Chapter V

Cu enhanced quasi–free excitonic photoluminescence in Co-Sputtered Ag$_{1-x}$Cu$_x$ (x= 0.05, 0.1 and 0.2) thin films grown on fused quartz substrates iodized at ambient

5.1 Introduction

The Ag-Cu binary system is quite interesting because its alloys are classic examples of relative ineffectiveness of alloying and thus has the possibility of existing as metastable solid solutions over the entire range of compositions [1,2]. Earlier studies on Su-substituted AgI thin films by Senthil Kumar [3,4] and on nano/micropowders by Bharathi Mohan [5,6] and Shahi [7,8] have recognized the unusual effect of Cu on the physics of AgI. The most interesting aspect of these Ag-Cu solid solutions is the crucial role played by Cu in stabilizing the $\gamma$-phase of AgI when iodized and favourably enhancing the optical properties, as would be demonstrated in this chapter. As 30% vacancies in the fcc structure of Ag lattice, are available for the smaller Cu atoms the latter would control the motion of Ag$^+$ ions in the AgI lattice upon iodization thus ensuring stability of the zincblende structure reinforced at the Ag-I band level, with Cu induced reduction in lattice parameter.

In present study we have chosen the RF magnetron sputtering technique to prepare quasi amorphous Ag-Cu thin films in which Cu promotes layer type growth. The RF sputtered films will have more disorder and display stain-induced thin films growth depending upon the plasmon environment. This helps us to slow down the growth kinetics, thus providing an attractive controllable platform for studying formation of $\gamma$-AgI nano particle growth through structural, microscopic and optical probes. Relative to the sputtering of Undoped Ag and the evaporation of cu-doped Ag, the inherent disorder associated with sputtering coupled with the Cu-advantage are expected to result in delayed formation of gamma AgI upon iodization reducing the possibility of wurtzite formation even in thicker films. A dramatic consequence of these development is the observation of Cu-enhanced quasi-free excitonic photoluminescence in the blue region at 300K.
5.2 Deposition of Ag-Cu thin films

Thin Ag-Cu alloy (at wt % 5, 10 and 20 Cu) films thickness of 5 and 15 nm were deposited on fused silica substrates by RF Co-Sputtering method. The highly pure silver and copper metal targets (Aldrich, 99.999) are used for thin films depositions. The desired composition ratios of 5, 10 and 20 % (by atomic weight %) were obtained by placing appropriate size of Cu metal pieces placed on the top of the 2 inch Silver target(cathode dia: 2inch). This target was placed on the RF cathode for prior deposition. Here we have used up sputtering or sputter-up process to deposit Ag-Cu alloy films. Initially, the sputtering chamber was evacuated to a base pressure of 2x10^-6 Torr after loading the cleaned substrates on to the substrate holder placed inside the vacuum chamber. All the films were deposited at a fixed RF power 15 W. A working pressure of 10 mTorr was constantly maintained using high pure argon (purity: 99.999%). The argon pressure was 10 sccm to achieve uniform rate of deposition. The target to substrate distance was fixed at 15 cm. It was observed that without any heating, the un-cooled substrate temperature increased to about 50-80°C during the deposition, presumably due to ion bombardment. To avoid this undesirable substrate heating the substrate was kept at distances greater than 15 cm (even though scattering will be more). A few batches of thin films of pure Ag and of Ag-Cu (5, 10 and 20%) composition with thickness of 5 and 15 nm were deposited at room temperature and the rate of deposition was maintained constant during the entire depositions. The above conditions were found favorable for the formation of homogeneous, amorphous alloy films, and the actual composition ratio of coated films was analyzed using EDAX. The average thickness of the films was determined by using AMBIOS XP-1 profilometer.

Iodization: Iodization of these thin films was done an hour-glass type chamber. Iodine kept at the bottom of the lower half of the chamber sublimes at room temperature and slowly (over durations ~ tens of minutes) deposits on the Ag_{1-x}Cu_{x} alloys films kept at the top of the chamber kept in a dark room [9-11]. Thus iodization was carried out for selected durations in the range of 30 to 720 min.
Substrate clean: Fused silica substrates were cleaned with piranha solution for 30 minutes (1:3 ratios: 30% hydrogen peroxide/concentrated sulfuric acid). *(Caution piranha solution reacts violently with most organic materials and should be handled with extreme care).*

Following the deposition of Ag-Cu thin films, a series of characterization techniques probing the structural, microstructure and optical properties of the films were performed. The stiochiometry of the films was established by Energy dispersive X-ray analysis (EDAX) analysis as described in chapter 2. The crystal structure of Ag, Ag-Cu and AgI films deposited on fused silica substrates as a function film thickness and Cu concentration were characterized using X-ray diffraction (XRD) technique. Following the XRD measurement, Dynamic Force microscope (DFM) was employed to measure the surface morphology of the films, which provided high resolution images. The room mean square roughness (rms roughness) was also determined using DFM. Optical band gap (Eg) of cation stabilized AgI films deposited on fused silica substrates were determined from the spectral absorption data obtained from UV-Visible spectrophotometer. The band development of iodized Ag-Cu films was monitored by the photoluminescence a study using a Fluorolog@-3 Spectrofluorometer has been used in the UV/Visible range 300 to 800 nm with scanning rate of 200 nm/min at different excitation levels. A correlation between the structural, microstructural and optical properties of AgI films is discussed.

### Table 5.1 Sputter deposition parameters of Ag and Ag-Cu thin films

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tbody>
<tr>
<td>Power density (W/cm²)</td>
<td>15 W</td>
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<tr>
<td>Substrate to target distance (cms)</td>
<td>15 cms</td>
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<tr>
<td>Working pressure (mTorr)</td>
<td>10 mTorr</td>
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<tr>
<td>Ar pressure (sccm)</td>
<td>10 sccm</td>
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<tr>
<td>Substrate types</td>
<td>Fused silica substrates.</td>
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<td>Substrate temperature</td>
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Chapter V  
RF Sputtered Cu doped AgI Thin Film

5.3 Structural characterization of γ-AgI films deposited on fused silica substrates

5.3.1 Lattice parameter and iodization time dependent strain measurement

The crystal structure of γ-AgI thin films grown at two different film thickness which is 5 and 15 nm with 5, 10 and 20% Cu concentrations on fused silica substrates were analyzed by XRD θ–2θ scans using Cu Kα radiation (λ=1.54Å) and are shown in figure 5.1,5.2. The as-deposited Ag and Ag-Cu alloy films were found to be quasi-amorphous in nature as revealed by XRD patterns without any detectable Bragg peaks [12-17]. Without any further post deposition treatment, these films were then iodized systematically to determine whether the disordered structure would yield stable γ-AgI thin films and offer a more fundamental platform to monitor the evolution of the crystal structure and electronic band structure (It is pertinent to think of nanostructure development as a nucleation and growth phenomenon from a frozen liquid). XRD pattern of 5nm Ag films iodized at 30 to 360 min shows figure 1 the gradual AgI structure development. Over short time iodization up to 30 min there is no evidence for AgI structure development observed because of RF sputtered Ag films will have more disorder and strain because of low thermal energy arresting surface diffusion on sputtered Ag particles and therefore it delays the formation of AgI which is favorable for stabilizing metastable γ-AgI structure [10,11]. After 30 min iodization, there is small peak development absorbed around 20=27.54 which is characteristic of γ-AgI. As iodization time is further increased from 30 to 180 min there is a gradual increase in the (111) plane intensity. The enhancement of intensity is due to increase of crystallinity suggesting that the rate of generation of γ-AgI nanoparticles in these 5 nm Cu doped Ag films is relatively higher than in 5 nm Undoped Ag films [9-11,17-20]. Upon further iodization for 180 to 360 min the (111) reflection intensity starts to decrease slowly, possibly due to small impurity phase formation which is wurtzite β (100) and β (101) at low Bragg angles. Figure 5.1 (ii) shows the structure of 15 nm Ag films iodized at up to 24 hr. Iodization of 15 nm thick Ag films shows amorphous nature an-indication of lack of development of long range order. Nano-crystallization begins after 60 min iodization of thick Ag films. After a prolonged iodization up to 360 min we could see only stable γ-AgI (111) plane with very high intensity Thereby the expected goal of delayed and disorder controlled fabrication of zincblende AgI films is achieved. In the case of long time iodization 24 hr mixed phase of minor wurztite β-AgI phase with (100), (102) and (103)
planes and major zincblende phase (111) structures of AgI were observed for thicker films [10,11].

Figure 5.1: XRD pattern of (i) 5 nm (ii) 15 nm Ag thick films iodized for different times.

Figure 5.2: XRD pattern of 5 nm thick (i) $\text{Ag}_{0.95}\text{Cu}_{0.05}$ (ii) $\text{Ag}_{0.90}\text{Cu}_{0.10}$ and (iii) $\text{Ag}_{0.80}\text{-Cu}_{0.20}$ Ag-Cu films iodized for different times (a) 30 min (b) 60 min (c) 180 min and (d) 360 min (e) 720 min and (f) 24 hr.
The ratio \( R \) of the relative percentage of \( \beta \) and \( \gamma \)-AgI could be determined by using the relation

\[
R = \frac{I(111)_{\gamma} + I(002)_{\beta}}{I(100)_{\beta} + I(101)_{\beta}}
\]

Figure 5.2 (i), (ii) and (iii) shows the structure evolution in Cu doped (5, 10 and 20 %) Ag-Cu thin films 5nm thick. The \( \gamma \)-AgI nanoparticles were clearly seen upon progressively iodized Ag-Cu metastable alloy thin films under ambient condition (300K and ~760 mm pressure). Cu induced disorder in Ag films (initially upto 60 min iodized) enables growth of \( \gamma \)-AgI nanoparticles. After 180 min iodization around 2\( \theta \)=23.75\( ^{\circ} \) the \( \gamma \)-AgI (111) zincblende structure pattern observed with very small intensity. As iodization time is increased to 360 min the intensity of the (111) plane increased with no impurity phase (\( \beta \)-AgI) being observed. But in the case of undoped AgI films after 180 min iodization there is strong overlapping between \( \beta \) and \( \gamma \) AgI structures co-existing in the iodide film. The Cu substitution thus stabilizes the metastable zincblende structure of \( \gamma \)-AgI besides assisting in particle size reduction due to the possibility of reinforcing the Ag sublattice in AgI aided by enhanced covalency of the Ag-I bond. Doped Cu ions could either occupy the vacant interstitial position in the Ag lattice or substitute Ag ions thereby depleting Frenkel defects in the AgI lattice and arresting the random motion of the Ag\( ^{+} \) ions. Although the Ag-Cu binary system has only metastable solubility in view of their positive heat of mixing, there is a natural tendency for Cu to stabilize \( \gamma \)-AgI zincblende structure especially because zincblende CuI is the most stable phase.

Figure 5.3 (i), (ii) and (iii) shows the XRD of Cu doped (5, 10 and 20 atomic wt %) Ag-Cu thin films thickness of 15 nm. Short time iodization (60 min) of 5% Cu doped Ag films shows there is a strong Ag (111) plane: there is no evidence for AgI formation due to film thickness as well as Cu induced disorder nature. Prolonged iodization of Ag-Cu alloy shows the strong Ag crystalline fcc structure with only two diffraction peaks appearing in the spectra, namely the (111), (200). The low angle (111) Ag peak is the most intense in the pattern, which implies a slight preferential orientation of the Ag grain along the (111) crystallographic direction [21-26].
Figure 5.3: XRD pattern of 15 nm thick (i) Ag$_{0.95}$Cu$_{0.05}$ (ii) Ag$_{0.90}$Cu$_{0.10}$ and (iii) Ag$_{0.80}$-Cu$_{0.20}$ iodized for different times (a) 60 min (b) 180min (c) 360 min and (d) 720 min and (e) 24 hr.

In figure (ii) and (iii) the iodization time increased to 3 to 24 hr shows the β-AgI phase observed for 15 nm thicker films and proportions of which increases with increasing iodization time reflecting the iodine-rich regions in these films favor that the condition, (Ag/I)$\leq$1. The wurtzite structure of β-AgI (2H) and zincblende structure of the metastable γ-AgI (3C) [27] differ in the stacking sequences, and they can be regarded as different polytypes so called γ-AgI films shown in figure 5.3. γ-AgI film contains more or less stacking disorder, exhibiting only traces of the β (100) and β (111) line. This is evidence of γ-phase being stabilized by non-stiochiometry and strain due to a difference in the thermal expansion coefficients between the AgI film and substrates. The 5 nm Ag films iodized at 360 min show reddish colour, suggesting iodine deficiency, while the 15 nm Ag film iodized at 24 hr exhibit pale yellow colour. These stacking faults are usually associated with (111) planes of crystallites, which are prone to ‘ABABAB’ type of
hexagonal close packing instead of ‘BCABCABC’ type of cubic close packing the existence of two polymorphs [28], γ-AgI and β-AgI, with the same first neighbor coordination of Ag by I atoms and propensity of β-AgI to grow into big micro crystal, thus offering a stiff competition to the nucleation and growth of γ-AgI nanoparticles making the study of nanoparticle structure growth process an attractive challenge.

However, the peaks become intense and narrow with increase in iodization time, which indicates that crystallinity improves with increase in iodization time. Interestingly it was observed that the iodization influences the direction of preferred orientation of γ-AgI films on fused silica substrates. Perhaps the Si-O tetrahedral banding in SiO₂ substrate encourages this. The evolution of preferred orientation in polycrystalline thin films can be analyzed from the viewpoint of energy minimization. The total energy in any film deposited on a substrate is the sum of three components: (1) the surface energy of the film, (2) the film–substrate interface energy, and (3) the strain energy in the film [25].

Figure 5.4 clearly shows the qualitative analysis of thickness and iodization time dependent changes in γ-AgI lattice parameter (a) and average stain (ε) calculate from XRD pattern. Lattice parameter of γ-AgI (111) peak for 5 nm thin film is initially, short time iodization shows very high (6.61Å) which shows there is the compressive residual stress present in the initial iodization time [10]. Upon prolonged iodization the lattice parameter starts decreasing slowly and finally matching with 6.495Å JCPDS standard value for γ-AgI. This means Cu progressively substitutes Ag ions thereby depleting Frenkel defects in the AgI lattice, thus arresting the random motion of the Ag⁺ ions and internal stress gets relaxed in the AgI matrix. However, for 15 nm thick films the lattice parameter decreases crosses the JCPDS value during short time iodization finally 6.641Å after 24 hrs iodization due to defects and multiphase AgI (γ and β) phase [23].
From the peak shift in the XRD pattern, average strain ($\varepsilon$) was calculated using the following relation 

$$
(\varepsilon) = \frac{[d_{\text{observed}} - d_{\text{reference}}]}{d_{\text{reference}}} \times 100\%
$$

where $d_{\text{observed}}$ and $d_{\text{reference}}$ are the interplanar spacing of $\gamma$-(111) and reference from JCPDS respectively. Figure 5.4(b) shows calculate average strains of $\gamma$-AgI for two different thickness 5 and 15 nm. The short time iodized 5 nm AgI films shows the average strain is positive and it is very high (1.89 %) at 30 minutes iodization suggesting the presence of compressive stress at room temperature. On prolonged iodization the average strain decreases slowly and finally approaches zero strain or free strain state at 720 minutes. It clearly shows the strain relaxation in defects free film realized by iodization. In 15 nm thick Ag films iodized at (1-24 hr) show that the compressive stress becomes the tensile stress (the calculated values of strain is negative) for 24 hr iodization time while compressive stress (strain is positive) increases with the increasing iodization time 24 hr resulting in the production of more $\beta$-AgI. This strain arises possibly due to the formation of Frenkel defects.

**5.4 Surface microstructure characterization of AgI thin films grown on fused silica substrates**

The two dimensional and its corresponding three-dimensional, DFM image of AgI and Cu doped AgI films deposited on fused silica substrates at two different film thickness (5 and 15 nm) and different iodization time shown in figure 5.5 to 5.10. Figures
5.5 and 5.6 show the microstructure of as deposited 5 nm and 15 nm thick Ag films. The surface morphology of as deposited Ag film consists of uniform spherical size particles with average particle sizes of 25 and 35 nm [10,11,17,29]. Surface roughness (rms) of the as deposited films is 1.23 and 3.26 nm as shown in figure 5.11. With increasing the film thickness the surface to volume ratio decreases and in turn grain size and surface roughness increases. The iodization process induces AgI grain growth leading to a significant increase in lateral grain growth and a striking difference in the morphology between Ag-I bonds depending upon iodization time. Figure 5.5 and 5.6 (b) and (c) all show Ag to be passivated at the top by a thin I$_2$ layer and at the bottom by the unconsumed Ag layer (core-shell) after the 60, 360 and 720 minutes iodization of 5 and 15 nm Ag films [30-33].

In short time iodization initially favours core-shell type grain growth the core being Ag while shell is AgI (to be discussed exhaustively in the chapter 6). Depending upon the iodization time, the iodine will diffuse (lateral diffusion) in to the Ag surface and stabilizes the Ag-I bond formation [30-31]. When iodization time increased to 360 minutes the shell thickness increases which shows the development of $\gamma$-AgI zincblende structure. Upon prolonged iodization grain size increases from 24 nm to 55nm and from 35 to 83 nm for 5 and 15 nm films. Surface roughness of the films increased which are 1.23 to 3.2 nm and 3.26 to 6.46 nm for 5 and 15 nm films as clearly shown in figure 5.11. In short time iodization when the iodine flux is exposed to Ag surface the Ag grains start slowly growing and once the formation of Ag-I bond is complete the grain size and roughness of the films get stabilized which implies the uptake of iodine molecules is just enough to form Ag-I bond and AgI$_4$ tetrahedra. Further more 24 hr iodization shows the iodine rich regions in the system which would allow the formation of $\beta$-AgI wurtzite structure seen in XRD pattern [9-11,30].
Figure 5.5: DFM Surface micro structure (0.5 μm x 0.5 μm) of 5 nm thin Ag films (a) As deposited (b) 30 min (c) 360 minutes iodized.
Figure 5.6: DFM Surface micro structure (0.5 μm x 0.5 μm) of 15 nm thin Ag films (a) As deposited (b) 60 min (c) 720 minutes iodized.
Figure 5.7: DFM Surface micro structure (1 μm x 1 μm) of 5% Cu doped 5 nm thick Ag films (a) As deposited Ag (b) 60 min (c) 720 minutes iodized.
Figure 5.8: DFM Surface micro structure (1.5 μm x 1.5 μm) of 10 % Cu doped 5 nm thick Ag films (a) As deposited Ag (b) 60 min (c) 720 minutes iodized.
Chapter V                                           RF Sputtered Cu doped AgI Thin Film

Figure 5.9: Surface micro structure of 5 % Cu doped 15 nm thick Ag films (a) As deposited Ag (b) 180 min (c) 24 hr iodized.
Figure 5.10: DFM Surface micro structure (1 μm x 1 μm) of 10 % Cu doped 15 nm thick Ag films (a) As deposited Ag (b) 180 min (c) 24 hr iodized.

Figure 5.7 and 5.8 show DFM micrographs of 5, 10 and 20 % Cu doped 5 nm thin Ag-Cu alloy films iodized at different times. The purpose of Cu doping is to stabilize zineblende structure of γ-AgI besides assisting particle size reduction and control the growth assisted by sputter disorder. The surface morphology of the as deposited Ag-Cu
alloy film shows the well defined uniform spherical shaped nanoparticles with average grain sizes of 30 and 40 nm [13-15,34-38]. Significantly Cu arrests agglomeration in nanoclusters of Ag-Cu alloy systems. Because of lower atomic radius of Cu relative to that of Ag the amount Cu ions that go into silver sub lattice controls the grain growth. The short time iodization of Cu doped AgI shows the triangular shaped grain growth which provides direct evidence for Cu induced shape transformation shown in figure 5.7. As the Cu$^+$ ions are the reinforcing cations in to the sublattice of these Ag rich zincblende solid solutions, the identity of the phase that evolve thermally depends on the changes in the Cu$^+$ occupancies relative to the initial Zincblende lattice. The $\gamma$-AgI grain growth is clearly seen in progressively iodized Ag-Cu metastable alloy films under ambient condition. As more and more Cu atoms substitute Ag in AgI, the Ag-I bond progressively shortens and strengthen due to enhanced p-d hybridization, there by stabilizing robust $\gamma$-AgI grain growth.

Figure 5.11: Thickness and iodization time dependent (a) particle size and (b) surface roughness changes in Ag and 5 and 10% Cu doped 5 and 15 nm thick Ag-Cu thin films.

5.5 Optical properties of RF Sputtered Ag and AgI thin films

5.5.1 Surface plasmon resonance of Ag and Ag-Cu alloy films

Figure 5.12 shows the UV-visible optical absorption spectrum of 3-15 nm thick Ag films. Figure 5.12(a-d) shows thickness dependent surface plasmon resonance (SPR) of Ag thin films deposited on fused silica substrates [39-49]. 3 nm thin Ag film shows the SPR band maximum ($\lambda_{\text{max}}$) at 413 nm. Where as 5, 8, 10 and 15 nm thick films show the
Figure 5.12: Surface plasmon resonance spectra of (i) pure Ag films thickness of 3-15 nm (ii) 5, 10, 20 % Cu doped Ag films thickness of 5 nm (ii) 5, 10, 20 % Cu doped Ag films thickness of 15 nm. Figure 5.12 (a), (b) and (c) SPR peak maxima and FWHM (a) undoped (b) 5, 10, 20 % Cu doped Ag films thickness of 5 nm (c) 5, 10, 20 % Cu doped Ag film thickness of 15 nm. Thickness dependent SPR show shifts in the plasmon peak position towards red but Cu doped Ag films show shifts towards blue in the SPR.
SPR at 466, 432, 440 and 451 nm. Increase in absorbance value and shifting of SPR peak position in the higher wavelength region is in proportion to increase of Ag films thickness and subsequent formation of larger sized grains [50-54]. The full width and half maximum (FWHM) of the SPR of 3 nm thin Ag film is 63 nm. The shape of the SPR peak is very sharp an evidence for uniform distribution of Ag nano particles size of 25 nm. A systematic increase of SPR peak broadening with FWHM of 95, 115, 118 and 121 nm observed with increasing Ag films thickness merits explanation from Mie’s theory [39,40].

According to Mie’s theory, only a single SPR band is expected in the optical absorption spectra of spherical nanoparticles (NPs), whereas anisotropic particles can give rise to two or more SPR bands depending on the shape of the particles [41-43]. The $\lambda_{\text{max}}$ value shifted gradually towards the red region with the increasing of Ag film thickness due to decrease of interparticle distance and increase of volume fraction which causes the aggregation of Ag nano particles [51].

Figure 5.12 (ii) and (iii) shows the UV-visible optical absorption spectra attributed to surface plasmon resonance of 5, 10 and 20% Cu doped 5 nm thin Ag thin film. 5% Cu doped Ag films show a single peak in the visible blue range SPR band $\lambda_{\text{max}}$ at 413 nm [38,58-62]. The FWHM of the SPR line width is 82 nm which again gives evidence for uniform particle distribution and controlled grain growth. With increasing copper concentration up to 10% the SPR peak shifts to longer wavelengths side shown in figure 5.12(iiib). The peak position of Ag-Cu films typically show the formation of two distinct resonance peaks due to the anisotropic particles growth which gives the dipole and quadrupole resonance with redshifted broad resonance [38]. The SPR for pure silver and copper occur at 400 nm and 570 nm respectively. For Ag-Cu alloy films, in our study these resonances move to 424 and 572 nm for the pure metals. For bimetallic nanoparticles with 10% Cu substitution, an absorption peak is seen between 427 and 570 nm. With increasing Cu content, the SPR exhibits redshift, the existence of a single broad resonance peak is evidence of an alloyed particle rather than a phase-segregated system. Further increasing Cu content to 20% there is no change in Ag SPR $\lambda_{\text{max}}$ position but intensity of the second resonance increases. This result confirms that the nanoparticles are a bimetallic form of silver and copper and not just a physical mixture of silver.
nanoparticles and copper nanoparticles. The red-shifts of the SPR peaks with increasing copper concentration are attributed to the decrease in conductivity [55,56].

Figure 5.12 (iii) shows the Surface plasmon resonance of 5, 10 and 20 % Cu doped Ag film thickness of 15 nm. The 5% Cu doped Ag films showed the SPR maxima at 436 nm single resonance with line width FWHM of 96 nm. Undoped 15 nm Ag films shown the SPR $\lambda_{\text{max}}$ at 451 nm where Cu doped Ag film 436 nm the peak shift is observed 15 nm towards blue shifts. In the Cu doped 15 nm thick Ag films grain growth is controlled by doping Cu is seen clearly. On 20% Cu doping SPR peak shifts slightly towards higher wavelength, and an additional resonance can also be seen at the position of copper plasmon peak which becomes stronger and appears as a clear resonance with increasing concentration of Cu [55,56,60]. It is known from literature that the copper and silver exhibit very limited miscibility in the bulk. Therefore the optical absorption of 15 nm thick Ag films with some un-reacted copper shows the presence of free copper nanoparticles [61-62].

5.6 Exciton formation in Undoped and Cu doped AgI thin films

5.6.1 Exciton formation in AgI thin films

Figure 5.13 shows UV-visible optical absorption spectra of 5 and 15 nm thin Ag films deposited on fused silica substrates and these films were iodized at different time. Upon controlled iodization, flux-controlled iodine vapor is slowly deposited on the Ag surface and diffuse into silver lattice and replaces the interstitial atom by the action of several processes initiated by surface diffusion (lateral surface diffusion) at the gas-solid interface, and silver nanoparticles surface are eventually iodized [9-11]. RF sputtered silver iodide begins to grow on the surface at the ‘early’ stage of iodization (30 minutes) the core still remaining as silver constituting at Ag/AgI core-shell type of growth [34-33,63]. This type of growth chiefly depends on the surface morphology and surface roughness of the Ag film. The AgI formation delay depends on the preparation techniques and is thus a kinetically controlled process, determined by iodization time. In case of evaporated Ag films exciton formation took 15 min as has been observed because evaporated films are quasi amorphous due to thermal strain where as in the RF sputtered films formation took 30 min to begin AgI formation due to stress [10,11].
Short time iodization (15 minutes) of 5 nm Ag films shows the formation of exciton peak at 426 nm $Z_{1,2}$ zincblende AgI structure. Short time iodization shifts the SPR peak towards longer wavelength at 492 nm are shown in figure 5.13(ia). In short time iodization AgI nanoparticles grow on the surface of Ag films, where as bottom of the films remains as unconsumed layer of silver nanoparticles the two constituting an Ag@AgI core shell type structure. Thus an Ag/AgI interface is formed during short time iodization where AgI acts as a dielectric matrix in which Ag particles embedded or aggregated on the surface, which shifts the plasmon to the higher wavelength side and become close enough to interact electromagnetically with each other this makes the onset of plasmon-exciton transition. Moreover AgI films possess a large concentration of Frenkel defects, and stacking faults at the grain boundaries as a result of iodization process [64-67]. On prolonged iodization (at 30 minutes) SPR peak broadens and AgI exciton band intensity increases with peak position observed to shift from their initial $\lambda_{\text{max}}$ 419 nm and intensity of the absorption spectrum increased. The core–shell structures in which the AgI shell is forming gradually and engulfing the core Ag nanoparticle on its way to being converted fully into its iodide form and it can be seen that the size of the silver core is larger during the higher time iodization. The formation of the exciton peak at 426 nm ($Z_{1,2}$) is due to the dipole forbidden $4d^{10}-4d^9 5s$ transition in Ag allowed by the tetrahedral symmetry of Ag$^+$ ion in the Zincblende AgI structure and the resultant p-d hybridization [68-71]. The weak peak at 330 nm $Z_3$ is due to spin-orbit split $\Gamma$ valence of the spin orbit interaction, so that the growth of $Z_{1,2}$ and $Z_3$ exciton, respectively is seen in figure 5.13(i). When iodization time is further increased to 180 min the exciton peak position shifts to 435 nm (higher wavelength side) as also the intensity of the exciton peak increases and the absorption edge becomes very sharp [10,11]. Increase of exciton peak maximum gives evidence for increase in the crystallinity (as seen in XRD) which decreases the band gap energy. It must be mentioned that the growth and development of $Z_{1,2}$ and $Z_3$ excitons strongly reflects the valence band development in AgI upon progressive iodization, the corresponding energies and energy difference quantitatively determining the band structure. This is because the electrons in the exciton are essentially differing from the developing/developed valence band.
Upon iodization at 360 min the exciton peak shifts towards the blue region at 424 nm which shows strong quantum confinement effects in AgI thin film [72-75]. 5 nm thick Ag films iodized up to 360 minutes showed the fully developed $\gamma$-AgI structure. Upon long time iodization (720 minutes) shows the formation of the mixed phase $\beta$ and $\gamma$-AgI due to iodine rich region in the film. The exciton peaks $Z_{1,2}$ and $Z_3$ belong to the $\gamma$-AgI phase since they are very strong in the 5 nm AgI with high $\gamma$-AgI content. All these observations systematically characterize the very basic process of the band structure formation of AgI. 15 nm Ag films iodized at different time (same as 5 nm Ag films) shown in figure 5.13 (ii). The thick 15 Ag films for long time iodization do not favor stabilizing $\gamma$-AgI zincblende structure. While doing iodination of Ag films the AgI band...
structure forms as follows: the top of the valance band ($\Gamma^{15}$) is triply degenerate without spin orbit interaction in the zincblende structure. This degeneracy is reduced by spin-orbit splitting to a doubly degenerate states ($\Gamma^8$) and a singlet ($\Gamma^6$). The $\Gamma^8$ doublet gives the $Z_{1,2}$ peaks whose degeneracy is lifted due to some strain field changes at the crystalline surface (surface reconstruction or surface defects). With increasing film thickness, the saturation behavior of optical absorption unequivocally demonstrates strong particle size control particularly during the long term iodization regime and inhibits invariably the anisotropic growth and coalescence of the special crystal plane of the crystallites through Ostwald ripening process. This exciton spectrum can be interpreted along the same line as the absorption edges of other materials with wurtzite and zincblende structures. The strength of the exciton spectrum suggests direct allowed transition which by analogy with the other zincblende and wurtzite materials should occur at $k=0$ in the $E$ vs $k$ plot. These results are to be compared with the work of Cardona et al [68], Kondo et al [69] and Mochizuki et al [71] who measured optical absorption of AgI at temperature from 7K; through the superionic phase transition point Tc at 419K to 472K. The results obtained in the present case are at room temperature with is very rare and unusual because so far there are no studies so far on optical absorption of pure $\gamma$-AgI, the valance band degeneracy of which is lifted at room temperature.

Figure 5.13(iii) and (iv) shows the thickness and iodization time dependent exciton peak maxima and line width (FWHM). The iodization time dependent exciton band broadening makes it difficult to separate it form the interzonal absorption edge. To determine the $Z_{1,2}$ band parameter these peaks were fitted with Gaussian function. The iodization time dependent exciton peak maxima and line width of 5 and 15 nm thick Ag films shows of Ag@AgI nanostructure core-shell formation. Upon prolonged iodization peak position slowly decreases towards blue region with increasing iodization time, which is indication of quantum confinement effects decreasing upon iodization. In thick films intensity increases linearly with increasing iodization time. These results clearly indicate a thickness induced transition from $\gamma$-AgI to $\beta$-AgI upon increasing iodization time. With increasing film thickness, in short iodization initially forms the $Z_{1,2}$ exciton and prolonged iodization initiates the formation of bound exciton due to formation of Frenkel defects in the Zincblende AgI structure. Long time iodization (720 minutes) shows the bound exciton becoming quasi free exciton which is an indication of the formation of strain free stable $\gamma$-AgI zincblende structure. Where as in thickness induced
long term iodization $Z_3$ exciton get merged with $W_3$ exciton as seen in figure 5.13 (ii). Iodine rich areas show an exciton peak close to bulk value, which could be a reflection of the increase in the particle size decrease in the quantum confinement effect and a tendency towards formation of bulk band structure.

5.6.2 Cation stabilized exciton formation of Cu doped AgI thin films

In the previous chapter, we have employed XRD, UV-visible optical absorption and photoluminescence as monitors for AgI particle growth of Cu doped AgI thin films thickness of 5 and 15 nm by vacuum evaporation method. Presently optical absorption spectroscopy is used to study the evolution of AgI in the quasi amorphous Ag-Cu matrix upon progressive iodization for the period of 15 to 720 minutes using RF sputtered thin films. The crucial role of Cu in the formation of crystalline thin films is being ascertained. As the precursor films are quasi-amorphous, the rate of crystallization possibly controls the particle growth rate triggering changes in the exciton spectral feature and the development and stabilization of the energy band gap. For all three compositions (5, 10 and 20%) UV-visible optical absorption measurements were done at room temperature.

Figure 5.14 shows the room temperature optical absorption spectra of the progressively iodized metastable quasi amorphous precursor Ag-Cu films. Figure 5.14 (ia)a, (ib)a and (ic)a shows the 5, 10 and 20 % Cu doped Ag films. Short time (15 min) iodized 5 nm Ag film which exhibit a gradual development of features at 423 nm and 331 nm which is $Z_{1,2}$ and $Z_3$ exciton energy (2.931 eV) respectively as determined from the optical absorption spectrum of $\gamma$-AgI (Zincblende structure) [79]. These results have been observed for the first time in sputtered AgI films. These results clearly point to a thickness and Cu substitution induced stabilization of a robust $\gamma$-AgI zincblende structure. With increase of iodization time, the $Z_{1,2}$ exciton peaks intensity increases and SPR peak position shift at 458 nm towards the red region, which could be a AgI band structure development. This type of mixed plasmon-exciton formation could be termed ‘plexciton’ [80] observed in short time iodized films. Plexciton formation is the direct evidence of plasmon-exciton transition in iodized Ag films [12,13]. When iodization time increased, the optical density saturates and the degree of saturation depends on refractive index (n). In thin films, the optical density is expected to decrease linearly with increasing iodization time; since the filling factor becomes smaller. Careful comparison of these
Figure 5.14: Evolution of exciton absorption band at 422 nm during the progressive iodization of the Ag-Cu thin films thickness of 5 and 15 nm of various compositions of 5, 10 and 20 %. Figure (i) a, b and c. shows the data for 5 nm thin Ag film iodized for (a) 15 (b) 30 (c) 60 (d) 180 and (e) 360 minutes. Figure (2) a, b and c. shows the data for 15 nm Ag films iodized at thick Ag films iodized for (a) 30 (b) 60 (c) 180 (d) 360 (e) 720 minutes.
optical spectra for isochronal iodization up to 360 minutes of the three Ag-Cu composite films of 5 nm thickness reveals that the increasing Cu content farms facile AgI nucleation and saturable growth thereby effectively controlling resultant product particle size.

A general feature of the absorption spectra in our iodized Ag-Cu films is the appearance of strong exciton absorption peak edge around 422 nm ($Z_{1,2}$) and 330 nm ($Z_3$) characteristic of $\gamma$-AgI zincblende structure. This feature persists even upon a substantial increase of the Ag/Cu ratio, signaling the fact that Cu acts only as a catalyst for controlled particle growth and stabilization of defect free structure $\gamma$-AgI and thus does not evolve itself as CuI giving its own characteristic exciton bands. The optical property of AgI is enhanced by partial Cu substitution [4,79]. The intensity of the peak increases with the increasing iodization time. The evolution of $Z_{1,2}$ and $Z_3$ exciton absorption bands was observed at about 422 nm and about 330 nm which correspond to the two spin orbit components of exciton excitation in AgI. This absorption edge corresponding to unresolved excitons is due to the forbidden transition in the Ag$^+$ ions, which becomes resolved because of the tetrahedral symmetry caused by the p-d hybridization in the electronic structure of AgI. Besides, there is a strong UV band at around 330 nm characteristic of $\gamma$-AgI in copper substituted films. With increasing iodization time, the SPR of the Ag nanoparticles, being sensitive to changes in the refractive index of the medium at or near the particle surface, shifts steadily to longer wavelengths as seen in the inset shown in figure 5.14.

Prolonged iodization of Cu doped Ag films iodized at 60 and 180 minutes shows clearly $Z_{1,2}$ band formations. The width of the exciton peak decreases to 162 meV which evidences the development of strong Ag-I bond. The $Z_{1,2}$ exciton absorption becomes very sharp and band edge splits faintly into two bands for 60 minutes iodization. With progressive iodization the $Z_{1,2}$ exciton band grows to a single band shifting towards blue region and $Z_3$ band gets faint due to the Frenkel defects but the 330 nm $Z_3$ exciton peak intensity decreases which means 360 minutes iodized films are fully iodized [68,81]. In comparison with work of Cardona et al and Kondo et al increasing iodization time provides clear evidence of a ‘phase transition’ from amorphous to crystalline state in the 5 nm thick AgI film. The faint double peak structure arises from a splitting of the doubly-degenerate valence band $\Gamma_8$ with light and heavy hole masses due to the difference of
quantum size effects, or some crystal-field change at the crystallite surface (for example, surface reconstruction or surface defects).

From the work of Kondo et al, it is clear that the thin films surface have the effect to lower the nucleation activation barrier and grain growth activation barrier. It is interesting to note that the iodization induces the amorphous films to crystallize into the $\gamma$-AgI phase at room temperature without passing through the $\beta$-AgI phase. As is well known the valence and conduction bands in semiconductor retain their meaning (in a broad sense) even in the amorphous state, and the density of states (DOS) of the bands is almost unaltered by amorphous since the gross feature of electronic states is determined by the short range order. But the lack of the long range order in the amorphous states leads to the relaxation of the k-conserving and/or symmetry-imposed selection rule. Such a relaxation sometimes gives rise to a significant result, particularly in the case of indirect band gap semiconductors. In the case of AgI, where the amorphous AgI films transform to the $\gamma$-phase crystalline films, the situation seems to be somewhat different. $\gamma$-AgI is known to have a direct band gap at the $\Gamma$ points with the allowed types of optical transition matrix element the band edges.

The exciton bands in the nanocrystals (NCs) are characterized by a blue shift and inhomogeneous broadening that are caused by the relatively weak spatial confinement of the exciton in the small particles and by the (NC) size distribution and Cu impurity respectively [75-78]. While in un-doped 5 and 15 nm thick AgI films FWHM of the $Z_{1,2}$ exciton in $\gamma$-AgI NCs between 102 and 155 meV shown in figure 5.13 in the 5 % Cu doped AgI exciton line width varies with iodization time 139, 162 and 137 meV corresponding iodization time 15, 60 and 360 minutes respectively. The data reveal the internal structure of the 422 and 430 nm exciton states that is interpreted in terms of the electron–hole exchange interactions as well as a possible non spherical shape of the NCs. With increased Cu concentration the $\beta$-phase impurity decreases and it disappears at $x=10\%$. At room temperature the broadened exciton peak is isolated against the background of interzonal absorption shown in figure 5.14. The exciton band broadening causes definite difficulties in separating it from the interzonal absorption edge. As in bulk material, in NCs of $\gamma$-AgI, the lowest energy state ($Z_{1,2}$) is a $(1S_{3/2}, 1S_e)$ pair-state composed of a hole from the uppermost $J=3/2$ valence band and an $s$-type conduction band electron. By reduction of symmetry through the crystal field, in $\beta$-AgI the eightfold
degeneracy of this state is removed resulting in exciton states 330 nm four-fold degenerate. In bulk crystals, the \((Z_{1,2})\) exciton is split further by short- and long-range exchange interactions caused by the spatial overlap of the electron and hole wave functions [71-73].

Figure 5.14 (2a), (2b) and (2c) show optical absorption of the 5%, 10% and 20% copper substituted 15nm thick Ag-Cu films deposited on fused silica substrates with a dielectric constant different (larger) than glass substrate and thus expected to exercise better control over nanostructure formation and resulting properties. The short time iodized (30 min) Ag-Cu films have shown the immediate/rapid development of the \(Z_{1,2}\) exciton peaks at 423 nm along with Surface plasmon peak and no evidence of 330 nm \(Z_3\) band suggesting that the Cu substitution and higher thickness delay the \(Z_3\) formation due to surrounding inorganic Ag-Cu matrix strongly restricting further aggregation during the formation of AgI crystallites. More interestingly, this saturation behavior clearly shows the strong particle size control particularly during the short-term iodination regime and exhibits the anisotropic growth. The exciton absorption observed even in the amorphous state points to a very small exciton radius of AgI (0.61 nm) so small that it could exist within the short range order itself. However, no trace of CuI exciton was observed even (80:20 wt ratio). Probably Cu\(^+\) ions are dispersed as monomers in the amorphous environment, thus maintaining the electrical neutrality of the system each Ag\(^+\) ion is replaced by Cu\(^+\) ions [4,77].

The iodized AgI films show a number of intrinsic defects that are expected to be formed in the grain at the grain boundaries, on the surface or at the interface, leading to creation of energy levels within the energetically forbidden gap [82-84]. These separate defects levels can extend to form an energy band overlapping with the conduction band or valance band of AgI, thus giving rise to band tail states. It is well known that a decrease in particle size generally results in the blue shift of this peak due to enhanced quantum confinement. However the red shift is not too surprising when the effect of lattice composition (XRD figure) is taken into account. According to the bonding orbital theory of band structure for covalent semiconductors, such as AgI (its band structure is characterized by strong p-d hybridization-even stronger in CuI), energy bands are derived from the extension of molecular orbitals in unit cells. As the lattice parameter decreases, the overlap between the MOs in adjacent cells increases, leading to broadening of the band.
This generally results in a decrease of band gap, as observed in many semiconductors and insulators. Moreover, a decrease in lattice parameter results in reduction of electron-hole distance in the exciton, leading to strong electron-hole interaction and a larger binding energy of the exciton (the exciton binding energies in AgI eV). These Cu$^+$ ions may also absorb light at their respective exciton energies, but this absorption might be irretrievably submerged by the strong absorption of the host Ag$^+$ ions, the small ionic radius of the Cu$^+$ ions is considered favorable for the substituting in a unique manner. This observation shows the important role for Cu in the rapid nucleation of the metal halide thus providing a new method for obtaining nanostructures for basic and applied research [4].
5.7 Photoluminescence study of nanostructured Silver iodide thin films

5.7.1 Thickness and iodization time dependent band structure development of AgI thin films

Figure 5.16 (i) and (ii) shows room temperature photoluminescence (PL) spectra of 5 and 15 nm thick Ag films grown on fused silica substrates by RF magnetron sputtering technique and these films were iodized at different times. Further, these iodized 5 and 15 nm Ag films are excited at 355 nm which is higher than the AgI band gap (bulk AgI 2.82 eV) to study band structure formation of γ-AgI zincblende structure [79-81]. As a source of the excitation the monochromatized light of a high pressure Xenon lamp was used.

Figure 5.16 (i) show the room temperature emission spectra of 5 nm thin Ag films iodized at 15 to 720 minutes, the iodized Ag films shown emission at 2.90 eV which is from Z1,2 exciton. AgI (zincblende structure) and two sub-bands which is appears around at 3.03 eV and 2.70 eV [11,26,27,71-74,68,82,83]. In the direct band semiconductor the emission will appear at same in excitation wavelength. The emission spectra display an intense three-finger pattern with three prominent emission bands probably seen for the first time at room temperature. The first weak emission band at around 2.90 eV arises from the excitonic absorption peak but does not appear to be from the bottom of the conduction band, thus possibly corresponding to a shallow trap state or intrinsic near band edge state slightly below the conduction band [27,84]. The intensity of the emission peak associated with this weak luminescence is low in short time iodized films; the PL line is very broad. The assignment of the broader emission line with small energy shifts remains uncertain.

Upon increasing iodization time (i.e increase nanocrystals radius) the energy shift varies from 2.90 eV to 2.79 eV (290 meV). Besides, from the excitation/ emission scheme one would expect a resonance behavior parallel to that of the lower energy line, whereas that is not in the case. For these reasons a different origin may have to be considered, e.g. strain splitting of the states A_T and/or A_F. Assuming bimodal nanocrystals size distribution, the two processes could also be due to the short-range electron-hole exchange interaction in each of the two distributions. Since in that case the excited states A_T and the emitting states A_F each are different, this interpretation would qualitatively explain both the different emissions and different PL line widths. As prolonged iodization shows the strong intensity enhancement in strong emission band at 2.90 eV and also emission band shifts towards blue region this could be due to increase in the crystallinity.
Figure 5.16: Room temperature PL spectra of as deposited (i) 5 nm Ag and (ii) 15 nm Ag thin film iodized for (a) 15 (b) 30 (c) 60 (d) 180 (e) 360 (f) 720 min. The non-linearity in the band gap show the changes in lattice parameter due to the Cu atoms going in to the sub-lattice position.

as well as quantum confinement effects (seen in XRD patterns). The band edge emission is red-shifted from the band edge absorption peak by 24 to 55 nm, with smaller nanocrystals showing larger shifts. Likewise, the relative intensity of deep trap emission varies from zero in large nanocrystals to peak intensity on the order of the intensity of the band edge emission for small nanocrystals [72-74,85].

Even after 720 minutes of iodization the single emission band remains unresolved which is supposed to appear at 2.82 eV at room temperature. This observation implies
that the majority of the charge carriers i.e electron hole pairs decay primarily via non-radiative pathways (shown by the remaining sub-bands appeared at 3.03 eV and 2.70 eV. Due to strong binding of the electron- hole pair the non radiative decay is attributed to fast electron- hole (D-A) recombination mediated by high density of deep trap states involving exciton- phonon interaction or some crystalline defects or impurities. Also as these are very thin films the grain sizes are in the nanometer range (seen in figure 5.11) the surface area to volume will be high. Thus there is a possibility of unsaturated dangling bonds, which act at shallow surface traps to effectively enhanced the PL properties.

Coulomb interactions between donors and acceptors in a semiconductor cause the recombination energy to be distance dependent. The recombination energy of a distant donor-acceptor (D-A) pair is given by $E = E_g - (E_D + E_A) e^2/\varepsilon r$ where $E_g$ is the band gap energy, $E_D$ and $E_A$ are the binding energies of the donor and acceptor and the last term is the Coulombic interaction of the D-A pair separated by $r$. This gives rise to discrete line spectra in semiconductors where the electron-phonon coupling is weak. In the case of AgI with strong electron-phonon coupling the peak of the resultant broad emission should shift to lower energies with time after excitation. The broad emission observed in room temperature photoluminescence (PL) from AgI is reasonably expected to result from D-A recombination. The intent of this investigation is to establish the nature of this broad emission and to explore to what extent it is affected by quantum confinement. The long time iodization induced redshift of the emission peaks following increased excitation energy is indicative of a coulombic interaction between the donor and accepter sites and long time iodization increases the grain size from 24 nm to 55 nm, the increase in particle size decreases the quantum confinement effect in $\gamma$-AgI due to decrease of confinement effect the energy shift will be towards the redshift shown in figure 5.16 [72-74,85-87]. The intrinsic Frenkel defects such as interstitial silver ions ($Ag_i$) and silver ion vacancies ($V_{Ag}$) would have the proper coulombic interaction.

In figure 5.16 (ii) the PL spectra of the 15 nm $\gamma$-AgI film on a fused silica at room temperature. The iodization time dependent emission intensity peaks for the $\gamma$-AgI films are observed at 2.85, 2.84, 2.82 and 2.80 eV corresponding to iodization times of 30, 60, 180 and 720 minutes respectively. The bands are accompanied by at least two shoulders at 3.01 eV and 2.67 eV shown in figure 5.16 (ii). The 2.85 eV band is close to the $Z_{1,2}$ and 2.80 eV emission band is closed to $W_1$ exciton absorption peaks. Other shoulders and low intensity peaks arise from excitons trapped by exciton-phonon interactions, or some
crystalline defects or long time iodization induced $\beta$-AgI impurities as seen in thick films. With increasing iodization time the low intensity peaks shift toward longer wavelength and, passing through $T_c$ (crystallization temperature) it shifts abruptly to about 2.80 eV which is slightly shorter than the absorption trace of $\gamma$-AgI band position. This suggests that some luminescence states are above free exciton band in $\beta$-AgI. We suspect that the two emission bands on the low energy side of the $Z_{1,2}$ emission (around 2.80 eV in figure 5.16(a)) is due to electron–hole recombination at point defects or to smaller aggregates that have formed besides the NCs during longer time iodization. Except for the low energy region of the $Z_{1,2}$ band, this dependence does not show a clear correlation with the exciton absorption peaks demonstrating that energy transfer processes in the sample actually are important.

The compositional behavior of the structure of Cu doped AgI is characterized by Vegard’s Law, which states that, lattice constant changes linearly with composition, as seen in figure 5.4a. Other physical properties such as band gap often vary nonlinearly as seen in figure 5.16. To a first approximation, the variation is quadratic: The sources of nonlinearity are threefold: (i) the changing lattice constant alters the band structure; (ii) the atoms in the alloy have different electro-negativities, deforming the electron distribution; and (iii) anion-cation bond lengths and angles must relax in order to accommodate the differently sized constituents [88,89].

5.7.2 Room temperature photoluminescence study of Cu doped AgI thin films deposited on fused silica substrates

Figure 5.17 shows the PL emission spectra of 5, 10 and 20 % Cu-doped 5 nm thin Ag films. The emission bands centered at 2.82 and 2.91 eV are likely to be caused by the radiative recombination associated with the Cu$^+$ states replacing the Ag$^+$ lattice sites (which is mandatory for reducing the Ag-I lattice parameter upon Cu-substitution [6], which could be formed during the systematic iodization of Ag films [6,23]. The strong direct gap semiconductor AgI emission feature has been shown to be blue shifted. In smaller NCs, the luminescence arising from the direct recombination of exciton is absent, and this is attributed to surface effect [85]. In contrast the radiative excitonic recombination in AgI is dramatically reduced in the smaller size particles. While the surface of AgI is to play an important role in exciton recombination dynamic at smaller size [71-73].
Figure 5.17 (i) shows the PL spectra of 5% Cu doped Ag films displaying a broad emission band that ranges from 410 nm to 550nm (3.05 eV to 2.4 eV). The broad peak centered at 2.82 eV and 2.89 eV for 15 and 360 min iodization. The short time iodized 5 % Cu doped Ag films shows the broad emission peak and shoulders at 3.02 and 2.67 eV at energies greater than the emission energies of both the bulk γ and β-AgI excitons. When silver iodide clusters are excited, not only the emission of silver iodide clusters, but also the emissions of Ag clusters were observed. Similarly, when Ag clusters are excited, both the emission of AgI and Ag clusters were detected. This demonstrates that energy or charge carriers can transfer from Ag clusters to AgI clusters and vice versa. It is interesting to find that the emission of AgI clusters is stronger than that of Ag clusters when excitation is at the absorption band of Ag clusters. Similarly the emission of Ag clusters is stronger by indirect excitation into the excited states of AgI clusters than that by direct excitation into the excited states of Ag clusters. These phenomena indicate that energy transfer or carrier migration between AgI and Ag clusters is a dominant process in photo excitation.

* This is different from the possibility of interstitial occupation of Cu in the fcc lattice of Ag

Details about the interaction and energy transfer between the two clusters are not very clear now, but they are probably related to the structure of the two clusters [90]. Thus a type of composite clusters i.e., clusters each containing some Ag as well as AgI, may be formed upon partial iodization. Each of these composite clusters may have two domains with a sharp boundary separating the Ag from AgI. The structure of the composite AgI-Ag clusters is probably similar to that of mixed CdS-CdSe and ZnO nanoparticles [88,89].

Upon prolonged iodization the emission peak is due to exciton emission (but broad with a low energy tail) at 3.02 eV, redshifted by 70 meV. This red shift is a clear evidence of donor-acceptor recombination [10,11,92-95]. The red shifted PL peak also suggests a Coulombic interaction among the defects. Thus silver ion interstitials and silver ion vacancies could be the defects responsible for the D-A recombination. In particular, the intensity of this blue emission (centered at 440 nm (2.82 eV)) is enhanced by doping of Cu. This luminescence can be explained tentatively as follows.

During photo-excitation of AgI films it is likely that free electrons can be shallowly trapped at the bottom of the conduction band and in addition be coulombically attracted by the interstitial species (e.g., Ag⁺ [i]). On the other hand, because the degree of
covalency in AgI is already sufficient to prevent hole self-trapping even at the room temperature and because silver iodide exhibits a relatively stronger covalent tendency as compared to AgBr (e.g. ionicity values of AgI (0.77) < AgBr (0.85) [13]), the self-trapped holes such as those of AgI$_6$ may be eliminated. Therefore, holes are probably trapped at the vacancy-compensated divalent cations (i.e., Ag$^{2+}$ [Vac] and Cu$^{2+}$ [vac]). The extra holes provided by the charge transfer reaction between Cu$^{2+}$ and Cu$^{+}$ ions are also considered. The Cu$^{2+}$ ions can be formed as a result of the trapping of photo holes by the Cu$^+$ ions; subsequently, under a light energy $h\nu \geq 2.2$eV ($\leq 564$nm), the reverse of this reaction will release a free hole according to the reaction: $\text{Cu}^{2+} \rightarrow \text{Cu}^{+} + h^+$. 

![Figure 5.17: Room temperature PL spectra of 5 nm thick (i) Ag$_{0.95}$Cu$_{0.05}$, (ii) Ag$_{0.90}$Cu$_{0.10}$ and (iii) Ag$_{0.80}$Cu$_{0.20}$ films iodized for (a) 15 (b) 30 (c) 60 (d) 180 (d) 360 min. As the Cu concentration is increased there is a strong intensity enhancement as well as the exciton luminescence peak shift from 2.82 to 2.90 eV due to the confinement effects.](image-url)
Finally, we suggest that an increase in the concentrations of Cu may increase the amount of AgI: Cu$^+$ species in our samples. Therefore, the possible mechanisms for the 440 nm emission can be attributed to the DA radiative recombination from the electron-trapped donor site (e.g., Ag$^+$ [i]: e$^-$) to the hole-trapped acceptor site such as Cu$^{3+}$ [vac] and Ag$^{3+}$ [Vac]. Other processes such as the DA recombination from an electron trapped Ag$_n^+$ bulk species to an acceptor site such as Cu$^{3+}$ [vac] should also be considered.

Figure 5.18: Fluctuations in the energy gap and PL line width (FWHM) observed in 5, 10 and 20 % Cu doped 5 nm thick Ag-Cu films iodized at different times. The peak shift is due to Cu$^+$ in lattice substitutional position also their may be some kind of compositional fluctuations.
Figure 5.17 shows the normalized emission spectra of 10 and 20% Cu doped 5 nm Ag thin films iodized at different durations in the range 15-360 min. The 10% Cu substitution into AgI, produces a single intense band 427 nm assigned to the radiative recombination of $Z_{1,2}$ excitons. This is the most important change brought about by Cu substitution that too at room temperature—not seen in the literature so far. The spectral structure of the 429 nm peak assigned to D-A recombination of $Z_{1,2}$ excitons changes with iodization time as shown in the inset. The shift in band indicates that there are several shallowly trapped exciton states. In such cases, the lower energy trapped excitons tend to populate higher energy trapped exciton states with increasing Cu content.

The short time (15 min) iodized films shows the broad band at 2.89 eV (427 nm) further iodization at 30 min the broad band becomes narrowed and blue-shifted 2.89 eV, which is close to the intensity maximum (427 nm) of pristine AgI. Therefore, it should be interpreted that the Cu doping delays the iodization as well as controls the surface trapped exciton seen clearly. The narrow peak of the $\gamma$-AgI luminescence spectrum on figure 5.18 (ii) shifted by the same amount in the presence of copper and this shift also corresponds to change of effective band gap. The observation of gradual evolution of the optical band gap together with the development of the step like absorption and the corresponding luminescence spectra for AgI is very significant from the point of view of particle growth and associated quantum confinement effect in $\gamma$-AgI. We believe that copper is executing an extremely important role in the stabilization of the quantum confinement effect in the I-VII semiconductor. The very small thickness of the films, the extended metastable solubility of Cu in Ag and the condition for the growth of quasi amorphous film have all helped in the stabilization of $\gamma$-AgI quantum dot structure at room temperature.

The absence of any characteristic feature of $\gamma$-CuI or $\beta$-AgI in the optical spectra of Ag(Cu)I films quite significant, this reflects the fact that the amorphous AgI formed at the initial stage of iodization relaxes to achieve much better defined short-range order than that in CuI before the crystallization process takes place and a complete nanocrystalline film is obtained at 360 minutes iodization. Essentially the role of Cu is to qualitatively change the thin film growth mode from a simple layered type growth to a layered plus island type growth mode after all these film thickness is 5 nm via formation of mixed Ag-Cu cluster as evidence from the optical spectra figure 5.14. Thus the strain-induced size control by Cu helps in the confinement of exciton in $\gamma$-AgI nanoparticles and inhomogeneity of the PL peak observed even at room temperature represents the particle size distribution as reflected by its FWHM shown in figure 5.18. The PL lineshape
analysis was done by fitting all the PL spectrum using Gaussian functions. The FWHM of the luminescence peak decreases with increasing iodization time but there is not much change in PL line shape as shown in figure 5.18. The nonlinearity in the band gap points to the presence of Cu$^+$ in lattice substitutional position also suggests some kind of compositional fluctuations present in the systems [88,89]. However, precise characterization of the exciton energy levels and wave function and the identification of the traps responsible for luminescence must await low-temperature measurements and also time resolved PL investigations.

5.8 Summary

In summary, structural, microstructural exciton and photoluminescence properties of Cu substituted metastable $\gamma$-AgI films with thickness of 5 and 15nm on fused silica substrates by RF magnetron sputtering have been studied. The systematic iodization of Ag-Cu alloy films has apparently yields continuous $\gamma$-AgI films through 5, 10, and 20 % Cu substitution. Cu stabilized $\gamma$-AgI formation shows the AgI particle growth leading to the long term stable $\gamma$-AgI phase. The lattice parameter of the $\gamma$-AgI zincblende structure systematically reduces upon Cu substitution in accord with our earlier work on Ag$_{1-x}$Cu$_x$I (0$<x<1$) nanopowders [6] which gives the evidence of changing the phase transition temperature upon Cu substitution.

The Cu doped $\gamma$-AgI films reveals $Z_{1,2}$ and $Z_3$ exciton transitions with increased broadening of $\gamma$-AgI nanoparticles due to the effect of disorder produced during the course of iodization in 5 and 15 nm AgI thin films. The Cu doped AgI films have shown blue shift in the exciton maxima which could be effect of decreasing particle size and thus shown increasing the band gap 2.91 eV at RT (2.82 bulk $\gamma$-AgI at RT). The exciton energy blue shift upon Cu substitution due to Cu$^+$ in lattice substitutional position.

PL characterization of Cu doped AgI thin films thickness of 5 and 15 nm shown the very strong emission peak at 2.91 eV. The strain induced size control by Cu helps in the confinement of exciton in AgI nanoparticles and the inhomogeneity of the PL peak observed even at room temperature represents the particle size distribution as reflected by its fwhm narrowing upon iodization. Thickness and Cu doping favors the quasi free AgI nanoparticles formation which enhances PL emission intensity at RT and more
importantly a drastic reduction in shallow-trap luminescence. Quantum confinement results in the loss of the longer lived components of the D-A emission.

Taking cue from the quartz-substrate induced results described and discussed above it would be fascinating to consider the effects of using a soft substrate such as polyvinyl alcohol on the nature of Ag nanostructure formation and AgI nanoparticle shape/size evolution upon iodization. Results of such an investigation form the basis of the next chapter.

References


