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Influence of temperature dependent morphology on localized surface plasmon resonance in ultra-thin silver island films

N. Venugopal*, Anirban Mitra

Department of Physics, Indian Institute of Technology, Roorkee, Uttarakhand 247667, India

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ABSTRACT

Dependence of morphological evolution and variation of corresponding localized surface plasmonic properties of the ultra-thin Ag island films deposited by thermal evaporation at different substrate temperatures have been investigated. It has been observed that the particle diameter, height, aspect ratio, surface coverage, roughness and particle density of the films are strongly dependent on the substrate temperature and film thickness. Depending on the trend of the shift of localized surface plasmon dip overall thermal process is divided into two stages: in first stage apparent change in localized surface plasmon dip takes place with the shift towards the shorter wavelengths. In the second stage, it is red shifted. Both these changes can be attributed to the change of morphology of the Ag island films. Strong temperature dependence between the morphological evolution and optical properties variation has been observed. Bandwidth, position and relative intensity of localized surface plasmon resonance induced absorption dip have been correlated with various morphological characteristics. Effective medium extended Maxwell–Garnett theory is used to simulate the optical transparency of these Ag metal island thin films. With the increment of substrate temperature up to 250 °C these silver metal island thin films exhibit high optical transparency in the range 600–1100 nm.

1. Introduction

Quantization of collective oscillations of free electrons in metal leads to the formation of plasmons. Plasmons can be generated in metal island film with the excitation of electromagnetic radiation of particular frequency. Displacement of the conduction electrons with excitation of incident electromagnetic radiation can polarize the charges. This polarization of charges creates a restoring force Conduction electrons oscillating under this restoring force with a characteristic frequency is known as plasmon frequency [1,2]. When the frequency of incident electromagnetic radiation matches with the characteristic frequency of the metal island film resonance occurs. At resonance maximum energy of the incident electromagnetic radiation can be absorbed by the metal island film. Refractive index of the metal island film has strong dependence on the frequency of incident electromagnetic radiation as well as the other parameters of metal island film like size, shape, geometry of metal nanoparticles and surrounding medium. This plasmon frequency can be tuned for different applications in organic light emitting diode (OLED), solar cells, optical filter, sensors etc.

Anti reflection (AR) coating based metal nanostructures have been widely used as optical components like solar cells, flat panel displays, transparent conductive oxide and light emitting diode to increase the transmittance of incident light and prevent disturbances from external light [3–7]. In recent years, plasmonic metal–dielectric nanostructures have attracted a great interest due to their high potential in diverse fields such as plasmonic biosensors [8], photocatalytic [9], metamaterials [10,11] and 1D metal–dieletric photonic crystals [12].

In this paper, we present our experimental study of morphological evolution of ultra-thin silver films (mass thicknesses 1 nm, 2 nm and 4 nm) at various substrate temperature (50–450 °C) and corresponding optical properties. We also simulated our experimental results of optical properties by using effective extended medium Maxwell–Garnett theory. Our experimental results show that silver metal islands on glass substrate have maximum absorption (1 – T), neglecting reflection, in the range 400–900 nm for the metal island films of mass thickness 4 nm. Varying the substrate temperature this can also be tuned. In this range solar spectrum is very intense and most of the a-Si, c-Si, GaAs and CIS based solar cells are highly efficient in this range. Our observations may have potential applications for plasmonic based solar cells.

* Corresponding author. Tel.: +91 011332285652; fax: +91 011332273560.
E-mail addresses: venu9dph@iitr.ernet.in (N. Venugopal), mitrafph@iitr.ernet.in (A. Mitra).

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2. Experimental details

Ag island thin films were prepared using thermal evaporation method under the base pressure of 1×10^{-5} Torr. These films were deposited at various substrate temperatures staring from 50 to 450 °C with an interval of 50 °C and source-to-substrate distance was kept at 20 cm. Ag thin films were deposited at a rate of 0.5 Å/s. Substrate heater consisted of two quartz plates with coiled tungsten-wire heater positioned between them. Mass thickness of the films was measured using a quartz crystal thickness monitor. Substrate temperature was measured using thermocouple inbuilt in vacuum coating unit. Surface morphology of silver metal island thin films was characterized using Field Emission Scanning Electron Microscope (Model: Quanta 200F FEG and FEI Netherlands) and Atomic Force Microscope (NT-DMT, NTEGRA model). Optical transmittances of all the thin films were measured in the range 300–1100 nm using UV–vis spectrometer (SHIMDZU-UV1800).

3. Results and discussion

3.1. Morphology

To understand the cause of the thermal induced optical properties of Ag nanoparticles Field emission scanning electron microscopy (FESEM) and atomic force microscopy (AFM) are used to provide a quantitative description of morphological evolution. Morphology of Ag ultra-thin films of mass thickness 1, 2 and 4 nm were studied with increasing substrate temperature starting from 50 °C to 450 °C. We have divided the whole substrate temperature range into two regimes, one is in the lower substrate temperature range 50–250 °C and another is in the higher temperature range 300–450 °C. As the substrate temperature increases distinct phases have been developed in the following order hillocks, worms, holes, islands and complex structures respectively.

Typical AFM and FESEM images of ultra-thin silver film of mass thickness 1 nm deposited on glass have been shown in Figs. 1–3. Initially at the lower substrate temperature regime from 50 to 100 °C, Ag island films are of anisotropic shapes, inhomogeneous sizes. Particles are distributed closely to each other. In this regime Ag island films with small particle diameter, large particle density and aspect ratio are formed during the vacuum evaporation process in which the Ag nanoparticles are nucleated and coalesced on the corning glass substrate. There is no significant change in morphology below 97 °C as it is expected that the crystal grain growth starts above 97 °C due to surface migration of Ag atoms according to Thorton's structural model [13]. However, when the substrate temperature enters into the range 150–250 °C, small change in the structure of the film from hill to valley hillock occurs. Due to the non-uniform thickness of the island film structure faster surface diffusion has been occurred in this range. This results in increasing the aspect ratio and decreasing the particle density and elongation. There is no significant change in diameter of the particles but the inter particle separation distance increases. Furthermore at the substrate temperature range 300–350 °C hill to valley structures evolved into more regularly isotropic nanoparticles changing from spheroid to ellipsoidal (elongated) shapes. In this regime particles become round shape compared to low substrate temperature regime and having inhomogenous distribution of sizes with increasing inter-particle distance as shown in Figs. 1–3. Particle shape distribution of silver islands becomes more spherical and well separated. In this range particle diameter and height have been increased while aspect ratio, surface coverage and particle density decreased. Further elevating the substrate temperature in the range 400–450 °C the rounded shape islands transform into anisotropic worm like island films and complex island shapes having low aspect ratio. Diameter and height of the particles of these island films are large while the particle density and surface area are quite low.

Images corresponding to the mass film thickness of 2 nm have been presented in the Figs. 4–6. At low substrate temperature regime, Ag island film exhibits morphology similar to 1 nm. These films have anisotropic shapes, high particle density and large surface coverage. They also have low aspect ratio and inhomogeneous size distribution as the deposition temperature is below 100 °C. At 100 °C temperature there is signature of continuous film with hole nucleation as evidence shown by the AFM images. This temperature promotes the formation and percolation of holes. At 150 °C these particles become spheroid and well separated with large aspect ratio, particle density and low surface coverage. In the higher substrate temperature range 200–300 °C hill to valley hillocks growth is occurred with the increment of particle diameter, height, and decrement of aspect ratio and surface coverage area. In the range 350–450 °C particles become rounded shape having broad range particle size and shape with the decrement of separation distance.

AFM and FESEM images of silver island film of thickness 4 nm are presented in Figs. 7–10. In the low substrate temperature range 50–100 °C due to large mass thickness of Ag, these films consist of round shape elongated particles with inhomogenous size distributions. Inter particle separation, aspect ratio, particle density and roughness of these films are large having worm like structures at 100 °C. Further increasing temperature from 150 to 200 °C, particles become well separated with isotropic round shapes. In this range particle diameter increases while particle height decreases with uniform particle size distribution. At substrate temperature 250 °C, particles have inhomogeneous size and well separated distribution but large diameter and height. Further increasing the substrate temperature from 300 to 400 °C particles sizes and height have been increased while aspect ratio and particle density decreased. Shapes of the particles again become isotropic with inhomogeneous sizes.

AFM images as shown below each having different *z* scales. The island height continuously changes with substrate temperature in all Ag ultra-thin films. The silver islands appear larger in size and closer in spacing as determined from the semi-contact mode. AFM images as compared with those in corresponding FESEM silver nanoparticles seem to be more rounded, closer to each other and have larger diameter. This is because of resolution of AFM which is not as high as that of FESEM while AFM can provide more information about the island height. Combination of FESEM and AFM provides a reliable description of the 3d morphology and topography of the ultra-thin Ag films at different substrate temperatures. FESEM and AFM images have been shown for all the studied samples, but the main results derived from AFM images and their analysis are presented in Tables 1–3. In order to study effect of film thickness and substrate temperature on the morphology of the film parameters like particle diameter, height, aspect ratio, roughness, surface coverage and particle density are determined from AFM images. Morphological features of the films depend on both substrate temperature and film thickness. Modification in morphology of Ag ultra-thin films, due to difference in thermal expansion coefficient between the substrate and the metal is mainly responsible for this. Growth of hillock finally induces the formation of some holes and eventually growth of holes which take place mainly through the surface diffusion. Finally holes percolate leading the formation of larger silver islands.

Morphological variation of the ultra-thin Ag films with the change of substrate temperature, mean diameter of islands, height etc. increase consistently from thin island films to isolated nanoparticles. Silver islands were also reshaped from isotropic islands to anisotropic worm. Theses films initially show a continuous hillock structure at low temperature. In fact, no obvious increment of height and diameter of the nanoparticles have been observed