Effect of deposition rate and vacuum content on the structure of Ag films deposited on to pure and doped substrates.
6.1. INTRODUCTION:

In chapter 2, we have discussed in detail how the various experimental parameters influence the different stages of the film growth. It was also mentioned that the influence of the experimental parameters on nucleation decides the future trend for the grain structure of the vacuum deposited films.

In chapter 5, we have already seen how the silver films grow epitaxially on doped NaCl and KBr substrates at room temperature in contrast to the polycrystalline growth on pure substrates. To investigate in detail this peculiar behaviour of doped substrates measurements were made to evaluate quantitatively grain size dependence on the rate of deposition, and, the vacuum content of the system during deposition which is presented in this chapter.

6.2. Experimental:

Thin films of silver were prepared by vacuum deposition from a molybdenum boat at different deposition rates, on to freshly cleaved KBr, AgSO₄ doped KBr, and PbSO₄ doped KBr crystals grown as described in chapter 5, (dopant concentration 2% by weight), both in high vacuum (10⁻⁵ torr) and low vacuum (5 x 10⁻⁵ torr) in the thin film preparing unit described in chapter 4, fig. 4.1. The different deposition rates were determined for different source heating currents through the boat by noting the time required for the same
amount of silver to completely evaporate, in each case. The thickness of silver film was determined by multiple beam interferometry and thereby the deposition rate was computed in terms of thickness of the film deposited/second. Since silver does not wet molybdenum, there will not be much change in boat resistance as silver evaporates. Thus the films were prepared for different deposition rates in high vacuum as well as low vacuum, and, were examined by selected area diffraction technique in the electron microscope.

To minimize the effect of impurities, the substrates were cleansed by ionic-bombardment and were also degassed for a long time in the case of high vacuum studies. The power supply to the boat was stabilised so that the fluctuations in the mains could be eliminated.

6.3. Results:

6.3.A. High vacuum experiments:

Figs. 6.1 to 6.4 show electron micrographs a selected area diffraction patterns of silver films deposited on (a) pure KBr (b) AgSO₄ doped KBr (c) PbSO₄ doped KBr, at deposition rates of (1) 2Å/sec (2) 6Å/sec (3) 15Å/sec (4) 50Å/sec respectively. The grain size and grain density of these films are condensed in table
Table: 6T.1.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Deposition rate A°/sec.</th>
<th>Grain size A°</th>
<th>Grain density x 10^10 cm^-2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>pure KBr</td>
<td>AgSO_4 doped</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>250</td>
<td>300</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>150</td>
<td>340</td>
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<td>3</td>
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<td>140</td>
<td>780</td>
</tr>
<tr>
<td>4</td>
<td>50</td>
<td>330</td>
<td>520</td>
</tr>
</tbody>
</table>

Figs. 6.5 and 6.6 are the plots showing the variation of grain size and grain density with the rate of deposition.

6.3.4.1. Pure KBr substrates:

(i) Grain size and grain density:

The grain size of the film on pure KBr decreases initially with the increase of deposition rate, up to 15A°/sec. and later on slowly increases. Thus the curve can be divided into two parts, viz., (a) an inverse dependence of grain size on deposition rate and (b) a direct dependence on deposition rate. The initial part of the curve seems to be in agreement with the theoretical prediction made.
during the discussion on nucleation in chapter 2. It was discussed in chapter 2, how deposition rate influences the critical nucleus size $r^*$ and the free energy of formation $\Delta G^*$ of the nucleus, which in turn governs the nucleation frequency $I$, and the nuclei density. It was theoretically deduced that a decrease in deposition rate which means a lowering of super saturation (a) increases the size of the critical nucleus $r^*$ and (b) decreases the free energy of formation $\Delta G^*$, increasing the nucleation frequency and hence the nuclei density.

Considering that the grain size of the film depends directly upon the critical nucleus size and grain density on nucleation frequency, a lower nucleation density leads to higher agglomeration, i.e. large grain size and small grain density, consequently. Accordingly grain size should decrease with the increase of deposition rate. The initial part of our curve just fits with this logic. Similar observations have been made by Campbell et al.\textsuperscript{174} for L.F and gold on carbon film. But these dependences hold good only qualitatively, as, during the growth of a continuous film grain growth and coalescence phenomenon lead to a noticeable variation in the dependence of grain size and grain density on the rate of deposition. A number of parameters in a not clearly known way seem to influence the whole process. This is evident from the exactly contradictory results of Sennet and Scott\textsuperscript{175} reported for silver films on formavar substrates. But Chopra et al.\textsuperscript{91} have
observed an increase in grain size with increasing deposition rate. They have shown that agglomeration and hence grain size increases with higher deposition rates. But these observations are for films between post nucleation and pre coalescence stage (II stage coalescence). As the film becomes more and more continuous the process becomes more complicated. The slow rise in grain size of silver film on pure substrate at higher deposition rate may be attributed to higher surface mobility of adatoms due to higher kinetic energy of depositing atoms. As discussed in chapter 2, the depositing atoms will still have a component of velocity parallel to substrate. Higher the evaporation temperature, higher will be the K.E. of adatoms and higher will be the surface mobility leading to higher agglomeration and consequently larger grain size. This is evident from the larger number of holes observed in the films (Fig. 6.4a) deposited at a rate of 50Å/sec.

(ii) Orientation:

The electron diffraction patterns in Figs. 6.1a...6.4a show the effect of deposition rate on the orientation of the films. At very low deposition rate (Fig. 6.1a) the film is having a slightly preferential orientation with higher deposition rates, the orientation deteriorates and a pure ring pattern is obtained (Fig. 6.3a). This is in accordance with the theory of nucleation, wherein at low deposition rates, better orientation is expected, because of lowering
of super-saturation (chapter 2). On the other hand at very high deposition rates (50Å/sec.) the orientation improves to an archy pattern (Fig. 6.4a). Though this seems to be in contradiction to nucleation theory, it is pointed out in chapter two, that at very high deposition rates, the orientation improves due to a very large increase in the number of nuclei which will have a controlling influence on orientation\textsuperscript{106,107}. This is in contradiction to the previous conclusions about grain size where it is pointed out that higher the nuclei density, lesser will be the agglomeration and hence smaller the grain size. But at very high deposition rate, the high K.E. of the vapour atoms may lead to large surface mobility leading to high agglomeration. Chopra et.al.\textsuperscript{91} have also observed improved orientation at high K.E. of vapour atoms. Hence though initial nuclei frequency will be large at very high deposition rates, there will be drastic coalescence leading to agglomeration and better orientation with larger grain size and less continuity.

6.3.A.2. Doped substrates:

(i) Grain size and grain density:

The results on doped substrates show peculiar structure of the film (Table 6T.1 and Fig. 6.5) compared to the pure substrate film. In this case also the grain size deposition rate curve can be divided into two regions, viz. (i) increase of deposition rate initially (ii) decrease of grain size at very high deposition rate in exact contrast to
the behaviour of the film deposited on pure substrates. The grain density falls initially with increase of deposition rate and slowly rises at higher deposition rates. This is contrary to the prediction made on the basis of the nucleation theory. It is already observed in chapter 5, that the nucleation on doped substrates is highly preferential, the nuclei on an average are bigger than those grown faster leading to earlier coalescence. Also, as a result of such non-uniform distribution of nuclei and their faster growth, the films contain many holes in contrast to the continuous films grown on pure substrates. In other words there is a higher tendency for agglomeration in films on doped substrates. This is evident from large number of holes present in these films (Figs. 6.2b to 6.4b, 6.2c to 6.4c). It has been discussed earlier in chapter 5, that dopant changes the surface energy of the substrate. The nature of the substrate surface plays a vital role in the mobility of adatoms. With increasing deposition rates, mobility is enhanced leading to higher agglomeration.

In the films on doped substrates, at higher deposition rates, it is clearly seen that the grain size is highly non-uniform. Some grains are very large compared to many others. These grains probably correspond to the preferential nucleation sites in the substrate. Since these were born earlier and grown faster to coalesce earlier, they remained larger in contrast to the smaller grains which must have come into existence in a later stage of growth. The bigger
grains all show the same tint whereas the smaller ones show a non-uniform tint (this will be discussed later). These bigger grains are mainly responsible for the change in the grainsize, since the smaller grains do not show much variation, i.e. with increasing deposition rate, the grains on the preferential nucleation sites must have grown faster.

At very high deposition rates, the grain size registers a fall on doped substrates. Here once again it is seen that (Fig. 6.4b and 6.4c) the typical big grains found so far, considerably reduce in number and size, leading to a fall in the average grain size, i.e. pockets of preferential nucleation must have considerably decreased. It is probable that due to high K.E. of vapour atoms, the surface mobility of adatoms becomes so great as to over run the preferential sites, thereby decreasing their dominance. The increase in the holes in the films with deposition rate, shows the higher agglomeration tendency on doped substrates. In the case of films on pure substrates, agglomeration is possible only by higher K.E. of vapour atoms whereas preferential nucleation centres are also involved in the case of films deposited on doped substrates.

The grain density also initially decreases and further slowly rises with deposition rate on doped substrates (Fig. 6.6) Slow rise of grain density in contrast to the steep fall of grain size may be explained due to larger number of holes appearing in later stages of growth.
In a nutshell, there seems to be fast growing islands on preferential nucleation centres in doped substrates which dominate the initial stages of growth. At very high deposition rates, the preferential nucleation sites seem to be less influential on the overall growth of the film.

(ii) Orientation:

The diffraction patterns in Figs. 6.1b and 6.1c show the monocrystalline growth of the film as already observed in chapter 5. With the increase of deposition rate, the decrease in the crystallinity is evident from the archy patterns seen in Figs. 6.2b, 6.3b and 6.2c, 6.3c. This is once again in accordance with the nucleation theory, as already discussed for films deposited on pure substrates. The uniform tint of the bigger grains suggests that they are contributing for the preferential oriented growth of the film. This further supports the prediction that they must be from the initial preferential pockets of nucleation.

At very high deposition rates (50Å/sec.), there seems to be a slight improvement in the orientation (Figs. 6.4b, 6.4c). This can be explained on the similar lines as for the improved orientation of films on pure substrates at very high deposition rates, as due to higher K.E. of the vapour atoms and a large number of nuclei in the initial stage of deposition.
6.3. A.3. Conclusion:

The grain size dependence on deposition parameter is a very complex phenomenon and no single theory has been able to explain the whole process satisfactorily. The behaviour of the film on both the doped substrates is similar and in exact contrast to the one on the pure substrate. Once again, as stressed in chapter 5, the dopant is mainly responsible for the peculiar observations. The films on doped substrates always show a better degree of orientation for all the deposition rates as compared to the film on pure substrates. From the table and graphs, it is clear that the grain size is larger on PbSO$_4$ doped substrate than that on the AgSO$_4$ doped one. This shows that the quality of dopant is also an important factor in the modification of the film growth.

6.3. E. Low vacuum experiments:

Figs. 6.7 to 6.9 show the typical micrographs and the selected area diffraction patterns of films deposited on to pure, AgSO$_4$ doped and PbSO$_4$ doped substrates. The average grain size and grain density at different deposition rates on these substrates are given in Table 6.2. Figs. 6.10 and 6.11 show the variation of grain size and grain density as a function of deposition rate.
### Table: 6T.2

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Deposition rate $\text{Å/sec.}$</th>
<th>Grain size $\text{Å}$</th>
<th>Grain density $\times 10^{10}$ $\text{cm}^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>pure $\text{AgSO}_4$</td>
<td>NaCl doped $\text{PbSO}_4$ doped</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>280</td>
<td>550</td>
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</tr>
<tr>
<td>3</td>
<td>30</td>
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</tr>
</tbody>
</table>

(i) Grain size and grain density:

Contrary to the high vacuum deposited films, grain size decreases with increasing deposition rate on the pure substrate, almost linearly. On the doped substrate also a similar trend is observed in the initial stages but not much change is seen later stages (Fig. 6.10). A large number of big holes appear in the films on the doped substrates, at higher deposition rates. One more prominent feature with the films on doped substrates is that the grain size tends to be more uniform at higher deposition rates.

The grain density increases with deposition rate on pure substrates. This is a direct consequence of fall in grain size with increasing deposition rate. On $\text{AgSO}_4$ doped substrates, though grain density registers a rise in the initial stages, it remains almost independent of deposition rate later (Fig. 6.11). This can be attributed to the
appearance of holes in films at high deposition rates, which compensates for the decrease of grain size observed at these rates.

In the case of films on the PbSO$_4$ doped substrates, the grain density traces a similar path. Compared to that of films on pure substrates, the variation of grain density with deposition rate is negligibly small.

In low vacuum, the number of gas molecules striking the substrate surface is very high in comparison to the metal atoms incident on it. Also the quality of vacuum considerably varies. The amount of water vapour and other impurities present will be higher as compared to those in high vacuum. All these individually and collectively influence the growth processes. The larger number of gas molecules striking the substrate will considerably affect the adatom mobility on the substrate. The very large grain size at low deposition rate in low vacuum films can be attributed to this fact. As a result of restricted mobility, the adatom clusters grow individually without coalescing leading to bigger grain size. As the deposition rate increases, the influence of gas molecules decreases resulting in a lowering of grain size. Compared to the films deposited in high vacuum, a larger number of irregular holes are present in low vacuum films. This can again be attributed to the complex nature of the influence of the number of impurities present in low vacuum.
though oxidation is a possibility in low vacuum films, no such case could be detected in diffraction patterns.

(ii) Orientations:

The diffraction patterns reveal the most astonishing fact that the epitaxial enhancement on the doped substrates still persists even in low vacuum. The extent of vacuum is a very important factor in deciding epitaxy. Lower the vacuum, the orienting influence of the substrate diminishes, resulting in deterioration of epitaxy. Ino and Watanabe have shown, how vacuum cleaving enhances epitaxy due to lesser coverage of the substrate surface by the residual gas atoms. In contrast to these observations, the films on the doped substrates still remain better oriented at as low a vacuum as $10^{-3}$ torr! This shows the dominating influence of doped substrates on epitaxy. At a deposition rate of $12\,\text{Å/sec.}$, the film on pure substrate exhibits predominantly ring pattern (Fig. 6.7a), whereas the films on the Ag$_2$O and Pb$_2$O$_3$ doped substrates show a strongly $<100>$ oriented growth (Figs. 6.7b and 6.7c).

As deposition rate increases, the degree of orientation decreases, as observed for the high-vacuum films (except for very high deposition rate) and the diffraction pattern of the film on the pure substrate changes over to a completely ring pattern (Figs. 6.8a and 6.9a). With higher deposition rates, the characteristic influence of the dopant continues to exist, which is evident by the archy diffraction patterns—
of the films on doped substrates (Figs. 6.8b, 6.8c and 6.9b, 6.9c). The tendency throughout remains to be for a \( <100> \) orientation.

6.4 Summary:

In high vacuum, the films on pure substrate become less grainy with increase in deposition rate, up to 15Å/sec. At very high deposition rate, agglomeration sets in, increasing the grain-size. Holes also start appearing in the films. Though the orientation decreases initially, the trend reverses for very high deposition rate.

On both \( \text{AgSO}_4 \) and \( \text{PbSO}_4 \) doped substrates, grain size increases with increase in deposition up to 15Å/sec., indicating higher agglomeration. When deposition rate is increased to 50Å/sec., grain size decreases. The films become less continuous as deposition rate increases. From a parallel epitaxy at low deposition rate, the orientation deteriorates up to 15Å/sec. and improves once again at 50Å/sec. deposition rate. The size distribution of grains in the films deposited on doped substrates remains highly non-uniform, as compared to the uniform size of grains in the films on pure substrate.

In low vacuum though, the grain size decreases with increase in deposition rate, dependence is not as evident as in films deposited in high vacuum. Both pure and doped substrates show similar trend, though the grain size is very
large on doped ones. From orientation point of view, the doped substrates still exhibit their characteristic influence on oriented growth.

Doped NaCl substrates (same dopant concentration) also showed qualitatively, a similar behaviour as compared to doped KBr substrates, highlighting the point that the dopant, immaterial in what parent crystal it is, influences the growth of the deposited film in almost a similar fashion.