7} mbar) by electron beam evaporation method in a MANTIS Q Prep-250 deposition unit. Thickness was measured *in-situ* by quartz crystal monitor and *ex-situ* by Rutherford backscattering spectrometry (RBS). RBS measurements were performed with 2 MeV He^+ ions using 1.7 MV accelerator facility at IUAC, New Delhi in a vacuum of 1×10^{-6} mbar. The He^+ ions were bombarded perpendicularly to the sample surface and backscattered ions were detected at an angle of 160° to the beam direction using silicon surface barrier detector.

The films were irradiated with 120 MeV Au^{9+} ions using the 15UD Pelletron accelerator at IUAC, New Delhi. Irradiation was done at two different fluences (3×10^{12} and 1×10^{13} ions cm^{-2}). The ions were incident perpendicular to the surface of the films. The ion beam was scanned over an area of 1×1 cm^2. The vacuum in the chamber during irradiation was 9×10^{-6} mbar. Irradiation induced sputtering was analyzed by *ex-situ* thickness measurement using RBS technique. Glancing angle X-ray diffraction (GAXRD) was done using Brucker D8 advance X-ray diffractometer with CuKα radiation ($\lambda = 1.5418$ Å) at 40 kV voltage and 40 mA current. GAXRD measurements in the 2θ range of 35–85° of as-deposited and irradiated gold films were performed at a glancing angle of 2° and a scan speed of 1° min^{-1}. Atomic force microscopy (AFM) measurements of the films were done to study evolution of surface morphology and microstructure before and after irradiation using 'Nanoscope IIIA' atomic force microscope of Digital Instruments. SERS was done on the films with surface plasmons of gold nanoparticles using 514 nm excitation lines from 50 mw Ar^+ laser. For SERS measurements we have taken acridine orange (AO) solution with concentration 1 mg/ml. Micro-Raman spectra of the films with 5 μl of AO solution were recorded in backscattering geometry using Renishaw inivia micro-Raman spectrometer.

3. Results and discussions

The GAXRD pattern of the pristine gold thin films of varying thickness (10–100 nm) (Fig. 1) and that of the films irradiated at different ion fluence (Fig. 2) consist of peaks corresponding to prominent reflection planes of bulk gold with cubic structure as reported in JCPDS file [Card No. 04-0784]. The position, intensity and width of each diffraction line were determined using pseudo-Voigt function. The lattice parameter of all the films was found to be ~4.072 Å. Irradiation with 120 MeV Au ions did not change the structure or the lattice parameter. The crystallite size estimated from the Scherrer equation, Culity [28] showed an increase with increasing thickness tending to saturate at higher thicknesses (inset 'a' of Fig. 1). Irradiation had a negligible effect on the crystallite size in the films of all thicknesses (inset 'a' of Fig. 2). Texture of the grains however showed a variation with thickness (inset 'b' of Fig. 1) as well as with ion fluence (inset 'b' of Fig. 2).

Texturing of different planes was calculated by comparing the intensity of the different XRD peaks of the films with that of the powder sample, where grains are randomly oriented. This comparison thus gives the degree of orientation along different reflection planes of the films with respect to the randomly oriented bulk

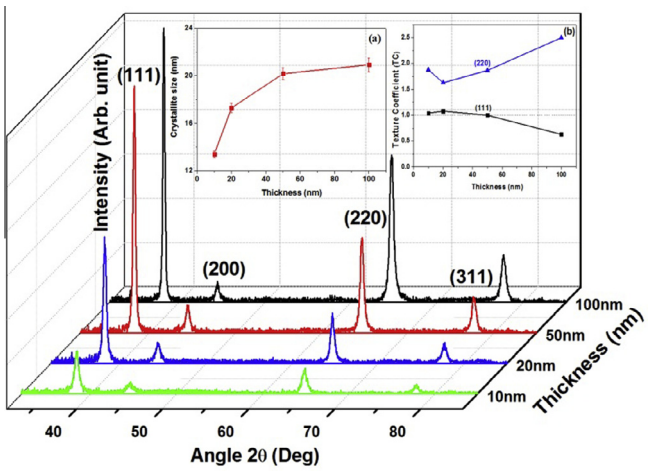

Fig. 1. GAXRD spectrum for 10, 20, 50 and 100 nm of gold thin films. The inset shows the variation of (a) crystallite size (b) texture coefficient of (1 1 1) and (2 2 0) peaks with film thickness.