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Sb-ASSISTED AgI NANOPARTICLE GROWTH IN THIN FILMS

P. Senthil Kumar, Swati Ray and C.S. Sunandana

School of Physics, University of Hyderabad, Hyderabad 500 046, INDIA

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Abstract. The growth of AgI nanoparticles by iodization of $Ag_{1-x}Sb_x$ thin films under ambient conditions has been investigated. Mechanically well ground mixtures of Ag and Sb were thermally evaporated onto microscopic glass slides. They were subsequently iodized at ambient temperature in the dark and characterized by XRD, SEM and optical measurements. Preliminary results infer that the addition of Sb favors the island growth of AgI, but greatly retards the rate of AgI particle growth, resulting in nanometric sized AgI particles. 5% Sb doped Ag films with optimal thickness (~ 200 Å) are found to be ideal for the formation and long term stabilization of γ-AgI thin films. Sb also plays a crucial role in controlling the exciton formation process.

1. INTRODUCTION

Nanoparticle growth of I-VII semiconductors such as AgI aimed at obtaining ordered nanostructure materials remains an actively pursued challenge in semiconductor nanophysics and nanotechnology [1]. In addition to realization of low dimensional systems (e.g. quantum dot arrays) with potential optoelectronic applications, such materials enable exploration of rich exciton physics.

Our earlier investigation [2] revealed that porous Ag foil obtained by "etching" offer as attractive a medium as an anodic alumina [3] for the AgI particle growth. Also, the isovalent Cu added as a minor component to Ag precursor films yields, upon iodization, more stable AgI nanoparticles [4] through island formation and retarded particle growth. However, aliovalent impurities such as Cd^{++} and Pb^{++} considerably enhance the iodization rate and yields only wurtzite β-AgI [5]. Thus we are led to explore trivalent impurities such as Sb or Bi to exercise a better control (than possible with Cu) over AgI particle growth, so that nanoparticle arrays could be conveniently assembled for device applications in a matrix free approach.

2. EXPERIMENTAL

Three precursor compositions (wt. %) *viz.* 99%Ag – 1%Sb, 95%Ag – 5%Sb and 87%Ag – 13%Sb respectively were chosen from the Ag-Sb phase diagram [6]. Mechanically ground mixtures of Ag and Sb were thermally evaporated onto micro glass slides held at room temperature at a pressure of $\geq 5 \cdot 10^{-5}$ Torr. These precursor films were iodized in a cylindrical chamber [2,4] using appropriate quantity of iodine. Preliminary structural and microstructural characterization of the iodized films were done using PHILLIPS powder X-ray diffractometer (Cu-K_α radiation) and a JEOL-SEM. Optical absorption measurements were carried out using a Shimadzu-3101 UV spectrophotometer to look at the exciton and band structure formation.

3. RESULTS AND DISCUSSION

The precursor films show progressively increasing structural disorder by way of broader XRD peaks relative to that of undoped Ag. The origin of this disorder must be sought in the formation process of the films itself, owing to the nature of the substrate

Corresponding author: C.S. Sunandana, e-mail: csssp@uohyd.ernet.in

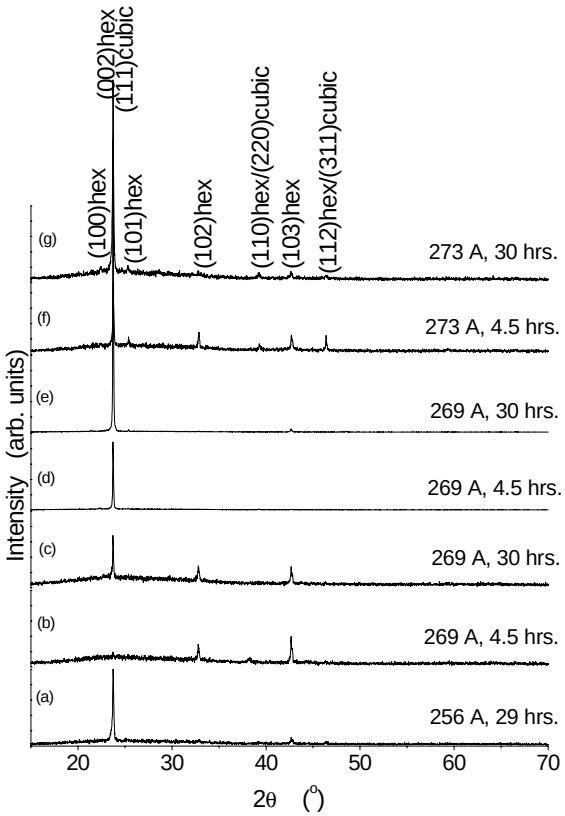

Fig. 1. Sb concentration, thickness and iodization time dependent evolution of the XRD patterns for (a) AgI, (b) and (c) $Ag_{0.99}Sb_{0.01}I$, (d) and (e) $Ag_{0.95}Sb_{0.05}I$, (f) and (g) $Ag_{0.87}Sb_{0.13}I$ thin films. Note the oriented γ-AgI film growth particularly in 5%Sb doped films.

(glass) and also to the strain effects. The ionic size mismatch ($r_{Sb}/r_{Ag} \approx 2$) is also expected to introduce extensive defects and disorder in the Ag lattice and induce formation of rather small Ag-Sb clusters. Sb favors island formation in the presence of a silver sublayer [7] even in thicker films, thus promoting upon iodization, considerably arrested surface diffusion and reduced aggregation. Iodization of these films as a function of thickness and time delineate these aspects vividly as revealed by XRD (Fig. 1) and SEM (Fig. 2). As the slower attack of halogen vapors on silver surface [8] yields strongly oriented layers of the halide lattice, Sb addition unmistakably favors the oriented γ-AgI film growth right from the nucleation stage itself.

The distribution of particle sizes (20 – 40 nm) in the iodized films calculated using the Debye-Scherrer formula awaits a more-detailed investigation of the variation of particle sizes with compositions/thickness and will be published elsewhere.

The representative SEM micrographs of the iodized films – reminiscent of the fundamental work on nucleation, growth and coalescence of Ag films [9] – clearly reveals the formation of uncoalesced islands. Retarded iodization rates (~ 3 times the duration compared to that of undoped Ag films) and nanoparticle "decoration" emerge as the most spec-

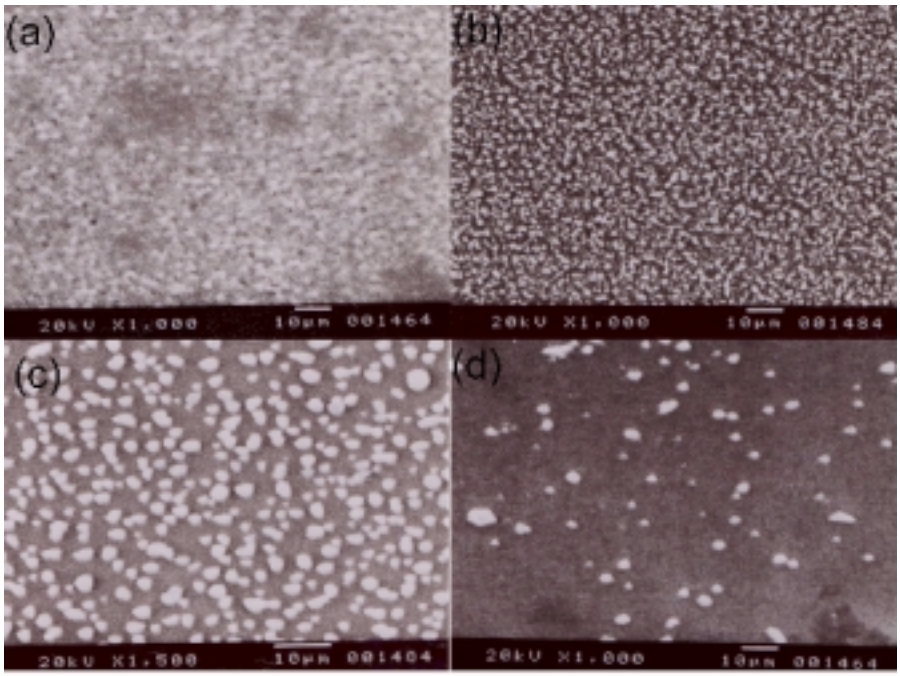

Fig. 2. Effect of Sb doping on the AgI island formation in thin films as revealed by SEM. (a) AgI thin film of thickness ~ 260 Å, iodized for 4.5 hours, (b) $Ag_{0.99}Sb_{0.01}I$ thin film of thickness ~ 150 Å, iodized for 5 hours, (c) $Ag_{0.95}Sb_{0.05}I$ thin film of thickness ~ 150 Å, iodized for 5 hours and (d) $Ag_{0.87}Sb_{0.13}I$ thin film of thickness ~ 275 Å, iodized for 4.5 hours.

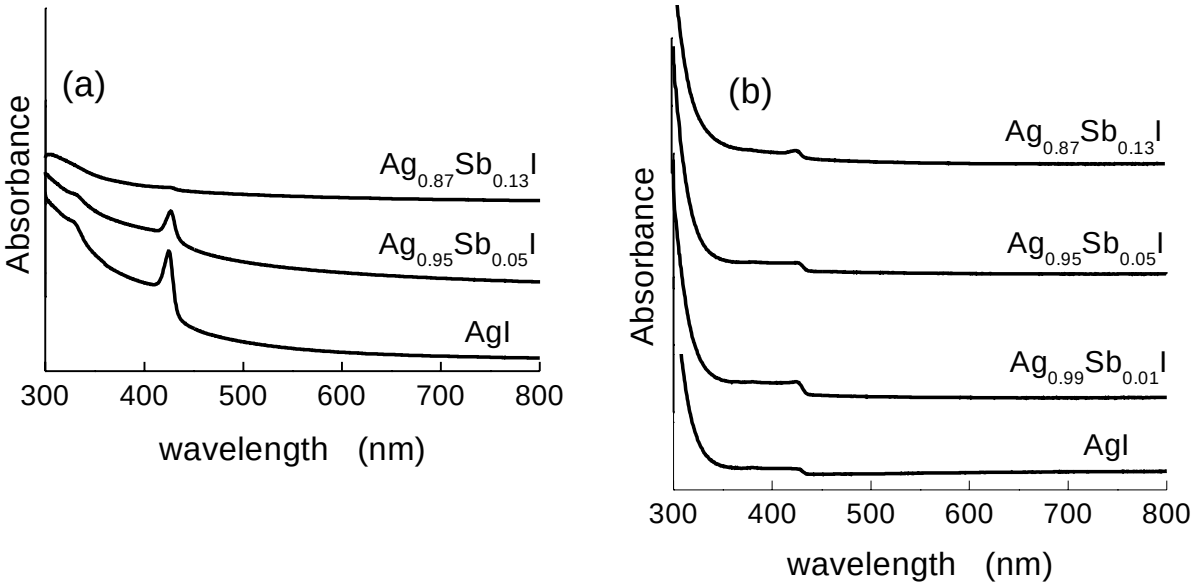

Fig. 3. UV-visible absorbance spectra of undoped and Sb doped films of thickness 151 Å iodized for (a) 4.5 and (b) 24 hours. Note the systematic retardation in AgI formation as clearly revealed in (a) by the diminishing 420 nm peak with increasing Sb concentration.

tacular effects of Sb-doping on AgI particle growth. From the application point of view, ~ 200 Å thin, 5%-Sb doped Ag films upon iodization for 20 hours yields stable γ-AgI films, with arrays of nearly spherical particles (Fig. 2). However, both 1% and 13%-Sb doped Ag precursor films respectively contain rich physics by way of Ag structure stabilization and kinetics of iodization with respect to the formation of mixed ($\gamma + \beta$)-AgI films, iodization time being a crucial parameter.

The optical absorption spectra shown in Fig. 3 exhibits the feature of a semiconductor with a direct band gap. Sb considerably controls the exciton formation in AgI films through its particle size and porosity dependence. The 420 nm exciton peak, sharp rise in absorption below 320 nm and the long wavelength tail due to the intrinsic Frenkel disorder, all systematically characterizes the very basic process of the band structure formation of AgI starting from the nanocluster level. The spatial and time dependence of the increasing size of the crystallites was corroborated with our earlier measurement [10] to be due to decrease in quantum confinement of the excitons and is being investigated in detail.

To conclude, we have demonstrated that ambient iodination of Ag-Sb alloys is a convenient way of synthesizing AgI nanostructures, in a unique formation mechanism that is being explored for the first time to the best of our knowledge.

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