Chapter VII

Superionic phase transition in AgI and (Ag-Cu) I thin films: A Preliminary Impedance Spectral Study

7.1 Introduction

Iodized Ag, Ag$_{0.90}$Cu$_{0.10}$ and Ag$_{0.80}$Cu$_{0.20}$ thin films-especially the partially iodized ones are interesting mixed conductors (ionic and electronic) besides being important for elucidating the role of interfaces in conductivity enhancement and ion transport in two-dimensional ionic conductors. Although there are many investigations of ionic conductivity on bulk AgI monocrystal/poly-crystalline samples [1-9] and there are only very few previous electrical studies on thin films [10-14] that emphasize the above aspects and thus a preliminary attempt was made (basically to complement our studies on microstructural and optical properties reported in previous chapters) to look at the superionic phase transition through DC conductivity derived from impedance measurements at selected temperatures and frequencies in the range 300 to 470K and 40 Hz to 1 MHz on 40 nm thick AgI, Ag$_{0.85}$Cu$_{0.15}$I and Ag$_{0.80}$Cu$_{0.20}$I films deposited on Pt/Si single crystal substrates. With respect to the AgI nanopowders [15-17] we have observed a ~ 3 order enhanced conductivity in the low temperature phase. Further the structural phase transition to alpha AgI is observed at 420 K. In Cu doped AgI films there is a lowering of conductivity throughout the temperature range besides an absence of phase transition in the same temperature as expected. The conductivity of Cu doped AgI is diminished compared with that of undoped AgI thin film.
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7.2 Deposition of Ag and Ag-Cu films on Pt/Si single crystal substrates

Thin Ag and Ag-Cu alloy thin films thickness of 40 nm were deposited on (111) oriented Pt/Si single crystal substrates by RF co-sputtering method. The pure silver and copper metal targets (Aldrich, 99.999 %) are used for thin films depositions. The desired composition ratios of pure Ag, Ag$_{0.90}$Cu$_{0.10}$ and Ag$_{0.80}$Cu$_{0.20}$ (by atomic weight %) alloy films 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 film. Initially, the sputtering chamber was evacuated to a base pressure of $2 \times 10^{-6}$ Torr after loading the cleaned Pt/Si substrates on to the substrate holder placed inside the vacuum chamber. All the films were deposited at a 15 W RF power. 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. The rate of deposition was maintained constant during the entire depositions. The above conditions were found favorable for the formation of homogeneous, alloy films, although the resulting composition ratio was analyzed using EDAX. The thickness of the films was determined by using AMBIOS XP-1 profilometer. These films were characterized by XRD using a wide angled X-ray powder diffractometer (INEL Model CPS120) and a position sensitive detector with Co Kα (1.7889Å$^6$) radiation. The surface micros structures of the films were examined by SPA 400 Atomic Force Microscopy (AFM) operated in the non contact dynamic force mode.

**Iodization**: Iodization of these thin films was done an hour-glass type chamber with dimension of 10 cm height x 6 cm diameter. Iodine kept at the bottom of the lower half of the chamber sublimes at room temperature and slowly deposits on the Ag$_{1-x}$Cu$_x$ alloys films kept at the top of the chamber kept in a dark room. Thus iodization was carried out for selected durations in the range of 180 to 720 min.

7.3 Structural characterization of Ag and Ag-Cu alloy films deposited on Pt/Si substrates

Figure 7.1 shows the XRD pattern of as deposited 40 nm thick Ag and Ag-Cu alloy films deposited on Pt/Si substrates. These films were systematically iodized at different times for determination of structural characteristic. Uniodized 40 nm thick Ag films consist of two strong prominent peak (111) and (220) reflections which is
characteristic of \(fcc\) cubic Ag structure. Further systematic iodization at 720 min of these films shows the development of mixed phase of \(\gamma\) and \(\beta\)-AgI structure in which \(\gamma\)-AgI zincblende structure as a major phase. This diffraction pattern consists of number of prominent peaks characteristic of a substantial amount of \(\beta\)-AgI minor phase and \(\gamma\)-AgI is a major phase [5,9]. The presence of additional weak reflection, which are attributed to the co-existence of two phases. In thick films stabilizing \(\gamma\)-AgI zincblende single phase structure cannot be stabilized easily at room temperature (discussed in previous chapters) 10 and 20 % of Cu substitution on to Ag film stabilizes the zincblende phase co-existing with the wurtzite possibly due to the fact that the films are not ultrathin(<10 nm). Even at 40 nm thick films the Cu substitution apparently helps to stabilize the zincblende phase as a major phase by reinforcing the cation sublattice of \(\gamma\)-AgI which has the smaller unit cell than of the wurtzite or \(\beta\)-AgI [7]. However 40 nm thicknesses is found to be quite suitable for electrical measurements because they are continuous [10,11].

![Figure 7.1: XRD pattern of 40 nm thick (a) as deposited Ag (b) Ag film iodized for 720 min (c) Ag\(_{0.90}\)Cu\(_{0.10}\) alloy film iodized for 720 min (d) Ag\(_{0.80}\)Cu\(_{0.20}\) film iodized for 720 min deposited on Pt/Si substrates.](image)

### 7.4 Surface morphology

The surface morphology of the 40 nm thick Ag and Cu doped Ag films iodized at 720 min shown in figure 7.2. Undoped AgI films shown the uniform smaller grains with average grain size \(\sim\)50 nm with RMS of the iodized film is 3.5 nm. In 10 and 20 % Cu doped AgI films are shown anisotropic grain growth with average grain size 80 and 150
nm for 10 and 20 % Cu substitution. Surface roughness increase the as function of iodization time and Cu substitution.

Figure 7.2: DFM images of 40 nm thick (a) Ag (b) Ag_{0.90}Cu_{0.10} (c) Ag_{0.80}Cu_{0.20} films iodized for 720 minutes. These films were deposited on Pt/Si single crystal substrates.
7.5 Impedance measurement

7.5.1 Fabrication of M-I-M structure

The frequency and temperature dependent impedance measurement of 40 nm thick AgI and Cu doped AgI films grown on Pt/Si substrates were characterized at low frequencies (≤ 1 MHz) using the MIM structure. The top electrode of 300μm² area of the MIM structure was fabricated using the shadow mask techniques. The measurement were carried out from 40 Hz to 1 MHz using Agilent 4294A impedance analyzer (shown in chapter 2).

The schematic cross section and top view of the M-I-M structure fabricated is shown in figure 7.3.

The top and bottom electrodes of the M-I-M (Au/AgI/Pt) structures were connected to the impedance analyzer through two tungsten needles mounted on their respective micropositioners in a custom made probe station with heating and cooling base. The modulus of impedance |Z| and phase constant θ were measured from impedance analyzer. The real and imaginary part of the complex impedance were calculated using the following equations

\[ Z' = |Z| \cos(\theta) \]  \hspace{1cm} (7.1)

\[ Z'' = |Z| \sin(\theta) \]  \hspace{1cm} (7.2)

The bulk resistance of the sample is determined from the Z’, Z’’ plot by extrapolating the curve to the Z’ axis at the low frequency side. The DC conductivity of the samples was determined from these bulk resistance.
Figure 7.4(a) shows the complex impedance plots as $Z'$ vs $Z''$ plotted at various frequencies at selected temperatures. A general feature of this family of plots is the presence of a single semi-circle followed by an almost linear rise in impedance at higher frequencies. This represents a Debye-type relaxation [1]. The three low-temperature plots ($T<T_c$) form a closely spaced group widely separated from the two high-temperature ($T>T_c$) plots (after the phase transition). Figure 7.4(b) represents the temperature dependence of the real part of impedance and figure 5c shows the temperature-dependence of the imaginary part of $Z$. Figure 7.4(c) reflects the trend of impedance plot of figure 7.4(a) with clearly separated groups for high and low temperature regions [6].

Figure 7.4: (i), (ii) and (iii) shows the complex impedance spectra for the LT and HT (inset) phase of 40 nm thick Ag film deposited on Pt/Si substrates and iodized for 720 min.
The plots of figure 7.4 (a) were analyzed by extracting the real part of impedance value at point where the semi-circle intersects the Z’ axis. This latter value represents the true impedance which is usually used to obtain DC conductivity. A plot of log sigma dc vs 1000/T may now be drawn to get the conductivity profile of the AgI thin film sample.

Figure 7.5: Complex impedance spectra for the LT and HT (inset) phase of 40 nm thick Ag$_{0.90}$Cu$_{0.10}$ alloy film deposited on Pt/Si substrates and iodized for 720 min.

Figure 7.5 (a-c) and 7.6 (a-c) show real and imaginary components impedances, Z’ and Z” ($Z^* = Z' + i Z''$) as functions of frequency and temperature, for 10% and 20% Cu doped AgI films respectively. A comparison to figure 7.4 shows qualitative changes upon Cu doping. Mainly conductivity changes marginally with temperature with no conductivity phase transition anomaly in the impedance plots [18,19]. A similar
conductivity vs temperature graph was drawn which reflects the effect of doping and the absence of anomaly as expected. The 300 K impedance plot of figure 7.5 (a) is very interesting as it is widely separated plots for \( T > 300 \) K w.r.t. the 300K plot. This plot is very similar to the impedance plot obtained by Watts et al [12] for Ag-AgCl mixed conductor films obtained by co-sputtering as in our case. This feature could arise from interfacial (substrate-thin film) contribution to conductivity which is characteristic of thin films [10-11].

Figure 7.6: Complex impedance spectra for the LT and HT (inset) phase of 40 nm thick \( \text{Ag}_{0.80}\text{Cu}_{0.20} \) alloy film deposited on Pt/Si substrates and iodized for 720 min.
7.6 DC Conductivity

Figure 7.7 show the conductivity profiles of AgI and Cu-doped AgI thin films as log sigma \( \text{vs} \) 1000/T plots with sigma derived from figure 7.4, 7.5 and 7.6. There is an abrupt jump in conductivity at the superionic phase transition temperature in undoped AgI (420K) but the low temperature conductivity is considerably enhanced by ~ three orders of magnitude relative to the bulk emphasizing the effect of dimensionality on conductivity especially the possible role of interfaces in enhancing ion diffusion. Another important feature is the considerably reduced slope (0.1eV) relative to bulk which strongly suggests facile ion motion in the films although the exact mechanism is yet to be ascertained. A tentative explanation is that there exist preferred conducting channels along the interface region, with a high concentration of defects (vacancies) around the insulator/conductor boundary or space charge region that may favor the faster migration of Ag\(^{+}\) ions.

![Figure 7.7: Arrhenius plot of the temperature dependent of the dc conductivity of 40 nm thick (a) undoped Ag film (b) Ag\(_{0.90}\)Cu\(_{0.10}\)I (c) Ag\(_{0.80}\)Cu\(_{0.20}\) films iodized for 720 min.](image)

Doping of Cu into AgI reduces the transport number for Ag\(^{+}\) because CuI is not an ionic conductor in this temperature range 300-580 K. In fact it is a p-type semiconductor in the temperature range. Therefore one expects to observe a reduced conductivity in the low temperature region as is observed. Equally importantly, Cu-doping shifts the phase transition temperature to \( T \gg 420 \) K due to reduction in lattice parameter and the
strengthened AgI bond which becomes more covalent than in Undoped AgI. However measurement of actual transition temperatures is deferred until a high temperature measuring set up is designed and developed [20].

These results which involve defects and interfaces are broadly relate to and supplement the earlier work on EPR of nanopowders of AgI and AgI-CuI solid solutions [21] and the present work on structural and optical properties of AgI and Ag-CuI thin films discussed in earlier chapters.

A detailed investigation of conductivity of AgI and Ag\textsubscript{1-x}Cu\textsubscript{x}I (0<x<1) films as function of thickness and different substrates is expected to throw more light on conduction mechanism besides helping to optimize the film properties for thin film battery and sensor applications.

References