Chapter VIII

Conclusions and Suggestions for Future Work:

Before stating the conclusions and pointing to directions for future research, it would be appropriate to mention that the major gain of this thesis effort is an insight into quasiparticle (plasmons and excitons) production and their transformation through a systematic oxidation of a two-dimensional noble metal nanostructure, witnessing in the process an \textit{ab initio} development of the electronic band structure of a direct gap I-VII semiconductor.

Based on the experimental research work reported in the present thesis -essentially focused on the optical and electrical behaviour of ultrathin nanostructured films of the I-VII semiconductor and Ag$^+$ superionic conductor gamma AgI the following conclusions emerge:

1. (a) short term (15 minutes) and (b) long term (360 minutes) iodization of vacuum evaporated 5 nm and 15 nm thick Ag films to Iodine vapours in the in-house developed iodization reactor yields nanostructured AgI films with zincblende (gamma) (case (a)), and zincblende (major) and wurtzite (beta) minor phases (case (b) as characterized by XRD, AFM and TEM supplemented by SAED. Extended (12 hr) iodization destabilizes the gamma phase and brings about an interpolytypic transition to beta AgI.

2. RF magnetron sputtering technique was applied to fabricate quasi amorphous Ag-Cu alloy thin films in which Cu promotes layer type growth with more disorder and in built strain-induced due to the plasmon environment, enabling retarded growth kinetics, thus providing an attractive controllable platform for studying formation of $\gamma$-AgI nano particle growth.

3. Surface plasmons are readily detected in ultrathin rough Ag films whose properties show dramatic thickness dependence.

4. Short-term iodization of evaporated pristine Ag films 5 and 15 nm thick exhibit the co existing plasmonic and excitonic absorption characteristic of zincblende phase AgI shell-Ag core nanoparticles.

5. Long-term iodization of evaporated pristine Ag films 5 and 15 nm thick results in the formation of zincblende phase AgI with characteristic ($Z_{1,2}$ and $Z_3$) excitons formed form the complete consumption of Ag plasmonic electrons. This could
be called ‘plasmon-exciton transition’ indicating the conversion of core-shell nanoparticles to full-fledged AgI nanoparticles.

6. Sputtered Ag pristine thin films 5 and 15 nm exhibit considerably delayed iodization kinetics so that one always gets a minor wurtzite AgI phase along with the major zincblende phase. The natural roughness of these Ag films result in intense blue-shifted SPR which gradually get converted to zincblende excitons in 5 nm films and both zincblende and wurtzite excitons in 15 nm films due to enhanced thickness. Such films could be used in molecular detection using SERS technique.

7. Photoluminescence of Ag films obtained by evaporation and sputtering show upon iodization weak excitonic luminescence accompanied by weaker and broad shoulders due to Frenkel defects and stacking faults acting as surface traps. This could be identified as shallow donor-acceptor recombination centres existing in the forbidden gap. The shoulders are much weaker in sputtered films indicating lower defect concentrations than in evaporated films.

8. (a) Thermally evaporated Cu-doped (5, 10 and 20 at %) Ag films 5 nm thick exhibits upon iodization zincblende structure and sharper and more intense blue shifted SPR than pristine Ag films. Upon iodization they exhibit $Z_{1,2}$ and $Z_3$ excitons- the latter with enhanced intensity. Most interestingly the room temperature photoluminescence spectra of these films (with 5, 10% Cu) show a single sharp and intense peak due to Cu-enhanced excitonic photoluminescence with negligible concentration of defect raps.

(b) Sputtered films exhibit these same features with even sharper excitonic PL. These changes are accompanied by reduction in the band gap. Optical absorption of 20% Cu doped Ag films show both Ag and Cu SPRs and upon iodization exhibit exciton features of both zincblende and wurtzite structures-the latter one a minor phase probably arising from composition fluctuations. Cu substitutionally doped into AgI enhances the excitonic PL by drastic reduction of Frenkel defects and increasing the oscillator strength for absorption by strengthening Ag-I bond which is also responsible for nonlinearity in band gap with respect to iodization time.

9. Ag films (5 nm thick) sputtered onto PVA substrates show enhanced SPR (with respect to films on glass and fused silica substrates). Also PVA supports Ag particles with different sizes and shapes (spherical in uniodized Ag and
triangular, trapezoidal and bipyramidal in iodized Ag films. TEM and SAED have helped visualization of shape evolution and characterization of zincblende structure respectively. Enhanced–intensity single sharp PL characteristic of defect-free excitonic luminescence is observed. These γ-AgI/PVA films could be used to develop flexible devices.

10. Impedance spectra of iodized (a) Ag and (b) Ag-Cu thin films (which show mixed conduction and thus make true DC ionic conductivity measurements very difficult) give (a) enhanced Ag⁺ ionic conductivity relative to bulk and show the anomaly at superionic phase transition (as in the well known bulk AgI) and (b) reduced ionic conductivity and absence of the conductivity anomaly in Ag-Cu due to the reduced defect concentration and off-critical ionicity of the Ag-I bond.

**Suggestions for future work**

1. Low temperature PL of all the sputtered and evaporated, and, iodized AgI thin films investigated in this thesis would enable temperature dependence of excitonic intensities and linewidths to be obtained providing insights on exciton dynamics.

2. Nonlinear optical properties of AgI and Cu-doped AgI thin films could be investigated using Z-scan for evaluation of these films for optical limiting and SHG applications.

3. Extending the impedance spectroscopy measurements to the study of conductivity phase transitions in Ag-Cu I thin films would provide motivation to look at AC conductivity relaxation and develop models for ion diffusion in thin films.

4. Development of optoelectronic and flexible microbattery elements based on gamma AgI and composite Ag-AgI thin films on PVA substrates could be a worthwhile project.

5. Mechanisms of (a) thin film formation (b) plasmon-exciton phase transition and (c) ab initio band structure development in gamma AgI could be explored in a semi-quantitative approach. This could also involve elucidation of thin film formation and microstructure development –crucial inputs to physical property enhancement.
Research Publications: (In refereed international journals)


2. M.Gnanavel and C. S. Sunandana, ‘Iodization time dependent Surface plasmon to exciton transition and Photoluminescence study of Core shell Silver Iodide thin films sputtered on PVA Substrates. (accepted for *Journal of Nano science*).


Manuscripts (to be communicated)


2. M.Gnanavel and C.S. Sunandana, Thickness and composition dependent plasmon-exciton transition and photoluminescence study of cation stabilized Co-Evaporated Ag-Cu nanostructured thin films iodized at ambient.

3. M. Gnanavel and C. S. Sunandana, 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. M. Gnanavel and C. S. Sunandana, Impedance Spectroscopic studies of Superionic phase transition in AgI and (Ag-Cu) I thin films.

International conferences


5. M. Gnanavel and C. S. Sunandana, Thickness dependent Surface plasmon-Exciton transition in ultra thin silver/silver iodide films. Inter national on Fiber Optics and Photonics (PHOTONICS-2008) at IIT Delhi, Delhi, India (Oral presentation).


ACRHEM: work presented at (National and International Conferences)*


*Does not form part of the PhD Thesis.