CHAPTER III

PIECE OF HIGH CONDUCTIVITY SOLID ELECTROLYTE

(COUNTERIONIC SOLID) RbAg₄I₅
This chapter reports the results obtained on \( \text{RbAg}_4\text{I}_5 \) films similar to those reported for \( \text{KAg}_4\text{I}_5 \) in Chapter II. \( \text{RbAg}_4\text{I}_5 \) is thermodynamically more stable than \( \text{KAg}_4\text{I}_5 \). The disproportionation temperature for \( \text{RbAg}_4\text{I}_5 \) is 28°C\(^1\) as compared to 37°C of \( \text{KAg}_4\text{I}_5 \). As such devices based on \( \text{RbAg}_4\text{I}_5 \) would have greater shelf-life when stored at room temperature. This has led to a large number of studies on \( \text{RbAg}_4\text{I}_5 \). The films of \( \text{RbAg}_4\text{I}_5 \) have been obtained by Kennedy et al\(^2\), Takahashi et al\(^3\) and Knoteck and Seager\(^4\) by vapour deposition technique. The electro-codeposition method developed by us for \( \text{KAg}_4\text{I}_5 \) is applied here to obtain films of \( \text{RbAg}_4\text{I}_5 \) and the results are reported below.

(3.1) EXPERIMENTAL

Experimental arrangement is the same as discussed in Chapter II. For deposition of films of \( \text{RbAg}_4\text{I}_5 \), an aqueous solution of PbI was prepared in place of KI which was used for obtaining \( \text{KAg}_4\text{I}_5 \) film. The results reported below are those for films annealed at 150°C for 3 hours in dark.
3.2 RESULTS & DISCUSSIONS

(a) **Thickness of the film as a function of electrolysis Temperature**:

The thickness of the film deposited at the silver anode was studied as a function of time when the electrolysis was carried out at a current density of 7 mA/cm$^2$ at different temperatures in HbI aqueous solution at pH = 3. Figure 3.1 gives the thickness of the film at the anode as a function of time for six temperatures viz. 10, 20, 30, 40, 60 and 80$^\circ$C. The dotted portion of the curve indicates the region where the film had a tendency to chip off after annealing. From Figure 3.1 it is obvious that (i) the thickest film which could be obtained and which does not peel or chip off after annealing is deposited at 10$^\circ$C, (ii) the thickness of the film deposited at 10$^\circ$C is maximum for various intervals of time, (iii) the thickness first varies linearly and then levels off slowly with time. The conclusion (iii) can be explained as done for $\text{KAg}_4$I$_5$ in Chapter II. First and second conclusions suggest that the film deposited at 10$^\circ$C has least built-in mechanical stress. This is not confirmed by indirect measurement of stress through back side film thickness measurements as discussed in the next paragraph. However, the apparent fast rate of growth at 10$^\circ$C temperature may be due to the presence of voids in the film which is also indicated by low electrical conductivity values reported later in this Chapter.
FIG. 3.1: THICKNESS OF RBAq_{4}I_{6} FILM AS THE FUNCTION OF TIME.
For a qualitative idea of the stress in the front side film, the back side film thickness was also measured as discussed in Chapter II. The backside film thickness obtained at different electrolysis temperature when the front side thickness was 75 μ is given in Figure 3.2. It is obvious that the back side film thickness is almost independent of electrolysis temperature indicating that the stress in front side film responsible for back side film formation does not vary much on electrolysis temperature.

(B) 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, 20, 30, 40, 60 and 80°C and annealed in the dark at 150°C for about 3 hours are given in Figure 3.3. The conductivity of the films of the same thickness as a function of electrolysis temperature are shown in Figure 3.4.

It is obvious from Figure 2.3 and Figure 3.4 that conductivity for all thicknesses are maximum for 30°C. Further, from Figure 3.3 we observe that in general, the conductivity in the beginning varies slowly with thickness but then decreases rapidly with increasing thickness.
FIG. 3.2: STRESS IN RbAg$_4$I$_5$ FILMS VS ELECTROLYSIS TEMPERATURE.
FIG. 3.3: VARIATION OF ELECTRIC CONDUCTIVITY WITH THICKNESS OF THE FILMS OF RBAg₄I₅

THICKNESS (MICRONS)
FIG. 3.4

THE RELATIVE CONDUCTIVITY OF DIFFERENT THICKNESS FILMS OF RbA$_{4}$I$_{3}$ DEPOSITED AT DIFFERENT ELECTROLYSIS TEMPERATURE

Conductivity (Ohm·cm$^{-1}$)

ELECTROLYSIS TEMPERATURE $^\circ$C

- 20 µ
- 40 µ
- 60 µ
- 80 µ
This is because at higher thicknesses, only a small number of silver ions are being able to diffuse through the thick ionic film to react with the Rubidium and iodide ions to form a new layer of $\text{RbAg}_4\text{I}_5$ and thus the favoured stoichiometry would be $\text{Rb}_2\text{AgI}_3$ which is a lower conductivity compound.

The high ionic conductivity (0.19 ohm$^{-1}$cm$^{-1}$ at 30°C) of the film deposited at the electrolysis temperature of 30°C can be attributed to the fact that the film is predominantly of $\text{RbAg}_4\text{I}_5$. The conductivity vs temperatures studies indicate the presence of a small amount of AgI also. These results are discussed later.

(C) Temperature variation of electrical conductivity

Figures 3.5 and 3.6 give the temperature variation of electrical conductivity of the films deposited at different temperatures viz. 10, 20, 30, 40, 60 and 80°C. Results for two thicknesses of the films namely small ($\sim 25\mu$) and large ($\sim 30\mu$) are given. In each case, it can be seen that there is a sudden increase in conductivity at 150°C indicating the presence of AgI (very small in the low thickness film prepared at 60°C).

At lower temperatures the high conductivity is mostly due to the presence of $\text{RbAg}_4\text{I}_5$. The low temperature slope has been analysed in terms of Arrhenius plot
FIG. 3.5: TEMPERATURE VARIATION OF ELECTRICAL CONDUCTIVITY OF FILMS OF RbAgI$_5$ (SMALL THICKNESS).

$\sigma T$ (ohm$^{-2}$ cm$^{-1}$ K$^{-1}$)

$\frac{1}{T} \times 10^3$ (°K$^{-1}$)
FIG. 36 TEMPERATURE VARIATION OF FILMS OF RbAg₄I₅ (LARGE THICKNESS).
(see eq. 2.2 & 2.3). The values of the pre-exponential factor (A) and the activation energy $\Delta E$ are given in Table 3.1. This table also gives the values of the electrical conductivity at 30°C ($\sigma_{30}$) and 230°C ($\sigma_{230}$) extrapolated from experimental data. The electrical conductivity of films obtained on different electrolysis temperatures are individually discussed below.

10°C film:

It can be seen from Table 3.1 that the activation energy of low thickness films ($\sim 25 \mu$) is found to be 0.06 eV which is smaller than for RbAg$_4$I$_5$ bulk material (0.1 eV). A jump in conductivity around 150°C is an indication of the presence of AgI in these films as discussed in Chapter 1. The extent of conductivity jump would be an indication of the relative amount of AgI present in these films. Thus, it can be concluded that these films contain a relatively large amount of AgI together with RbAg$_4$I$_5$. If this conclusion is true, then the room temperature conductivity of the films should be low since $\beta$-AgI (room temperature phase) is a low conductivity compound. This is found experimentally true ($\sigma_{30} = 0.0088 \text{ ohm}^{-1}\text{cm}^{-1}$). On the other hand, the presence of AgI should result in an increase in the net activation energy. Since $\beta$-AgI film has a larger value
Table 3.1  Some conductivity parameters of electro-codeposited films of Rb\textsubscript{2}AgI\textsubscript{4} at different electrolysis temperatures. The results are given for two films thickness viz. small (26\textmu) and large (90\textmu).

<table>
<thead>
<tr>
<th>Temperature of electrolysis (^\circ\text{C})</th>
<th>Thickness</th>
<th>(\sigma_{30}) \text{Ohm}^{-1}\text{cm}^{-1}</th>
<th>(\sigma_{230}) \text{Ohm}^{-1}\text{cm}^{-1}</th>
<th>A</th>
<th>(\Delta E) \text{eV}</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>small</td>
<td>0.0088</td>
<td>0.71</td>
<td>1.6</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>large</td>
<td>0.0062</td>
<td>0.12</td>
<td>0.39</td>
<td>0.052</td>
</tr>
<tr>
<td></td>
<td>small</td>
<td>0.06</td>
<td>0.19</td>
<td>0.18</td>
<td>0.085</td>
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<tr>
<td>20</td>
<td>large</td>
<td>0.0094</td>
<td>0.11</td>
<td>1.2</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>small</td>
<td>0.137</td>
<td>4.9</td>
<td>0.6</td>
<td>0.085</td>
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<tr>
<td>30</td>
<td>large</td>
<td>0.03</td>
<td>0.077</td>
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<td>0.011</td>
<td>0.083</td>
<td>0.83</td>
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<td>40</td>
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<td>0.0044</td>
<td>0.026</td>
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<td>0.045</td>
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<tr>
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<td>0.0012</td>
<td>0.0024</td>
<td>0.086</td>
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<tr>
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<td>0.004</td>
<td>0.084</td>
<td>0.046</td>
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<tr>
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<td>0.476</td>
<td>0.06</td>
<td>0.054</td>
</tr>
<tr>
<td>80</td>
<td>large</td>
<td>0.007</td>
<td>4.17</td>
<td>1.2</td>
<td>0.044</td>
</tr>
</tbody>
</table>
of activation energy 0.36 eV as compared to 0.1 eV of 
\( \text{PbI}_4 \). This is in contradiction with the experimental value of 0.06 eV which is even lower than the value of activation energy for \( \text{PbI}_4 \). However, these two self-contradictory conclusions can be reconciled if we postulate the presence of some metal colloids (or electronic conduction). As discussed in Chapter II, the presence of electronic conduction tends to decrease the net activation energy.

The results of large thickness films are also the same as those for small thickness films.

20°C film:

The room temperature conductivity of the small thickness films are not as low as those of 10°C film. The extent of conductivity jump at 150°C is much smaller. Both these suggest that the film has lesser amount of conductivity compound \( \text{AgI} \) in these \( \text{PbI}_4 \) film. This is also confirmed by the fact that the activation for these films (0.09 eV) is comparable to that of \( \text{PbI}_4 \) (0.1 eV). This slightly small value of activation energy forbids us to rule out completely the presence of metal colloids particularly because of the fact that the small amount of AgI present in the film would ordinarily increase \( \Delta \).
Results of large thickness films indicate the presence of a relatively greater amount of AgI in these films. This is also supported by a larger activation energy and small room temperature conductivity for these films.

30°C film:

The low thickness films obtained at this temperature are probably the best films that can be obtained using our electro-codeposition method. The value of activation energy and room temperature conductivity, which is very near to that of bulk RbAg₄I₅, indicate that the film is predominantly of RbAg₄I₅, though arguing as above for 10°C and 20°C films, the presence of some amount of metal colloids and AgI can not be completely ruled out.

This electrolysis temperature is expected to be favourable since the compound RbAg₄I₅ is known to be thermodynamically unstable below 28°C. Hence the favoured stoichiometry will be above this temperature. This is in conformity with the results which we have obtained.

The large thickness films deposited at this electrolysis temperature are also having conductivity parameters best comparable to RbAg₄I₅ vis-a-vis those for
same thickness but deposited at other electrolysis temperatures. However, the low thickness film has better electrical conductivity than the high thickness film prepared under similar conditions.

40°C film:

The room temperature conductivity ($\sigma_{30}$) of small thickness films is much lower than those expected for the bulk. This indicates the presence of a large number of some low conductivity compound like $\text{Rb}_2\text{AgI}_3$ and $\text{AgI}$. But $\text{AgI}$ is present only in small quantity judging from the extent of conductivity jump at 150°C. Also the activation energy is very low. These two facts together suggest that $\text{Rb}_2\text{AgI}_3$ and metal colloids are present in large quantities in these films.

Results for the large thickness films are qualitatively similar except for the fact that the conductivity is much lower than the low thickness film. This indicates the presence of relatively larger amount of $\text{AgI}$ or $\text{Rb}_2\text{AgI}_3$ alongwith metal colloids in the so-called film of $\text{Rb}_4\text{Ag}_4\text{I}_5$.

60°C film:

The temperature variation studies given in Figure 3.5 show that small thickness films deposited at
this electrolysis temperature are containing very small amount of AgI. Hence in view of the very low room temperature conductivity of these films, the large amount of \( Pb_2AgI_3 \) is postulated, as the activation energy also is very low. The presence of some amount of metal colloids also cannot be ruled out.

Large thickness films have a very low room temperature conductivity indicating a larger amount of AgI contained in them.

**80\(^\circ\)C film:**

The conductivity values for low thickness films are similar to those of 20\(^\circ\)C films and hence similar conclusions can be drawn. However, there is one important difference that the activation energy for 80\(^\circ\)C film is much smaller than \( PbAg_4I_5 \) or that of 20\(^\circ\)C film. It means that 80\(^\circ\)C film has more metallic colloids in it. The larger thickness film, apart from more metallic colloids, possesses more AgI also judging from a very steep rise in conductivity at 150\(^\circ\)C.

(D) **Effect of thermal annealing in light:**

All the results discussed above are for films annealed at 150\(^\circ\)C for 3 hours in dark. The effect of light during annealing was also studied to check out the
possible photolysis reaction as discussed in Chapter II for $\text{I}_5\text{g}_4 \text{I}_5$. For $\text{RbAg}_4 \text{I}_5$ films, we found that annealing in light does not change the electrical conductivity parameters much as compared to those annealed in dark. The typical conductivity parameters for films annealed in dark and Mercury light are shown in Table 3.2. The two values are within reasonable experimental agreement indicating that the effect of light is small.

(E) CONCLUSION

In concluding it can be said that predominantly $\text{RbAg}_4 \text{I}_5$ films can be obtained on silver substrate by electro-codensation method. The best films are obtained at an electrolysis temperature of 30°C as against 45°C for $\text{KAg}_4 \text{I}_5$. The effect of light during annealing is negligible as against $\text{KAg}_4 \text{I}_5$ where it was an important factor.
Table 3.2 The selected conductivity values and activation energy for electro-codeposited RbK$_4$I$_6$ film at different electrolysis temperatures for samples annealed in dark and in light. The values given in parenthesis are those for annealed in dark while the value is for films annealed in light.

<table>
<thead>
<tr>
<th>Temperature of electrolysis $a_0$</th>
<th>Thickness</th>
<th>$\sigma$ at 30 °C ohm$^{-1}$cm$^{-1}$</th>
<th>$\sigma$ at 230 °C ohm$^{-1}$cm$^{-1}$</th>
<th>$\Delta E_{AL}$ eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>small</td>
<td>0.009 (0.0038)</td>
<td>0.312 (0.71)</td>
<td>0.07 (0.06)</td>
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<td>0.007 (0.0062)</td>
<td>0.11 (0.12)</td>
<td>0.06 (0.052)</td>
</tr>
<tr>
<td></td>
<td>small</td>
<td>0.09 (0.06)</td>
<td>0.60 (0.49)</td>
<td>0.09 (0.085)</td>
</tr>
<tr>
<td>20</td>
<td>large</td>
<td>0.0096 (0.0094)</td>
<td>0.20 (0.11)</td>
<td>0.12 (0.13)</td>
</tr>
<tr>
<td></td>
<td>small</td>
<td>0.21 (0.19)</td>
<td>1.8 (4.9)</td>
<td>0.067 (0.085)</td>
</tr>
<tr>
<td>30</td>
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<td>0.09 (0.03)</td>
<td>0.12 (0.08)</td>
<td>0.10 (0.12)</td>
</tr>
<tr>
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<td>0.02 (0.011)</td>
<td>0.068 (0.083)</td>
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<tr>
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<tr>
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<td>0.01 (0.007)</td>
<td>6.98 (4.17)</td>
<td>0.046 (0.044)</td>
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</table>
References:


