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Optics of Quasiparticle Phase Transitions in Nanostructured Ag Thin Films

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Abstract

We describe and discuss XRD, AFM and optical absorption behaviour of nanostructured Ag films 2, 5 and 10 nm thick obtained by thermal evaporation. While all films are quasi amorphous, 2nm thick films exhibit nanotriangles in the nature of Mie particles which exhibit surface plasmon resonance (SPR). Increase of thickness produces a shape change from nanotriangle to spherical triangle and a red shifted SPR. Most interestingly systematic iodization throws up a quasi-particle transition namely plasmon-exciton transition even as Ag metal film is converted into an insulating/semiconducting AgI film.

Keywords: Nanotriangles, Iodized Ultrathin Ag films, Surface Plasmon Resonance (SPR), Plasmon-exciton transition

1. Introduction

Nanostructured noble metal films (ex: Ag) with thicknesses ≤ 10 nm support plasmon oscillations. Such films are discontinuous and consist of isolated islands each of diameter less than 100 nm and typically 30 nm involving large surface to volume ratio of crystallites constituting the film. These structures could therefore be modeled as 2D nanoisland lattices or as 2D photonic lattices of voids separating the islands. Electrons in metals form a dense fermion gas with strong electron-electron interaction. Virtually all electrons are simultaneously involved in the Coulomb interaction. Both individual and collective behaviour is exhibited by these electrons. For electromagnetic wavelengths larger than Debye length all electrons collectively behave as a uniform elastic medium showing organized longitudinal oscillations. Behaving as bosons, these so-called ‘plasmon’ oscillations can be created on the surface of metal films by external

electromagnetic/electric fields propagate along the surface. Behaviour of electrons is as individual particles for wavelengths less than Debye length in which case screened Coulomb interaction prevails. The interaction light with metal surfaces is strongly enhanced when the surface is patterned on a wavelength scale.

Nanostructures supporting localized plasmons are the subject of intense research for their applications in plasmonics including nanophotonic devices [1], chemical sensors [2], optical filters [3], left handed materials [4]. These surface plasmon resonances in thin films [5] largely depend on the size, shape, metallic material and the surrounding dielectric matrix. Ag being easily iodizable offers a wonderful opportunity to examine the possibility of quasiparticle formation and ‘transitions’

Brief iodization of these ultra thin metal films causes a controlled depletion of electron density leading to a gradual disappearance of plasmons and a progressive build-up of excitons and valence band structure of AgI. The decay of plasmons in Ag is apparently closely connected with the buildup of electron-hole pairs in AgI as found in our recent iodization experiments [6, 7]. In this paper we discuss experimental results on plasmon formation in ultrathin Ag films and plasmon-exciton transition when subjected electromagnetic radiation in progressively iodized Ag films. An area of fundamental scientific interest, and possible future applications, would be the study of the optical properties of discontinuous metal films in the presence of electric fields and currents applied to the films. A large surface to volume ratio is the property which might be exploited in devices intended to monitor variables that can be detected by surface defects, such as conductivity modulation due to gaseous component adsorption [8].

2. Experimental

Ultra-thin Ag films were deposited on borosilicate glass dielectric substrates by thermal evaporation using a molybdenum boat. The starting material was portions of highly pure Ag wire (Aldrich, 99.999) placed in the boat which was thermally evaporated on to the cleaned borosilicate glass substrates kept at an ambient temperature. The glass substrates were kept at a distance of 20 cm from the source for deposition [5]. Films with thicknesses of 2, 5 and 10nm with (0.1nm/sec) rate of depositions, were coated on the cleaned glass substrates at room temperature. The thickness was measured using profilometer.

Iodization of Ag films was done in an hour-glass type chamber with dimensions of 10cm height \times 6cm diameter. Iodine kept at the bottom of the lower half of the chamber sublimates at room temperature and slowly deposits on the Ag films kept at the top of the chamber. Thus iodization was carried for selected durations in the range 5 minutes to 30 minutes. These films were characterized by XRD using a PHILLIPS low angle X-ray powder diffractometer with Cu K_{α} ($\lambda = 1.54056 \text{ \AA}$) radiation. To analyze the surface morphology, films were examined by SPA 400 Atomic Force Microscope (AFM) using non contact Dynamic Force Mode. SHIMADZU UV- 3101 spectrophotometer has been used for absorption studies at 300K in the UV/visible range from 300 to 600 nm with scanning rate 2 nm per second.

The substrates were cleaned as follows: substrates were first immersed in boiling 10% soap solution with 90% water, rubbed with cotton in cold water to remove weathering, kept in chromic acid up to boiling point for removing organic contaminants, washed in cold water to remove surface contaminants followed by ultra-sonification

in iso-propyl alcohol for 3-5min duration, and, finally these substrates were dried in air before loading in to the system for deposition.

3. Results and Discussions

3.1 X-ray Diffraction

Representative XRD patterns of as-deposited Ag thin films are displayed in Fig.1. It is apparent that thin films in the thickness 2-10 nm are by and large amorphous-possessing only short range order which is in keeping with the islanded nanostructured quasi-continuous films. XRD patterns show quasi-amorphous structure due to the nanocrystalline nature of silver particles. As thickness increases there is a subtle broadening of the peak that hints at a possible increase in quantities such as particle size which could be conveniently probed by AFM to be described later.

Ag films of thickness 2, 5 and 10 nm as evaporated on glass substrate and progressively iodized were characterized by XRD as shown in figure 2. When subjected to a controlled flux of iodine vapours realized in a figure of eight or hourglass jig with a 1 mm opening at the centre for brief durations 30 minutes. Figure 2 shows the growth of γ and β -AgI nanoparticles upon iodization over duration of 30 min, Fig 2(a)) silver nanoparticles are gradually converted into room temperature metastable phase γ -AgI(classified as $\gamma(111)$), is formed 30min iodization in thermally evaporated Ag film upon Ag film thickness increased the (111) peak develop progressively. Perhaps due to local iodine excess (b) and (c) show an additional peaks at $2\theta = 25.35^\circ$ which corresponds to β -AgI (101) plane $[(Ag/I)<1]$ of silver iodide nanoparticles. This is something unusual and rare in ultra thin films because in our previous study [7] it has been observed that the Zincblende structure of silver iodide is stable in rf sputtered films.

From these observations one would understand that the formation of β -AgI nanoparticles is possible on ultra thin films, suggesting both zincblende and wurtzite crystal structure are certainly possible as these films are grown on discontinuous silver films involving very large surface to volume ratio. Discontinuous films are inherently unstable and tend to exhibit poor reproducibility. Furthermore the enhancement in the intensity of XRD peaks with increasing film thickness could be due to a decrease in the surface area of Ag nanoparticles.

We wish to focus in this paper on the quasiparticles that characterize uniodized and iodized Ag films and a transition from one to the other as seen through optical absorption measurements of the so called Mie particle conduction electron resonance or surface plasmon resonance to be described later.

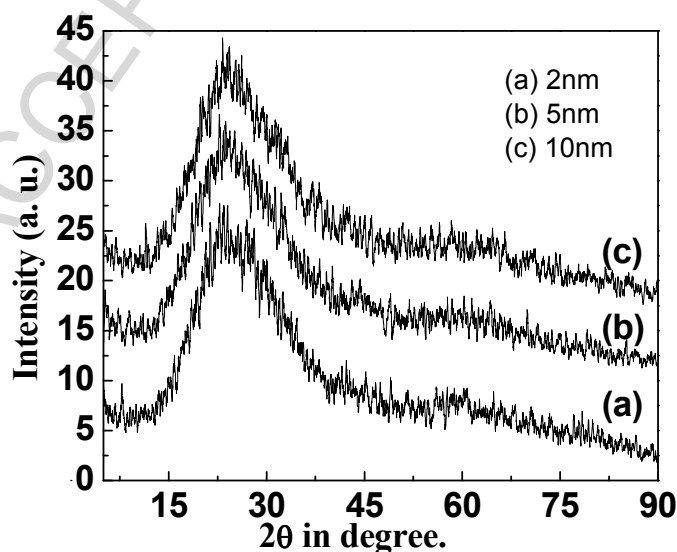


Figure 1 X-ray diffractograms of (a) 2 nm (b) 5 nm and (c) 10 nm Ag deposited on glass substrates. The broad peak around $2\theta = 61^\circ$ is due to formation of Hexagonal structure in Ag. The broad peak at $2\theta = 28^\circ$ (also observed in uncoated substrate) is due to amorphous background.

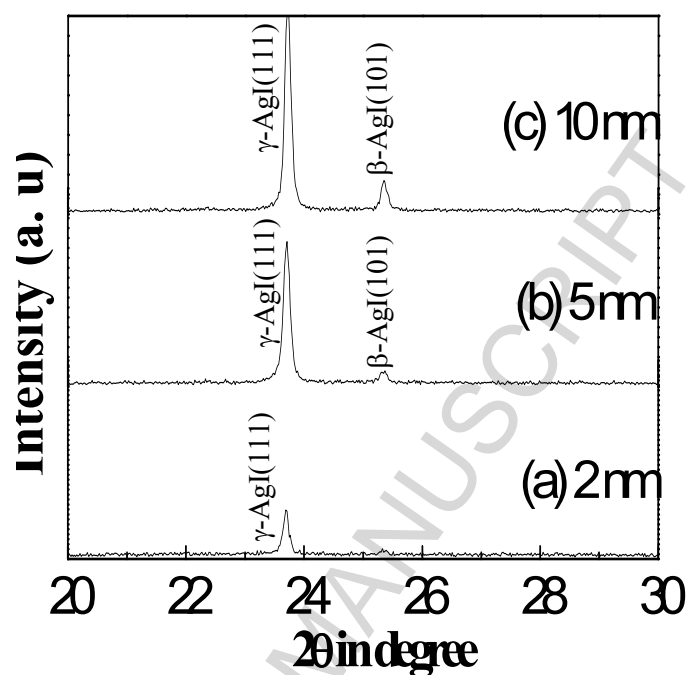


Fig 2. XRD of 30 minutes iodized silver films of thickness 2, 5 and 10 nm.

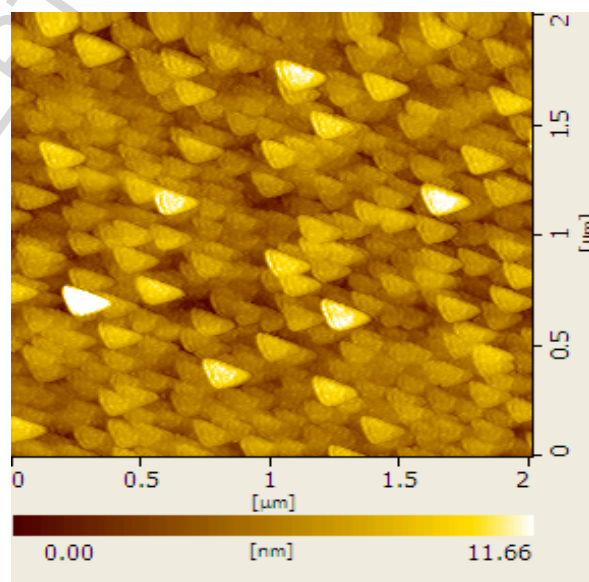


Fig.3. AFM of 2 nm Ag films showing several layers of Ag nanotriangles arranged in sparsely packed layers thus including considerable void space which probably facilitates iodization and formation of spherical AgI nanoparticles by providing sufficient “reaction volume”

3.2 AFM studies

To obtain a direct visual evidence of the size, shape and the distribution of nanoparticles or surface morphology, AFM images were recorded. Fig 3 shows the morphology of the 2nm Ag film which records the presence of triangle-shaped nano features that is unusually interesting. The layered stacks of such particles of near-uniform size and average edge length of 100-120nm, ultra-thin film suggests a growth process in which there is effectively arrested growth of ‘embryos’ especially when seen in the light of the XRD just described. We have in this case the equivalent of Ag nanoparticles stabilized in colloidal solutions [9]. we focus on the effect of thickness increase on the shape of these particles. Figures 4 (a) and (b) provide direct evidence for a change in the shape from flat triangular to ‘spherical triangular’ when the thickness is increased from 2 nm to 5 nm and 10 nm. In the case of a 10nm Ag film iodized for 30 minutes there is a increases in the size of ‘spherical triangular’ AgI nanoparticles and creation of void space. It is to be noted that the 2nm Ag film is already porous and this porosity helps maintain an I₂-rich environment suitable for the formation of wurtzite β -AgI as was the case with our study of Ag foils [10]. It would be naturally interesting and curious to seek by an optical probe such as optical absorption how the Ag nanostructures and their iodized counterparts respond to an electromagnetic field in the UV-visible region.

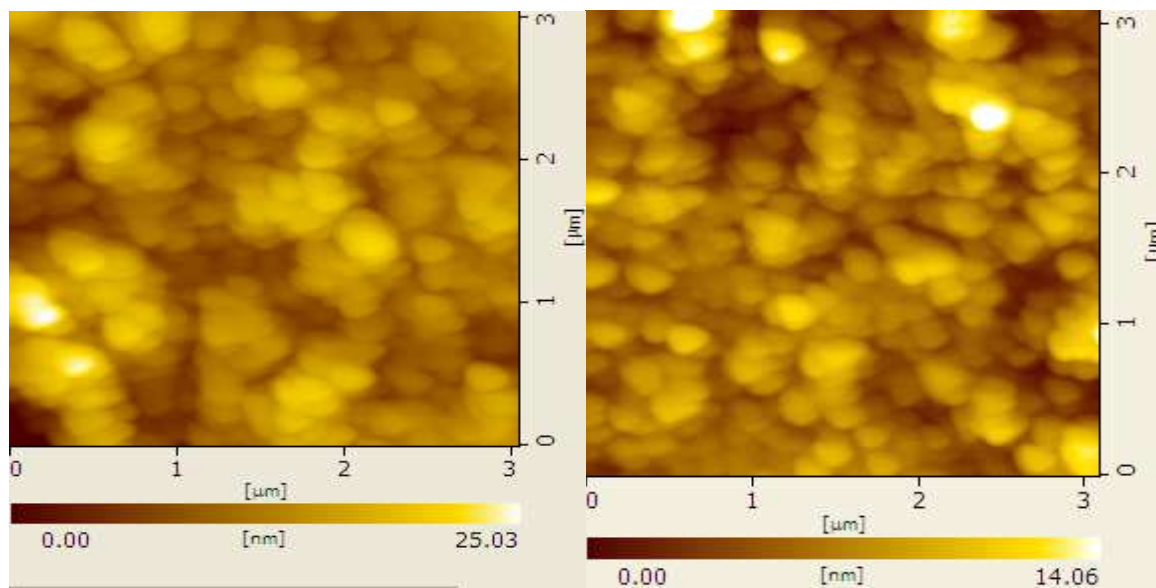


Fig 4 (a) AFM of 5nm Ag film note Shape changes of the Ag nano particles w.r.t 2nm thin film (b) 10nm Ag film Iodized for 30min Note the smaller size of Ag particles w.r.t those of 5 nm film and the Void space created.

3.3 Optical Absorption

Mie particles such as those triangular nanoparticles observed in our 2nm Ag films could give plasmon absorption band due to (i) surface conduction electron collective oscillations or surface plasmon resonance (SPR) and (ii) scattering of electrons in the inner particle surface especially when their sizes are small (say 5-60 nm) compared to electron mean free path (typically 100nm)[11]. The peak position and full width at half maximum of the absorption band depend on (a) type (b) size and (c) geometry of the particle as well as (d) on the difference between dielectric function between metal and surroundings. Moreover, when iodization is progressively carried out, the SPR absorption is expected to gradually decrease and as soon as the initial batch of AgI nanoparticles are formed (whose size could be as small as 13 nm) one expects to see the formation of the

exciton absorption band in the UV-Visible spectrum. We now describe and discuss results Optical absorption spectra of 2, 5 and 10 nm thick Ag films. Fig 5 shows 2nm thick films are made up of triangular nano particles of size 100-120 nm which give rise to an asymmetric surface plasmon resonance (SPR) maximum at 440nm. This is due to the plasma resonance effect as well as the displacement of the electronic cloud. The line shape of the 2nm thick films show the broad spectrum with symmetric line shape indicating the inhomogeneous interparticle distances. The asymmetry of the SPR peak suggests an unresolved second component which is normally resolved in the case of spherical nanoparticles. For silver nanoprisms, the plasmon absorption split into two bands corresponding to the oscillation of the free electron, But in our study due to larger particle size, and interparticle distances the second longitudinal plasmon absorption got merged in to the first SPR[12]. Figure 5(b) and (c) show that the longitudinal plasmon mode of the triangular particles is, indeed, more red shifted compared to thinner films. As the thickness is increased to 5nm the shape changes from triangular to disc. Edges of the triangles bend and tend to form Ag nanodisc particles with a decreased edge length (to below $\sim 100\text{nm}$) with enhanced surface area. Now the Mie resonance shows a red shift with the peak occurring at 457nm. This leads to the appearance of a more intense, more symmetric Lorenz-resonance due to increased surface to volume ratio resulting from reduced size. Finally 10 nm thick films show a further red shift around 44nm (peak at 484 nm) and their intensity increases linearly with increasing radius of the sphere as the thickness induced shape develops phase transition occurs. The thickness-dependence of the SPR maximum wavelength (λ_{max}) which is a measure of the plasmon energy is shown in Figure 6. λ_{max} increases linearly with thickness which must be understood as an effect

of increasing filling factor and increasing particle density and reduced void space-all of which influence the dielectric function of the thin-film nanostructure-substrate combination including the interface. Thus the two major effects of increase thickness are shape transition and increased inhomogeneous scattering contribution indication a distribution of inter particles distances further investigation into these and other aspects are in progress.

Fig 7 shows the typical response of a **10nm** Ag film as it is progressively iodized for 0, 5, 15 and 30 minutes. The peak marked SPR1 represents the plasmon Signature in the pure Ag film. Just a 5 minute exposure to the I_2 vapours creates a AgI film on a Ag background identified by the wurtzite exciton peak at ~ 420 nm[13] actually signaling the formation of the surface electronic structure. It is important to realize that it is very difficult to probe this development so easily by any other technique. Thus in the 5 minutes iodized Ag films the plasmon –exciton ‘transition’ has just begun. Further iodization sees the fuller development of the exciton structure by way of $W_{1,2}$ and W_3 and the suppression of plasmon peak, in the manner of a metal-insulator transition. A future work would examine the microscopic nature of this transition as well its connection to AgI thin film formation [14].

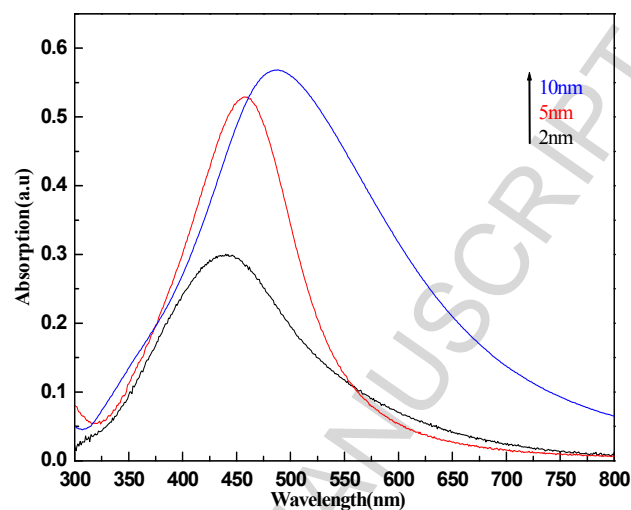


Figure 5. Optical absorbance spectra of as deposited 2, 5 and 10 nm thick Ag films.

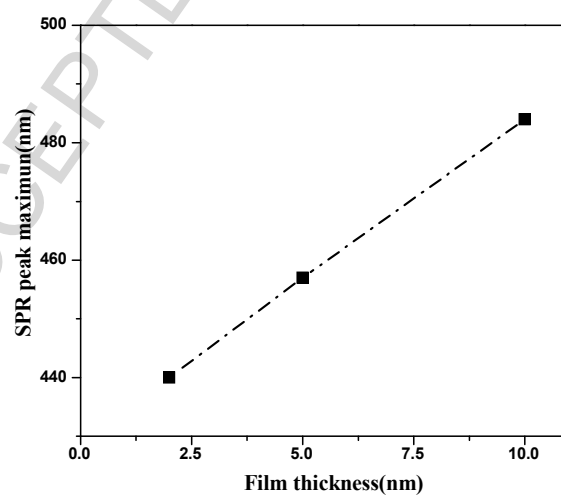


Figure 6. Films thickness vs observed SPR maximum

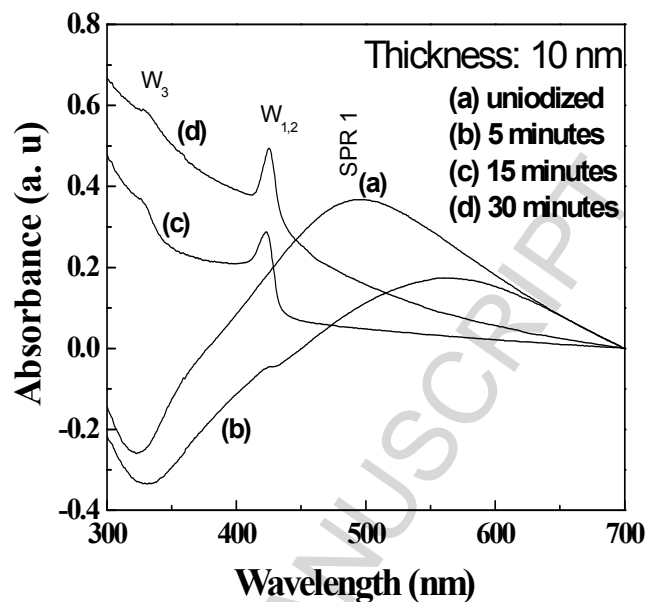


Fig 7. Iodization of a 10 nm thick Ag film brings about a plasmon-exciton ‘transition’ even as the metallic Ag becomes an insulating AgI.

Conclusions

In this work we have described and discussed XRD, AFM and optical absorption behaviour of nanostructured Ag films 2, 5 and 10 nm thick obtained by thermal evaporation. While all films are quasi amorphous, 2 nm thick films exhibit nanotriangles in the nature of Mie particles which exhibit surface plasmon resonance (SPR). Increase of thickness produces a shape change from nanotriangle to spherical triangle and a red shifted SPR. Most interestingly systematic iodization throws up a quasi-particle transition namely plasmon-exciton transition even as Ag metal film is converted into an insulating/semiconducting AgI film.

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References

1. L Hesselink, Photonics 2006, 8th Int. Conf. Optoelectronics, Fiber Optics and *Photonics*, Hyderabad, India Dec 13-16-2006, Abstracts 2 p.241.
2. J. J. Storhoff, R. Elghanian, R. C. Mucic, C. A. Mirkin, R. L. Letsinger, J. Am. Chem. Soc., **120**, 1959 (2002).
3. Y. Dirix, C. Bastiaansen, W. Smith, Adv. Mater. **11**, 223 (1999).
4. J. B. Pendry, Phys. Rev. Lett. **85**, 3966 (2000).
5. E. N. Economou, Phys. Rev. **182** 539 (1969).
6. D. Bharathi Mohan and C. S. Sunandana, J. App. Phys., **100**, 064314 (2006).
7. D. Bharathi Mohan, V. Sivaji Reddy and C. S. Sunandana, App. Phys. A, **86**, 73 (2007); D. Bharathi Mohan, K. Sreejith and C. S. Sunandana, Appl. Phys. **B89** 59(2007)
8. Z. H. Meiksin, Physics of Thin Films, **8**, 161 (1975).
9. M.H. Chowdhury, K Ray, C. D Geddes and J R Lakowicz, Chem. Phys. Lett. **452** 162 (2008) and references therein
10. J R G Patnaik and C S Sunandana, J Phys Chem Solids **59** 1059(1989)
11. U Schubert and N Husing, Synthesis of Inorganic Materials, Wiley-VCH 2005, p 366
12. X. Zheng, W. Xu, C Corredor, S. Xu, J. An, B. Zhao and J R Lombardi, J Phys. Chem. C, **111**, 14962(2007)

13. M Cardona, Phys.Rev.**129** (1963)690.

14. P Senthil Kumar and C S Sunandana, Proc. SPIE **4807**(2002)241

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