Preface

This thesis deals with the experimental research work carried out by the author on the fabrication of ultrathin (≤ 15 nm thick) silver and silver-copper alloy films by vacuum thermal (co) evaporation and (co) sputtering and their systematic iodization to produce zincblende AgI based nanostructures. A systematic characterization of these thin films has focused on the crystal structure microstructure and optical properties (optical absorption and photoluminescence) besides a preliminary study of the thin film electrical conductivity through impedance spectroscopy as AgI undergoes the superionic phase transition at 420 K.

The simple but effective means of iodization of Ag foils and thin films developed in our laboratory for about a decade and recognized and adopted by peer groups worldwide has helped investigate nanostructure development, thin film formation mechanism and such novel issues as plasmon-exciton transition in Ag and Ag-Cu ‘alloy’ films. This effort represents a logical continuation of a decade-long research programme on the semiconducting aspects of I-VII compounds of which AgI, CuBr and CuI are members. These are generally referred to as superionic conductors or solid electrolytes (ionic conductivities ~ 0.1 S/cm at or near ambient). They possess crystal structures with a large concentration of cationic Frenkel defects based on the partially covalent Ag-I/Cu-Br/Cu-I bond resulting in wurtzite/zincblende crystal structures (like III-V and II-VI compound semiconductors and also like ZnO) that eventually results in transitioned phases alpha AgI (bcc) and alpha CuBr/CuI(fcc) in which the metal cations form a kind of fluid of mobile ions. The physics of the wurtzite/zincblende phase transition though quite interesting is incompletely understood. The unusual nature of the Ag-I bond and the defects and disorder associated with the crystal structure play a crucial role in optical and electrical properties of both bulk and thin film forms of AgI and other superionic conductors.

This effort has thrown up such novel results as the development of core-shell type Ag@AgI nanoparticles and Cu-enhanced excitonic photoluminescence in Cu-doped AgI zincblende structured films. PVA polymer films have emerged as a very attractive active platform/matrix to look at shape-evolution of AgI nanoparticles that could be monitored by TEM and SAED techniques.
An impedance spectroscopy study on AgI and Cu-doped AgI thin films has revealed the superionic phase transition in AgI at 420 K in dc conductivity and the effect of Cu in controlling phase transition and overall conductivity reduction. This preliminary study has opened up a window on the study of ion diffusion in 2D systems.

This PhD thesis has probably helped understand basic concepts in solid state physics such as nature of quasiparticles (plasmons and excitons) and electronic energy band structure development in a direct gap semiconductor such as AgI besides providing recipes for fabricating optimal ultrathin nanostructures that could lead to device development. The novel plasmon-exciton transition reported here needs to be formulated and solved as a basic problem in condensed matter physics.