CHAPTER II

FIELD OF HIGH CONDUCTIVITY SOLID ELECTROLYTE

(SUPERIONIC SOLID) Cs$_4$I$_5$
The search of the new materials for solid state batteries, thin film coulometers and other electrochemical devices gave stimulus to the research in high conductivity solid electrolytes. Consequently, the discovery of cation disordered solid electrolytes $^{\text{Ag}_4\text{I}_5}$ ($^{\text{K},^{\text{F}},^{\text{H}_4}}$) with exceptionally high ionic conductivity $10^{-1}$ ohm$^{-1}$ cm$^{-1}$ at room temperature with very little electronic conductivity by Bradley & Greene$^1$ and Owens & Argue$^2$ was reported. Using one of these compounds, $^{\text{RbAg}_4\text{I}_5}$, a solid state electrochemical cell was reported by Scrosati et al$^3$, Takahashi & Yamamoto$^4$ and O'Keefe & Owens$^5$, and using $^{\text{Ag}_4\text{I}_5}$ by Chandra et al$^6$. The current density obtained by these authors was very small, of the order of a few mA/cm$^2$, because of the large internal resistances of these cells.

A possible solution of this is to develop the electrochemical cells using thin films of these materials. Not much work has been done on thin films of superionic solids. Recently, films of $^{\text{RbAg}_3\text{I}_7}$, $^{\text{Ag}_3\text{I}}$ and $^{\text{Ag}_{7}\text{I}_4\text{PO}_4}$ have been obtained by vacuum evaporation technique. Films of $^{\text{Ag}_3\text{SI}}$ and $^{\text{Ag}_{7}\text{I}_4\text{PO}_4}$ were ionically conducting but their properties did not coincide with those of the bulk material owing to decomposition during deposition. Films of $^{\text{RbAg}_4\text{I}_5}$ showed better electrical properties. However, Kennedy et al$^7$ did not rule out the possibility of the presence of traces of some compounds like $^{\text{Pb}_2^{\text{Ag}}\text{I}_3}$, $^{\text{AgI}}$ etc in their films of $^{\text{RbAg}_4\text{I}_5}$. The method of deposition of films of family of
compounds $\text{H}_2\text{Ag}_4\text{I}_5$ by vacuum evaporation technique is a complicated one. In this thesis we report a new and simple method of deposition of films of $\text{H}_2\text{Ag}_4\text{I}_5$ on a silver substrate by using an electrolytic method for the first time. In this method, the film on a silver substrate is obtained by carrying out electrolysis at different temperatures. Studies on electrical conductivity of those films are also reported in this chapter. Best quality films were obtained at $45^\circ\text{C}$ when the electrolysis was done at low current densities ($\sim 1 \text{ mA/cm}^2$). The effect of annealing under different conditions is also reported in this chapter.

(2.1) EXPERIMENTAL

(2.1.1) Deposition of the film:

The films were deposited on a silver substrate by electro-codeposition technique. Two silver plates were used as cathode and anode dipped in aqueous solution of $\text{KI}$. The silver plates were of high purity silver of dimension $1\text{ cm} \times 4\text{ cm} \times 0.4\text{ cm}$. These plates were first washed by using Ultrasonic cleaner. The two plates were held with the help of ebonite spacers as shown in Figure 1. The aqueous solution of $\text{KI}$ was freshly prepared by dissolving $\text{KI}$ in doubly distilled water. Solutions of different $\text{pH}$ were made dissolving different quantities of $\text{KI}$. For example, about $8\text{ gms of}$
FIG. 2:1: EXPERIMENTAL ARRANGEMENT FOR THE DEPOSITION OF THE FILM OF SUPERIONIC SOLID.
KI was added in a litre of water to prepare a solution of \( \text{HI} = 3 \). The solution was then filtered and used for the deposition of the film.

The solution was kept in a constant temperature bath. The two silver plates were immersed in this solution with the help of spacers as already shown in Fig.1. The electrolysis was carried out at different temperatures viz. 10, 32, 45, 60 and 90°C. Two current densities were used viz. 7 ma/cm\(^2\) and 1 ma/cm\(^2\). After electrolysis, it was found that a film was deposited onto anode. The thickness of the film was a function of time for which electrolysis was carried out as discussed later. The anode was taken out of solution and thoroughly washed with water. Care was taken that the water jet does not directly fall over the film. This film was then air dried.

(2.1.2) Measurement of thickness of the films:

The thickness of the films varied between 10 micron and 200 micron. Accordingly thickness could not be measured using an optical method. For the measurement of the thickness of the film, therefore, a low power microscope of a comparator was used. The plate was held vertically under the microscope such that the plate-electrolyte and electrolyte-air interface could be focussed. The crosswire of the microscope was first focussed onto the electrolyte-electrode interface and then on electrolyte-air interface. The difference of the two
readings gave the film thickness. The accuracy of measurement for low thickness film (\( \approx 25 \mu \)) was \( \pm 10\% \), while for high thickness film it was better than \( \pm 5\% \).

(2.1.3) **Measurement of the conductivity**

The base silver plate itself formed one electrode while the other electrode was painted over the film surface using colloidal silver paint. The area of the silver paint electrode was taken as the area of electrode for purposes of calculation of conductivity. From the measurement of resistance of the films, the conductivity (\( \sigma \)) can be calculated as,

\[
\sigma = \frac{1}{R} \cdot \frac{L}{A} \quad -- (2.1)
\]

where \( R \) is the resistance of the film, \( L \) its thickness and \( A \) is the area of the electrode.

For the conductivity measurement of these films special sample holder was fabricated as shown in Figure 2.2. It comprised of two electrodes of brass one of which was spring loaded for better contact. The whole assembly was put in a temperature controlled furnace. The temperature was measured by chromel-alumel thermocouple. The thermoe.m.f. was measured by a Keithley 160 digital multimeter. The resistance was measured by a Kelvin's low resistance bridge (Osaw Catalogue No. 2071). The minimum resistance
FIG. 2.2: EXPERIMENTAL ARRANGEMENT FOR THE MEASUREMENT OF RESISTANCE OF FILMS OF SUPERIONIC SOLIDS.
which could be measured was 0.0001 ohm. A polarization
effects are dominant when a d.c. current flows through these
electrolytes, care was taken that current flows only for a
very short time while balancing the bridge. To ensure that
polarisation effect was negligible, some of the d.c.
conductivity measurements were compared with a.c. conducti-
vity values measured at 1 Hz using Varconi Universal
bridge (UP 12700). Also, since the decomposition
voltage of these samples is 0.6 V, care was taken that
during measurement the voltage across the sample does not
exceed the decomposition voltage. For this purpose the
current through the bridge was adjusted such that the
voltage across the film never exceeded 0.2 V.

It may be remarked here that the resistance of the
film was of the order of the resistance of electrode itself.
So, the measured value of the resistance has to be corrected
for the resistance of electrodes. For this, first the
resistance of clean silver plate directly in contact with
upper electrode was measured at different temperatur-
es. This was subtracted from the resistance of film + silver
plate to get the resistance of the film for conductivity
calculation from eqn. (2.1). A typical set of measured
values are given in Table (2.1).
Table 2.1: Measured value of resistances of sample holder with silver substrate only and (silver substrate + film) at different temperatures. The actual values of film resistance and calculated conductivity values are also shown in the table. This result is for a film of 29 micron thickness prepared at 45°C at electrolysis current density of 7 mA/cm². The electrode area was 0.71x0.69 cm².

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Resistance in ohms of sample holder +film</th>
<th>Resistance in ohms of substrate +film</th>
<th>Resistance in ohms of film alone</th>
<th>Conductivity of the film (ohm⁻¹cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(1)</td>
<td>(2)</td>
<td>(3)</td>
<td>(4)=(3)-(2)</td>
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<tr>
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<td>0.035</td>
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<td>0.0766</td>
<td>0.222</td>
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<td>0.0855</td>
<td>0.0125</td>
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<tr>
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<td>0.0115</td>
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<td>1.67</td>
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<td>0.0030</td>
<td>1.92</td>
</tr>
<tr>
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<td>0.0027</td>
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<td>0.0024</td>
<td>2.42</td>
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<td>0.1512</td>
<td>0.0022</td>
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<td>0.159</td>
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<td>0.0021</td>
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<tr>
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<td>0.1630</td>
<td>0.0020</td>
<td>2.88</td>
</tr>
<tr>
<td>221</td>
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<td>0.176</td>
<td>0.0020</td>
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</tr>
<tr>
<td>240</td>
<td>0.180</td>
<td>0.1820</td>
<td>0.0020</td>
<td>2.83</td>
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(2.2) RESULTS AND DISCUSSIONS

( ) Formation of film

The morphology of the electro-deposited films as obtained above is likely to depend on a large number of interrelated factors and would be different from those of vapour-deposited films. The main difference in the case of electrodeposited film arises because of the environment about the silver plate consisting of ions and cations in water solution moving under the presence of an electric field. The important factors controlling the characteristics of electrodeposited films are:

- (a) temperature at which electrodeposition is carried out,
- (b) current density,
- (c) pH of the solution and
- (d) presence of additional agents or impurities.

The first study carried out by us is the thickness of the film deposited at the silver anode as a function of time when electrolysis was carried out at a current density of 7 mA/cm² at different temperatures in KI aqueous solution of pH = 3. Figure (2.3) gives the thickness of the film at the anode as a function of time for five temperatures viz. 10, 32, 45, 60 and 90°C. The dotted portions of the
FIG. 2-3: THICKNESS OF THE FILM AS THE FUNCTION OF TIME.
Fig. 3a: Thickness vs. Temperature of Electrolysis.

- Thickness (μm) vs. Temperature (°C)
- Curves for different times: 4 min., 3 min., 20 min., 30 min., 12 min.

(32)
The curve indicates the region where the films had a tendency to chip off after annealing. Figure 2.4 presents the results of Figure 2.3 in a different form where the thickness of the film is plotted as a function of the temperature of electrolysis for different intervals of time. From Figure 2.3 and Figure 2.4 the following conclusions can be drawn:

(i) The thickness first varies linearly with time and then levels off slowly with time,

(ii) the thickness of the film deposited at 45°C is maximum for various intervals of time and

(iii) the thickest film which could be obtained and which does not peel or chip off after annealing is obtained at 45°C.

The point (iii) indicates that the film deposited at 45°C has least built-in mechanical stress. The first rate of growth of film at 45°C (point - ii) also suggests the same. However, the first rate of growth may be suspected to be due to the presence of voids. If the film contains lot of voids, then the film is likely to swell up faster giving an apparent fast rate of growth of film. However, this would give rise to two very obvious effects viz.

(i) large built-in mechanical stress and (ii) low electrical conductivity due to the presence of grain boundaries.
both these are not likely to be true (mechanical stress is discussed in the following paragraph and the electrical conductivity results are discussed later in section (c)) suggesting that the low stress at 450°C film favours film formation mechanism. Though no direct measurements of stress could be carried out by us, the following interesting facts can be inferred.

In general the stress in films is known to be dependent on the temperature of the substrate during film formation. A large number of such studies are available on pure metallic or alloy films. The film may be under compression or tension depending upon the substrate temperature. For our case, an exaggerated schematic representation of the electrodeposited film is given in Figures 2.5(a) and 2.5(b). If the situation as given in Figure 2.5(a) is present, then there would be a stress component along the front surface of the silver anode which would help in slipping of the film along the edge "xy" resulting in a film formation at the back side of the anode. A situation like (b) would not favour the slipping and hence no or very little back side film formation would take place. In all our experiments we find a substantially thick back side film indicating the stress situation as given in Figure 2.5(a). The thickness of the back side film obtained at different temperatures is given in Table 2.2. If we take back side film thickness as a quantity proportional to the
FIG. 2.5: TWO TYPES OF STRESS SITUATION.
### Table 2.2

The thickness of the back side film obtained at different electrolysis temperatures.

Front Side Film Thickness = 100 \( \mu \)

<table>
<thead>
<tr>
<th>Temperature ( ^\circ C )</th>
<th>Average Back Side Film Thickness ( (\mu) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>35</td>
</tr>
<tr>
<td>32</td>
<td>21</td>
</tr>
<tr>
<td>45</td>
<td>30</td>
</tr>
<tr>
<td>60</td>
<td>76</td>
</tr>
<tr>
<td>90</td>
<td>16</td>
</tr>
</tbody>
</table>

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stress, then we can conclude that the stress is least around 30 - 40°C and 0 - 90°C. These results are presented in figure (2.6).

If the stress is small, the electrical conductivity should be relatively large as the "voids" are less. As such we should expect that the conductivity of the films prepared at 30 - 40°C or 80 - 90°C must be high. As discussed later, this is true for the low thickness films but not for the high thickness films obtained at 32 or 90°C. The low conductivity of the thick films may be due to the presence of a relatively large amount of some low conductivity compound in the films (see section C).

Now we go back and try to understand the thickness of the front side films as a function of time and temperature presented in Figures 2.3 and 2.4. The formation of the electrodeposited films can be understood along the following lines. The silver plate dipped in the aqueous solution of KI would have water molecules as well as cation I− and anions K+ from the solution adsorbed onto its surface. Generally, the cations and anions are surrounded by a sheath of water molecules i.e. they are hydrated ions. Under the influence of an electric field, these hydrated cations and anions move towards their respective electrodes.

At the silver plate, thermodynamically and chemically favoured compounds would be formed. In the compound
Fig. 2.6: Variation of stress in the films with the temperature of electrolysis.
\( \text{Ag}_4 \text{I}_5 \) there is more iodine than potassium, so this compound would be formed at the silver electrodes where more iodine is present i.e. at the anode. This is what we found experimentally. Once a layer of \( \text{Ag}_4 \text{I}_5 \) is formed over the anode, the process of growth of \( \text{Ag}_4 \text{I}_5 \) is then also governed by the diffusion of silver ion through this layer making itself available for the formation of the fresh layer of the compound. Hence in the beginning the rate of growth of the film would be fast, slowing down later as the thickness grows (see Figure 23). The diffusion would be controlled by: (i) \( \text{Ag}^+ \) ion diffusion coefficient in the compound, (ii) temperature of film and (iii) stress in the film. The \( \text{Ag}^+ \) diffusion coefficient is known to be very large in compounds of \( \text{Ag}_4 \text{I}_5 \) series. However, the presence of stress or grain boundaries would probably decrease this. Therefore, the rate of growth of films prepared at 30 - 45°C would be maximum, since the stress is small. Figure 2.3 and Figure 2.4 show that the rate of growth is maximum for 45°C and is fairly small for 30°C. This low rate at 30°C cannot be understood in terms of stress since at this temperature the stress is small. However, this could be due to the fact that at 30°C, the stoichiometry \( \text{Ag}_4 \text{I}_5 \) is not favoured. This is expected since the compound \( \text{Ag}_4 \text{I}_5 \) is known to be thermodynamically unstable below 35°C. The above argument would however suggest that the rate of growth at temperatures
80 - 90°C should also be very large, since stress is possibly small and also the compound Ag₅I₅ is thermodynamically favoured. But this is not in agreement with our observation. As discussed later, the electrical conductivity studies indicate that films prepared at 80 - 90°C have fairly large amount of AgI. AgI in this temperature range is in the low conductivity phase and inhibits fast Ag⁺ ion transport. Hence a low growth rate of films may be expected.

(m) Electrical conductivity versus film thickness:

The results for the electrical conductivity at room temperature as a function of thickness for all the films deposited at a current density of 7 mA/cm² at different electrolysis temperatures viz. 10, 32, 45, 60 and 90°C, and annealed in dark at 150°C for about 3 hours are given in Figure 2.7. The conductivity of the films of the same thickness as a function of the electrolysis temperature is shown in Figure 2.8.

It is obvious from Figure 2.7 and Figure 2.8 that the conductivity for all thicknesses is a maximum when the temperature of electrolysis is 45°C. This is more apparent for thick films. Further, Figure 2.7 reveals that, in general, the conductivity is at first constant with thickness, but then decreases rapidly. This is possibly due to the small number of silver ions being able to diffuse through the thick ionic film to react with the potassium
FIG. 27: ELECTRICAL CONDUCTIVITY AT ROOM TEMPERATURE AS A FUNCTION OF THICKNESS.
FIG. 2:8: CONDUCTIVITY OF THE FILMS OF THE SAME THICKNESS AS A FUNCTION OF ELECTROLYSIS TEMPERATURE.
and iodide ions to form a new layer of $\text{Ag}_4\text{I}_5$ and thus the covered stoichiometry of the upper layers in thick films would be $\text{K}_2\text{AgI}_3$ which is a lower conductivity compound.

The high ionic conductivity (0.22 ohm$^{-1}$ cm$^{-1}$ at room temperature) of the film deposited at the electrolysis temperature of 45°C can be attributed to the predominance of $\text{Ag}_4\text{I}_5$ in the film. However, from conductivity versus temperature studies (discussed later) it will be shown conclusively that all the films contained a small amount of $\text{K}_2\text{AgI}_3$.

The electrical conductivity of the low thickness (25 μ) film prepared at 60°C is comparable (though lower) to that of 45°C film but for large thicknesses (100 μ) the conductivity becomes very low. This could be explained if we assume that the mechanical stress in the film is large and also indicated by back side film thickness studies (see section ). In the films deposited at 90°C and 32°C, the conductivity is somewhat low even when the stress is low, since $\text{AgI}$ predominates in these films as discussed later. The low conductivity of these films may also partly be due to the presence of the low conductivity compound $\text{K}_2\text{AgI}_3$ in the film. This must be so for the 32°C film because the high conductivity compound $\text{K}_2\text{AgI}_5$ is unstable below 37°C and is known$^1$ to decompose into $\text{K}_2\text{AgI}_3$ and $\text{AgI}$. 
thus the presence of $\text{AgI}_{3}$ (and also AgI) could account for a lower conductivity.

(1) **Temperature variation of electrical conductivity**

Figure 2.9 gives the temperature variation of the conductivity of a film deposited at $45^\circ$C and annealed in dark at $150^\circ$C for three hours for heating and cooling cycles. For successive heating and cooling cycles similar curves are obtained for all the films deposited at different electrolysis temperatures. $\text{ABCD}$ is the first heating cycle, $\text{DF'E'F'}$ is the first cooling cycle, $\text{GH'G'H'}$ is the second heating cycle and $\text{J'M'H'M'}$ is the second cooling cycle. The first heating cycle curve $\text{ABCD}$ may be divided into three regions $\text{AB}$, $\text{BC}$ and $\text{CD}$. The portion $\text{AB}$ is a straight line and has been used to compute the activation energy value. After $\text{B}$ (i.e., around $150^\circ$C) the conductivity suddenly rises. This is attributed to the presence of AgI in the films. It is known that AgI remains in the low conductivity phase below temperatures $147^\circ$C and becomes a "superionic conductor" above this temperature. The region $\text{BC}$ in Figure 2.9 giving the total conductivity jump at transition temperature of AgI roughly indicates the
FIG. 2.9: TEMPERATURE VARIATION OF THE ELECTRICAL CONDUCTIVITY OF KA₄₄I₅ FILM (45°C) FOR SUCCESSIVE HEATING AND COOLING CYCLES.
relative amount of Ag present in the film. The portion 1.2 represents the total electrical conductivity of Ag plus AgI.

It is obvious from Figure 2.9 that the electrical conductivity shows hysteresis during subsequent heating and cooling cycles. The increase in conductivity during subsequent heating and cooling cycles may be attributed to the diffusion of silver into the film, the diffusion coefficient being large. A sizable part of this increase may be due to the establishment of a better contact between the film and the silver painted electrode.

Figure 2.10 and Figure 2.11 show the temperature variation of the electrical conductivity of the films deposited at different electrolysis temperatures (viz. 10, 32, 45, 60 and 90°C) for two thicknesses, small thickness of 25 µ and large thickness of 100 µ). All these studies are for the first heating cycle only i.e., the curve 10° of the Figure 2.9.

Electrical conductivity versus temperature behaviour in ionic solids is found to be generally Arrhenius type. However, in the literature there exist two different ways of graphically representing the behaviour viz.
FIG. 210 TEMPERATURE VARIATION OF THE ELECTRICAL CONDUCTIVITY OF FILMS OF $KAgI_5$ (SMALL THICKNESS).
FIG. 2.11: TEMPERATURE VARIATION OF THE ELECTRICAL
CONDUCTIVITY OF FILMS OF KAg_4I_5 (LARGE THICKNESSES).
\[ \sigma = \exp \left( - \frac{\Delta E}{kT} \right) \]  

(2.2)

and \[ \sigma T = A' \exp \left( - \frac{\Delta E'}{kT} \right) \]  

(2.3)

It has been found that generally both the plots log \( \sigma \) vs \( \frac{1}{T} \) and log \( \sigma T \) vs \( \frac{1}{T} \) comes out to be a straight line. However, the value of activation energy determined from the two slopes would be different. The value of \( \Delta E' \) is greater than \( \Delta E \) because of the presence of an additional term \( \log T \). Hence one has to be careful about the type of plots used while comparing the values of activation energy obtained by different workers. According to Lidiard\(^{12} \) the plot of log \( \sigma T \) vs \( \frac{1}{T} \) is better in investigating the transport behaviour. In this investigation we have evaluated both \( \Delta E \) and \( \Delta E' \). The results are given in Table 2.3 and are discussed below. The values given are obtained by a least square analysis of the experimental data in the temperature range \( \frac{10^3}{\Delta E} = 3.4 \) to \( 2.6^0k^{-1} \).

Table 2.3 also gives the values of \( \Delta E \) at 240°C and 30°C for films prepared at different temperatures for comparison purposes. It is clear from Figures 2.5, 2.7, 2.8 and earlier discussions that the conductivity and characteristics of small and large thickness films are different. So in discussions to follow, we have chosen two typical values of thickness namely 25 \( \mu \) (called small) and 100 \( \mu \) (called
Table 2.3 The values of conductivity at 240°C and 30°C for films prepared at different electrolysis temperatures namely small (25 μ) and large (100 μ)

<table>
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<tr>
<th>Temperature (°C)</th>
<th>Thickness</th>
<th>$\sigma_{30}$ (ohm$^{-1}$ cm$^{-1}$)</th>
<th>$\sigma_{240}$ (ohm$^{-1}$ cm$^{-1}$)</th>
<th>Activation Energy</th>
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<td>$k$ (eV)</td>
<td>$A$ (eV)</td>
<td>$\Delta E$ (eV)</td>
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<td>0.16</td>
<td>1.24</td>
<td>1.16</td>
</tr>
<tr>
<td></td>
<td>Large</td>
<td>0.03</td>
<td>0.07</td>
<td>0.013</td>
</tr>
<tr>
<td>90</td>
<td>Small</td>
<td>0.2</td>
<td>2.12</td>
<td>0.37</td>
</tr>
<tr>
<td></td>
<td>Large</td>
<td>0.056</td>
<td>3.78</td>
<td>2.31</td>
</tr>
</tbody>
</table>
Table 2.3 gives the values of various parameters for the two thicknesses.

10°C film: The low thickness films have $\sigma_{30} = 0.18$ ohm$^{-1}$ cm$^{-1}$ which is slightly smaller than the conductivity of bulk $\text{Ag}_4\text{I}_5$. This may be understood if we postulate the presence of a small amount of some low conductivity compound (e.g., $\text{Ag}_2\text{I}_3$, $\text{AgI}$) in these films along with $\text{Ag}_4\text{I}_5$. It is interesting to note that the sudden jump in conductivity at 150°C confirms the presence of AgI in the film. The activation energy value $\Delta E$ of 0.15 eV also seems reasonable for the composite film of $\text{Ag}_4\text{I}_5 + \text{AgI}$ (small amount). The values of $\Delta E$ for $\text{Ag}_4\text{I}_5$ is 0.1 eV$^{14}$ and 0.37 eV for AgI film$^{15}$. As such the composite film should have an intermediate value between the two as obtained by us. However, the composite film postulate is not so successful in explaining the conductivity results at high temperatures. For example, the experimental value of conductivity of the films at 240°C is 9.26 ohm$^{-1}$ cm$^{-1}$. At this temperature, the value of conductivity of AgI is 1.7 ohm$^{-1}$ cm$^{-1}$ and that of $\text{Ag}_4\text{I}_5$ is 0.32 ohm$^{-1}$ cm$^{-1}$. This unexplained high conductivity may be due to the presence of some metallic colloids or some grain boundary conduction

**Foot note:** The grain boundary generally decreases the conductivity but in some cases it has been found that activation energy for grain boundary conduction is lower than that of bulk conduction (see for example Kennedy et al$^{19}$ for AgBr).
The results of large thickness films are qualitatively similar to those of low thickness films with both \( \sigma_{30} \) and \( \sigma_{240} \) being smaller for large thickness films. This indicates that in large thickness films there is relatively more AgI and less metal colloids along with \( \operatorname{Ag}_4\text{I}_5 \).

32° C film: Following the reasoning given above and from Figures 2.7 and 2.8 and Table 2.2, it can be said that the film obtained at 32° C also contains AgI along with \( \operatorname{Ag}_4\text{I}_5 \). The low value of high temperature conductivity \( \sigma_{240} = 2.5 \text{ ohm}^{-1} \text{ cm}^{-1} \) suggests that the quantity of metal colloids in these films is small compared to that in the films prepared at 10° C.

45° C film: The film has the highest conductivity \( \sigma_{30} = 0.26 \text{ ohm}^{-1} \text{ cm}^{-1} \) which is nearly the same as bulk conductivity of \( \operatorname{Ag}_4\text{I}_5 \). The activation energy value 0.11 eV is also nearly the same as the bulk 0.10 eV. Therefore, the amount of AgI in these films is small though not negligible if we look at the results given in Figures 2.10 and 2.11 (a small rise in conductivity at 160° C). The high temperature conductivity \( \sigma_{240} \) suggests that the metal colloids are less than those in films obtained at 10° C.
$60^\circ$ film: The results on these films are confusing. As discussed earlier in section 5, the stress in these films is very large. The behaviour of the films thus would be stress-dominated and hence no firm conclusion is warranted regarding the composition of film as deduced from conductivity results. However, a few remarks may not be out of place. The extent of rise of conductivity at $150^\circ$ suggests from Figures 2.10 and 2.11 that the amount of AgI is relatively small, though the low value of $O_{30}$ would indicate a large amount of AgI. The low value of $O_{240}$ suggests a small amount of metal colloids though the small value of activation energy would indicate a large amount of metal colloids. This confusing situation further confirms the viewpoint that the relative conductivity values are more stress-dominated and not as much composition dependent.

$90^\circ$ film: The results are similar to those of the films prepared at $32^\circ$. Further, the magnitude of stress in $90^\circ$ and $32^\circ$ films are also of small magnitude as discussed in section 7. As such these results can be interpreted in the same way as done for $32^\circ$ film.

In view of the above, it can be concluded that

(i) film deposited at $45^\circ$ most closely approximates the behaviour of $Ag_{4}I_{5}$. (ii) AgI is present along with $Ag_{4}I_{5}$ in all the films though its amount varies from film
(i) there is a possibility of presence of metal colloids particularly in films prepared at 10°C.

The exact composition of the film could best be determined by x-ray studies which we have not been able to do.

2.3 Effect of current density of electrolysis:

So far we have been discussing the results obtained for the films deposited at an electrolysis current density of 7 ma/cm². The amount of ion transport (and hence the rate of formation of film) would change according to the current density. It is expected that the rate of growth of film at low current densities would be small for lower current densities. This is also evident from the results given in Table 2.4 which gives the thickness of the films obtained in 10 minutes at two current densities viz. 7 ma/cm² and 1 ma/cm², and at different electrolysis temperatures. From Table 2.4 or figures 2.3 and 2.4 it is clear that for 7 ma/cm², 45°C is a favoured temperature for the growth of film. However, this is not so for 1 ma/cm² current density. In this case, film thickness obtained at different electrolysis temperature are comparable and utmost we can say that it is least for temperatures 30 - 45°C.

The quality of the film is also affected by the electrolysis current density. The electrical conductivities
Table 2.4  Thickness of the films obtained in 10 minutes at two current densities viz. 7 ma/cm\(^2\) and 1 ma/cm\(^2\) and at different electrolysis temperatures

<table>
<thead>
<tr>
<th>Electrolysis Temperature (^\circ)C</th>
<th>Thickness of the Film ((\mu)) at current density of Electrolysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>7 ma/cm(^2)</td>
</tr>
<tr>
<td>10</td>
<td>100</td>
</tr>
<tr>
<td>32</td>
<td>76</td>
</tr>
<tr>
<td>45</td>
<td>163</td>
</tr>
<tr>
<td>60</td>
<td>95</td>
</tr>
<tr>
<td>90</td>
<td>94</td>
</tr>
</tbody>
</table>
of the films deposited at 7 ma/cm² and 1 ma/cm² are given in Figures 2.12(a) and 2.12(b). The extent of sudden jump of conductivity at 150°C is less for the films prepared at 1 ma/cm². This would mean that the amount of kg1 is reduced in these films and hence one should expect that the conductivity at 30°C (σ30) for films prepared at 1 ma/cm² must be greater than that for films prepared at 7 ma/cm². However, Table 2.5 gives the opposite result i.e. the values of σ30 for the films deposited at 1 ma/cm² have either comparable or lower conductivity than the films prepared at 7 ma/cm². This confusion may be resolved if we look at the results for σ240 and the discussion in section C where we postulated the metal colloids for the films prepared at 7 ma/cm². The smaller value of σ240 for films obtained at 1 ma/cm² (except for 90°C film where it is within experimental error) would suggest that the amount of metal colloids is considerably reduced as observed by us. A very sharp decrease in conductivity for 60°C film needs special mention. Though the behaviour of 60°C films, in general, is similar to that shown by other films, nothing conclusively can be said about this film since it is stress dominated as discussed earlier.
FIG. 212 (Q) ELECTRICAL CONDUCTIVITY OF THE FILMS
DEPOSITED AT 7 mA/cm² AND 1 mA/cm².
THE TAILED POINTS ARE THOSE FOR 1 mA/cm² WHILE UNTAILED POINTS
ARE FOR 7 mA/cm².
FIG. 76: ELECTRICAL CONDUCTIVITY VS
TEMPERATURE OF FILMS OF KAgI, DEPOSITED
AT 7 ma/cm² AND 1 ma/cm². TWINED POINTS
ARE FOR 1 ma/cm² AND CONTAINED FOR
7 ma/cm².
Table 2.5  Conductivity and activation energy of the films at 30°C deposited at 1 mA/cm² and 7 mA/cm².

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Current Density (mA/cm²)</th>
<th>Activation Energy (eV)</th>
<th>$\sigma_{30}$ (ohm$^{-1}$ cm$^{-1}$)</th>
<th>$\sigma_{240}$ (ohm$^{-1}$ cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1</td>
<td>0.11</td>
<td>0.21</td>
<td>1.41</td>
</tr>
<tr>
<td>7</td>
<td>0.15</td>
<td>0.08</td>
<td>0.18</td>
<td>2.5</td>
</tr>
<tr>
<td>1</td>
<td>0.07</td>
<td>0.17</td>
<td>0.25</td>
<td>1.5</td>
</tr>
<tr>
<td>1</td>
<td>0.11</td>
<td>0.05</td>
<td>0.26</td>
<td>2.3</td>
</tr>
<tr>
<td>45</td>
<td>0.08</td>
<td>0.16</td>
<td>0.21</td>
<td>2.0</td>
</tr>
<tr>
<td>60</td>
<td>0.05</td>
<td>0.16</td>
<td>0.20</td>
<td>2.1</td>
</tr>
<tr>
<td>90</td>
<td>0.12</td>
<td>0.21</td>
<td>2.3</td>
<td>2.1</td>
</tr>
</tbody>
</table>
Effect of thermal annealing in dark:

Figure 2.13(a) and 2.13(b) show the temperature variation of electrical conductivity of unannealed and annealed 25 μ thick $\text{K}_2\text{AgI}_3$ films deposited at different electrolysis temperatures. The annealing was done at 150°C for three hours in dark. Table 2.6 summarises some typical conductivity values and the activation energies for films of two thicknesses, namely small (25 μ) and large (100 μ). The effect of annealing on films prepared at different electrolysis temperatures is discussed below:

\[
\begin{align*}
(\sigma_{\text{U}})_{30} & < (\sigma)_{30}, & (\sigma_{\text{U}})_{240} & < (\sigma)_{240}, \\
\Delta\sigma_{\text{U}} & < \Delta\sigma.
\end{align*}
\]

Conductivity of unannealed and annealed films of 25 micron thickness is of the same order. However, the conductivity of unannealed films at 30°C i.e. $\sigma_{30}$ (0.11 ohm$^{-1}$ cm$^{-1}$) is somewhat lower than the conductivity of the annealed films of the same thickness (0.18 ohm$^{-1}$ cm$^{-1}$). The lower conductivity of unannealed film at 30°C may be accounted for by postulating the presence of low conductivity stoichiometry $\text{K}_2\text{AgI}_3$ and $\text{AgI}$ in these films which have an effect of lowering down the conductivity of these films.
Fig. 2.13 (a) Temperature variation of electrical conductivity of 25 μ thick unannealed and annealed films. Those with subscript A are for annealed films while with subscript U are for unannealed films.
FIG. 213 (b) TEMPERATURE VARIATION OF ELECTRICAL CONDUCTIVITY OF 25 μ THICK UNANNEALED & ANNEALED FILMS. THE SUBSCRIPT A STANDS FOR ANNEALED FILMS WHILE U STANDS FOR UNANNEALED FILMS.
Some typical conductivity values and the activation energies for unannealed and annealed in dark films of two thickness namely small (25 μ) and large (100 μ).

Table 2.6: Some typical conductivity values and the activation energies for unannealed and annealed in dark films of two thickness namely small (25 μ) and large (100 μ).

Subscript u stands for those of unannealed films while A stands for annealed films.

<table>
<thead>
<tr>
<th>Electrolysis</th>
<th>Temperature (°C)</th>
<th>Thickness cm</th>
<th>Conductivity Values</th>
<th>Activation Energies</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Small</td>
<td>Large</td>
<td></td>
</tr>
<tr>
<td>Electrolysis</td>
<td>10</td>
<td>0.11</td>
<td>0.18</td>
<td>8.46</td>
</tr>
<tr>
<td>Electrolysis</td>
<td>32</td>
<td>0.17</td>
<td>0.18</td>
<td>1.48</td>
</tr>
<tr>
<td>Electrolysis</td>
<td>45</td>
<td>0.24</td>
<td>0.26</td>
<td>15.0</td>
</tr>
<tr>
<td>Electrolysis</td>
<td>60</td>
<td>0.13</td>
<td>0.16</td>
<td>1.49</td>
</tr>
<tr>
<td>Electrolysis</td>
<td>90</td>
<td>0.17</td>
<td>0.23</td>
<td>1.24</td>
</tr>
</tbody>
</table>

Subscript u stands for those of unannealed films while A stands for annealed films.
But this does not explain the low activation energy value of 0.053 eV of these films, since the presence of AgI would tend to increase the activation energy (the activation energy of AgI film is 0.37 eV \(^{15}\) as compared to \(\Gamma e_4 I_5\) which is 0.1 eV \(^{13}\)). Further, the high temperature conductivity value \(\sigma_{240}\) is very large equal to 8.46 ohm\(^{-1}\) cm\(^{-1}\). This very high conductivity can also not be accounted for by postulating the presence of AgI and \(\Gamma e_4 I_5\) plus \(\text{AgI}_3\), since at this temperature the value of conductivity of \(\text{AgI}_3\) is \(\approx 1.7\) ohm\(^{-1}\) cm\(^{-1}\) and that of \(\Gamma e_4 I_5\) is \(\approx 0.32\) ohm\(^{-1}\) cm\(^{-1}\). This unexplained high conductivity is, as postulated in section (C), due to the presence of some metallic colloids. The presence of metallic colloids explains not only the unusually high conductivity at 240°C but also the lowering of activation energy in these films. The results \((\sigma_A)_{30} > (\sigma_U)_{30}\) and \((\sigma_A)_{240} > (\sigma_U)_{240}\) can be explained by assuming that on annealing, the internal stress is released resulting in an increase in conductivity.

32°C : small thickness

\((\sigma_U)_{30} \approx (\sigma_A)_{30} , (\sigma_U)_{240} < (\sigma_A)_{240}\) \(\Delta E_U \approx \Delta E_A\)

These films have more or less the same conductivity values as those of annealed films (section C) deposited at 32°C electrolysis temperature. As we know that internal stress in these films is not much (section h) hence
annealing does not seem to have much effect.

320°C : large thickness.

\[(\sigma_{30})_{240} \ll (\sigma_{30})_{240} \quad (\sigma_{240})_{240} \ll (\sigma_{240})_{240} \quad \Delta \sigma \ll \Delta \sigma_A\]

For large thickness films, the annealing does seem to show some effect. Since it is the case of large thickness films, the stress is likely to be large as compared to its corresponding value for low thickness films. As such, the slight increase in conductivity after annealing may be due to release of stress.

450°C : small thickness.

\[(\sigma_{30})_{240} \gg (\sigma_{30})_{240} \quad (\sigma_{240})_{240} \gg (\sigma_{240})_{240} \quad \Delta \sigma \ll \Delta \sigma_A\]

The conductivity of 30°C of these films is 0.24 ohm\(^{-1}\) cm\(^{-1}\) which is the same as that of bulk AgI. Also the activation energy is 0.16 eV (Table 2.6). The high temperature conductivity \(\sigma_{240}\) of unannealed films is very large \(\sim 15\) ohm\(^{-1}\) cm\(^{-1}\) and can be explained only by postulating the presence of metallic colloids. But the metallic colloids decrease the activation energy of these films which is against our observations. It seems, therefore, probable that metallic colloids and AgI present in the film combine together to form AgI, thus effectively decreasing the conductivity and increasing the activation energy.
The effect of annealing on these films is qualitatively similar to that of $45^\circ C$ low thickness films discussed above.

$45^\circ C$ : Large thickness.

$\sigma_{30} > \sigma_{30}'$, $\sigma_{240} > \sigma_{240}'$, $\Delta E_U > \Delta E_A$

$60^\circ C$ : Small thickness.

$\sigma_{30} \approx \sigma_{30}'$, $\sigma_{240} \approx \sigma_{240}'$, $\Delta E_U \approx \Delta E_A$

As has been discussed earlier in sections B & C, the results of these films are stress dominated. Therefore, nothing conclusively can be said about them. Since after annealing, the conductivity is not much affected, it can be said that in low thickness films obtained at $60^\circ C$ electrolysis temperature, the stress seems to be fairly large in large thickness films as discussed below.

$60^\circ C$ : Large thickness.

$\sigma_{30} < \sigma_{30}'$, $\sigma_{240} < \sigma_{240}'$, $\Delta E_U \approx \Delta E_A$

The conductivity at $30^\circ C$ of annealed film is approximately ten times that of unannealed film showing that a fair amount of stress has been released. Similar large increase is observed for the conductivity values at $240^\circ C$. A very large increase in conductivity on annealing does confirm our conclusion of high mechanical stress in
these films derived on the basis of back side film (see section A).

90°C : small thickness.

\[(\sigma_{H})_{30} < (\sigma_{A})_{30}, \quad (\sigma_{H})_{240} < (\sigma_{A})_{240}, \quad \Delta E_{r} = \Delta E_{f}\]

In the annealed films deposited at this electrolysis temperature, we have earlier postulated the presence of AgI and metal colloids in large quantity. In unannealed films, the conductivity at 30°C and at 240°C, both are lower than those for annealed films. It is expected that some of the stress present in these films is released after annealing and consequently an increase in conductivity results. However, the picture is not as simple as this. If we look at \((\sigma_{A})_{240}\) and \((\sigma_{H})_{240}\), it is found that \((\sigma_{A})_{240}\) is very large which cannot be explained unless we assume the presence of such larger amount of metallic colloids in annealed films than in unannealed films. This will mean that metallic colloids are more in number in annealed films in contradiction to the conclusion obtained above.

For large thickness films the effect of annealing is not as marked as for the low thickness films discussed above. However, qualitatively the effect of annealing on low and high thickness films is the same.
Effect of light during annealing:

No detailed study is available on the photolysis of AgI. However, Kaneda & Mizuki have measured Hall effect on RbAg4I5 in dark and in mercury light. They have concluded that free electrons are present when RbAg4I5 is excited by Hg light. It may be mentioned here that Hall effect results of Kaneda & Mizuki have been disputed by Knott & Eager who have not found any measurable Hall effect. The photoconductivity studies of Kennedy and Goodman are more relevant to present studies though their results are on AgBr and AgCl superionic solids. They found that photoionization yields Ag+ ion photocurrent. As such it is thought that annealing under light may yield different results than those annealed in dark.

Results of the films deposited at different electrolysis temperatures and annealed under Hg light for three hours at 150°C are given in Figure 2.14(a) and Figure 2.14(b) for small (25 µ) and large (100 µ) thickness films. The result of the films annealed in dark are given in section D. Table 2.7 summarizes the values of $\sigma_{30}$, $\sigma_{240}$, $\Delta E$ and $\Delta E'$ for films annealed in both dark and light. It is obvious from Table 2.7 that, in general, light is affecting both $\sigma$ and $\Delta E$. 
FIG 214 (ω) : ELECTRICAL CONDUCTIVITY

VS TEMPERATURE OF FILMS OF

KAg₄I₅ (~25 µ) ANNEALED IN

LIGHT.
Figure 2.14 (b) Electrical conductivity vs temperature of films of K\textsubscript{3}Ag\textsubscript{4}I\textsubscript{5} (\textasciitilde 100 \textmu m) annealed in light.
<table>
<thead>
<tr>
<th>Electrolysis temperature</th>
<th>Thickness</th>
<th>$\sigma_A$</th>
<th>$\sigma_{AL}$</th>
<th>$\Delta E_{A}$</th>
<th>$\Delta E_{AL}$</th>
<th>$\Delta E'_{A}$</th>
<th>$\Delta E'_{AL}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>Small</td>
<td>0.13</td>
<td>0.16</td>
<td>9.26</td>
<td>11.2</td>
<td>0.15</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td>Large</td>
<td>0.036</td>
<td>0.06</td>
<td>7.06</td>
<td>13.9</td>
<td>0.17</td>
<td>0.11</td>
</tr>
<tr>
<td>32</td>
<td>Small</td>
<td>0.13</td>
<td>0.17</td>
<td>2.46</td>
<td>1.63</td>
<td>0.08</td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td>Large</td>
<td>0.052</td>
<td>0.06</td>
<td>2.47</td>
<td>2.39</td>
<td>0.13</td>
<td>0.08</td>
</tr>
<tr>
<td>45</td>
<td>Small</td>
<td>0.26</td>
<td>0.26</td>
<td>3.23</td>
<td>3.01</td>
<td>0.11</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>Large</td>
<td>0.26</td>
<td>0.34</td>
<td>2.83</td>
<td>2.84</td>
<td>0.11</td>
<td>0.12</td>
</tr>
<tr>
<td>60</td>
<td>Small</td>
<td>0.156</td>
<td>0.21</td>
<td>1.24</td>
<td>1.71</td>
<td>0.05</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>Large</td>
<td>3.04 x 10^{-2}</td>
<td>0.032</td>
<td>0.07</td>
<td>0.21</td>
<td>0.04</td>
<td>0.05</td>
</tr>
<tr>
<td>90</td>
<td>Small</td>
<td>0.23</td>
<td>0.23</td>
<td>12.21</td>
<td>12.6</td>
<td>0.13</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td>Large</td>
<td>0.056</td>
<td>0.07</td>
<td>3.73</td>
<td>14.12</td>
<td>0.10</td>
<td>0.14</td>
</tr>
</tbody>
</table>
Following possible explanations may be offered for this :-

(1) In all the films some AgI is always present as discussed in section C. A portion of this AgI may photolyse according to the following equation:

\[
\begin{align*}
\text{(photon)} & \rightarrow h^+ + e^- \\
\text{AgI} & \rightarrow \text{Ag}^+ + \text{I}^- \\
\text{Ag}^+ + e^- & = \text{Ag} \\
\text{I}^- + h^+ & = \text{I} \\
\text{I} + \text{I} & = \text{I}_2 \\
\end{align*}
\]

(2) Formation of Ag metal colloids due to disintegration of \( \text{K}_5\text{Ag}_4\text{I}_5 \) according to the following reaction may take place:

\[
\begin{align*}
2\text{K}_5\text{Ag}_4\text{I}_5 & \rightarrow \text{K}_2\text{Ag}_3 + 7\text{Ag}^+ + 7\text{I}^- \\
7\text{Ag}^+ + e^- & \rightarrow 7\text{Ag} \\
7\text{I}^- + h^+ & \rightarrow 7\text{I} \\
\text{I} + \text{I} & \rightarrow \text{I}_2 \\
\end{align*}
\]

(3) We know that apart from \( \text{K}_5\text{Ag}_4\text{I}_5 \) another stoichiometry \( \text{K}_2\text{Ag}_3 \) is also possible in small amounts. This may
be effected by light according to the following reaction:

$$4K_2AgI_3 \xrightarrow{} KAg_4I_5 + 7^{+} + 7I^{-}$$

$$K^+ + e^- \rightarrow K$$

$$I^- + h^+ \rightarrow I$$

$$I + I \rightarrow I_2 \uparrow$$

(4) Minor changes in conductivity may be due to stress release under photon bombardment.

Now we would discuss these explanations one by one for different films.

10°C: Small and large thickness

$$(O_A)_{30} \sim (O_{AL})_{30}, (O_{AL})_{240} > (O_A)_{240}, \Delta E_A > \Delta E_{AL}$$

If explanation (1) is accepted, then we can account for the increase in conductivity at 240°C due to annealing and for the lowering of activation energy. It seems that major contribution is due to effect (1). Though, the conductivity at 30°C of light annealed and dark annealed samples are not much different but there is a slight decrease in conductivity on annealing in light. To account for the lowering of conductivity at room temperature (30°C) we have to consider a minor share from effect (2) also in which a low conductivity phase $K_2AgI_3$ is produced as a result of disintegration.
of $\text{Ag}_4\text{I}_5$ due to photon interactions. At these temperatures $\text{K}_2\text{AgI}_3$ is a favoured stoichiometry and hence this reaction could be triggered easily.

Possibility of effect of reaction (3) may be ignored, but that of (4) cannot be ruled out in view of the fact that this film has stress as discussed in section A. However, the above discussion is an oversimplification of the situation in view of the absence of chemical analysis or any other analytical data. More definite conclusion is not warranted.

32°: Small thickness.

$\text{K}_2\text{AgI}_3$ in large quantity; and $\text{Ag}_4\text{I}_5$ in relatively small amount with some metal colloids also (section C). On en-rolling under Hg light, AgI dissociates according to photochemical reaction (1), but dissociation of $\text{Ag}_4\text{I}_5$ as per reaction (2) is also favoured. However, it appears that the reaction (1) has a major contribution to the conductivity of these films in which the lowering of conductivity at room temperature due to the formation of $\text{K}_2\text{AgI}_3$ is compensated by conductivity of Ag metal colloids. Similarly, a rise in activation energy due
to formation of $K_2AgI_3$ is compensated by the lowering of activation energy due to metal colloids.

Possibility of effect of reaction (3) is unlikely since otherwise it would show up in an increase in room temperature conductivity. The effect (4) shall also be relatively small as the films deposited at this temperature has low stress (section A).

$32^\circ C$: Large thickness.

$\left( C_A \right)_{30} \cong \left( C_{AL} \right)_{30}$, $\left( C_A \right)_{240} \cong \left( C_{AL} \right)_{240}$, $\Delta E_A > \Delta E_{AL}$

Based upon the data on temperature variation of conductivity, it has been postulated earlier that these films have large quantities of AgI and $K_2AgI_3$ (section C). The occurrence of photochemical reaction (1) is therefore suggested on annealing under Hg light. This would account for the decrease in activation energy. However, $KAgI_5$ also dissociates according to reaction (3). The lowering of conductivity due to formation of $K_2AgI_3$ according to this reaction is compensated by an increase in conductivity due to effect (1). Hence we do not observe any effect on room temperature conductivity and at $240^\circ C$. 
As discussed earlier, the films deposited at this electrolysis temperature show the best electrical properties and possess least amount of mechanical stress. From Table 2.7, it is clear that neither $\alpha$ nor $\Delta E$ of these films are much affected on annealing in the presence of light. Figure 2.14(a) indicates that the electrical properties of films annealed in dark or light are nearly the same. Hence, it may be postulated that the effect (1) has only a minor contribution though it cannot be neglected since (1) is a well known photochemical reaction. As discussed earlier, the effect (2) and (3) are opposite to each other as far as the electrical conductivity is concerned. As such it can be said that the two effects are simultaneously present in such a way that the sum total effect is negligibly small as observed by us.

Since these films have minimum built in stress (section A), the contribution of effect (4) is also not much.

As we have seen earlier in section $\ell$ and Section C, the films deposited at this electrolysis temperature
are very interesting because of the large built-in stress in them. This stress prohibits us from making any conclusive remarks as regards the activation energy and the conductivity of these films. Annealing under light modifies both $\sigma_{30}$ and $\sigma_{240}$ while keeping the activation energy the same.

It seems, effect (4) is predominant in this case and modification of conductivities are only due to a further stress release under photon bombardment. However, in the absence of any detailed investigation on the stress in these films no definite conclusion is warranted.

90°c : Small thickness.

$$\sigma_A^{30} \sim \sigma_{AL}^{30}, \quad \sigma_A^{240} \sim \sigma_{AL}^{240}, \quad \Delta E_A \sim \Delta E_{AL}$$

Apparently there is no effect of light. It may be postulated as discussed for films deposited at 45°c, that the effect (2) and effect (3) act in a way such that the sum total effect is nullified.

Effect (4) can be somewhat ruled out in this case, as done for films deposited at an electrolysis temperature of 45°c discussed earlier. These films have also a small built-in stress, as discussed in section A.

90°c : Large thickness.

$$\sigma_A^{30} \triangleleft \sigma_{AL}^{30}, \quad \sigma_A^{240} \triangleleft \sigma_{AL}^{240}, \quad \Delta E_A \triangleleft \Delta E_{AL}$$

The probable composition of these films as
postulated in section C is $\text{Ag}_4 \text{I}_5$ and $\text{AgI}$ and metal colloids in small quantity. It is also postulated that stress in these films is small (section A).

Temperature variation of conductivity curve (Figure 2.14 b) shows that the relative amount of $\text{AgI}$ and metal colloids are considerably increased in these films after annealing under $\text{Hg}$ light. This may be because of the dominance of effect (2). The presence of metal colloids results in an increase in room temperature conductivity and also in $\Theta_{240}$.

The effect (4) shall be small since these films have small built-in stress as discussed in section A.

(G) *Effect of pH of the solution:*

Similar studies as discussed above were carried out on films deposited from KI aqueous solution of various pH values viz. 3, 8.5 and 9. Table 2.8 gives the results on the films deposited at 45$^\circ$C. It is obvious from the Table 2.8 that no substantial difference in the results are obtained due to change in pH.
The values of electrical conductivity $\sigma$ at 30°C and 240°C and the activation energy $\Delta E$ for films of $KAg_4I_5$ deposited at an electrolysis temperature of 45°C at 7 ma/cm² and annealed in dark are given for 100 micron thick film for different pH values of the electrolytic solution.

<table>
<thead>
<tr>
<th>pH of the solution</th>
<th>$\sigma_{30}$ (ohm$^{-1}$cm$^{-1}$)</th>
<th>$\sigma_{240}$ (ohm$^{-1}$cm$^{-1}$)</th>
<th>$\Delta E$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>0.26</td>
<td>2.32</td>
<td>0.11</td>
</tr>
<tr>
<td>8.5</td>
<td>0.256</td>
<td>2.96</td>
<td>0.106</td>
</tr>
<tr>
<td>9</td>
<td>0.26</td>
<td>2.30</td>
<td>0.109</td>
</tr>
</tbody>
</table>
In conclusion we can say that high conductivity ionic films of predominantly superionic solid $KAg_4I_5$ can easily be deposited on a silver substrate by a simple electrolytic method. The films deposited at 45°C show the best electrical properties. The films deposited at lower current density have less AgI and metal colloids than those obtained by electrolyzing at high current densities. The film deposited at 1 mA/cm$^2$ is mostly formed of $KAg_4I_5$. Thermal annealing in general improves the quality of the films. The presence of mercury light during annealing increases the conductivity of these films to some extent due to photolysis.
References:


