Study of Ag, Al & Au films deposited on pure & doped substrates at elevated substrate temperatures.
9.1. INTRODUCTION:

The fact that oriented growth of a film on a substrate can be achieved by raising the temperature of the latter is one of the earliest findings in thin film research. The phenomenon is usually termed 'epitaxy' and the temperature of the substrate is called epitaxial temperature (for the substrate-condensate pair). Though epitaxial temperature is characteristic of the substrate condensate pair, it depends upon various deposition parameters. The orientation of the epitaxial deposits is considerably influenced by the substrate temperature and deposition rate, although the nature of the substrate surface is also of fundamental importance. In this chapter an attempt is made to study epitaxy as a function of substrate temperature and deposition rate, and, the findings for Ag, Al and Au on a variety of substrates are presented.

9.2. Experiment:

Pure, AgSO₄ doped and PbSO₄ doped KBr crystals were grown by melt method. The dopant concentrations were about 2% by weight. Air cleaved crystals were heated in high vacuum in the substrate heater cum holder (described in chapter 4) to different temperatures and pure Ag (99.99%) was deposited on to them at different deposition rates from a molybdenum boat. The thickness of all the films was kept
constant at about 400Å°. After cooling the substrates to room temperature in high vacuum, they were taken out and the film was transferred on to the copper grids as mentioned earlier. Deposition was carried on to the pure and doped substrates in the same run so that the comparative study could be more reliable. In each run, two sets of crystals were placed and the results were compared. Whenever there was large variation in the results of two sets, they were discarded. The most consistent results were taken for the final analysis. Pure Al and Au were evaporated from tungsten helical sources. All other procedures were similar to those in Ag film studies.

9.3. Results and discussion:

9.3.1. Ag films:

Figs. 9.1 - 9.1a, 9.2 - 9.2a and 9.3 - 9.3a show electron micrographs and selected area diffraction patterns of Ag films deposited on to pure, Ag_2O_4 doped and PbSO_4 doped substrates respectively at a substrate temperature of 150°C and a deposition rate of 10Å°/sec. Figs. 9.4 - 9.4a, 9.5 - 9.5a and 9.6 - 9.6a are similar results of Ag films deposited at 180°C. Figs. 9.7, 9.8 & 9.9 are the selected area diffraction patterns of the film on the three substrates at 180°C, but, at a deposition rate of 20Å°/sec.

It is clear from the Figs. 9.1 to 9.6 that the films on the doped substrates are more discontinuous, having
a network of channels in contrast to the continuous films with holes in them, observed on pure substrates. The films deposited at 10Å/sec. on to all the three substrates at 150°C are highly <110> oriented. On the pure and on AgSO₄ doped substrates, archy rings are still present, whereas the rings are practically absent on the Pb doped substrates. In fact, the orientations are not pure <110>, but twinned, as is clear from the weaker spots lying at 1/3rd and 2/3rd the interspot distances. A comparison of these diffraction patterns, particularly the one of Fig. 9.3a with the theoretical pattern proposed by Menzer¹⁸⁵ (Fig. 9.3b) makes clear that this is due to twinning on all the planes of (111) tetrahedra of the initial nuclei.

As the substrate temperature is raised to 180°C, the orientations on all the three substrates change over to a strong <100>, although perfect epitaxy is obtained on PbSO₄ doped substrates only (Fig. 9.6a). The weak spots and rings present in Figs. 9.4a and 9.5a indicate the existence of polycrystalline grains and some twinning.

On increasing the deposition rate to 20Å/sec., the films on the pure KBr becomes highly twinned. This is quite clear from the extending spots in the four directions from the primary spots which are due to twinning and double diffraction (commonly observed for f.c.c. metals on rock salt) (Hirsch et.al.¹⁸⁶). On AgSO₄ doped substrates, the orientation changes to predominantly <110> once again, parti-
cularly so on PbSO$_4$ doped crystal (Figs. 9.7, 9.8, 9.9).

9.3.2. Al films:

Figs. 9.10 to 9.17 show a series of electron micrographs of Al films of about 400Å thickness, deposited on to pure and Ag$_2$SO$_4$ doped crystals at substrate temperatures 100°C, 150°C, 180°C and 250°C. The average grain size of the films on doped substrates is larger at all stages of study. The crystallinity of the films on doped substrates continuously improves with temperature which is evident from the growing grains of uniform tint. At 250°C, the films on the doped substrates do not show any grainy structure. But the films develop a lot of unfilled channels, making it less continuous in contrast to the films on pure substrates. These observations are exactly similar to those made on Ag films at high temperatures. Such observations have been reported by Tokutaka and Prutton. Figs. 9.10a, 9.11a, 9.16a and 9.17a are selected area diffraction patterns of the regions shown in Figs. 9.10, 9.11, 9.16 and 9.17 respectively. At lower substrate temperatures (~100°C). The films on pure KBr remain purely polycrystalline, except that the rings are grainy, whereas in the case of films on doped substrates <100> and <111> preferential orientations co-exist. This is clear from Figs. 9.10a and 9.11a.

At 250°C, the films on pure substrates show archy patterns with a mixture of <100> and <111> orientations. But on the doped substrates, the films exhibit a perfect (100)
epitaxy (Fig. 9.17a). The very weak spots observed are nothing but from another \(<100>\) orientation rotated by an angle of \(30^\circ\). This is due to \((100)\) twinning which is rarely observed in f.c.c. metals.

Figs. 9.13a and 9.15a are electron diffraction patterns of Al films on the doped substrates at \(150^\circ\)C and \(190^\circ\)C respectively. As temperature is increased to \(150^\circ\)C, the diffraction pattern (Fig. 9.13a) shows an \(<100>\) orientation along with polycrystalline rings. At \(190^\circ\)C (Fig. 9.15a), the film exhibits a perfect \(<100>\) orientation as well as a \(<111>\) orientation. From a comparison of the Fig. 9.15a with the C.R.L.P. net work shown in Fig. 9.15b it is clear that the diffraction pattern consists of a \(<100>\) orientation and two \(<111>\) orientations, rotated with reference to each other by \(30^\circ\). This is characteristic of many f.c.c. deposits. Figs. 9.18 and 9.18a are the regions of the selected area diffraction patterns of Al films on PbSO\(_4\) doped substrates at \(190^\circ\)C. It is clear from the figures that the PbSO\(_4\) doped substrates also yield similar results on the Al films as the AgSO\(_4\) doped substrates. Fig. 9.19 is precision diffraction pattern of the film on AgSO\(_4\) doped substrate at \(200^\circ\)C showing a clear domination of \(<100>\) orientation.

Experiments repeated with similarly doped NaCl substrates lead to almost similar results except for some quantitative differences.
9.3.3. Discussions:

As mentioned above a tendency for $\langle 110 \rangle$ orientation is observed on all the substrates at a lower temperature for Ag. The films on the doped substrates are found to be less continuous in the sense that they are having lot of unfilled channels. At higher substrate temperatures, the orientation changes over to a $\langle 100 \rangle$ epitaxial, maximum perfection being achieved on PbSO$_4$ doped substrates. On increasing the evaporation rate, the orientation again changes to a predominant $\langle 110 \rangle$ on doped substrates and a highly twinned $\langle 100 \rangle$ orientation on pure KBr. At all temperatures studied, best orientation is observed on PbSO$_4$ doped substrates. This is clear from the sharper diffraction patterns found for films on PbSO$_4$ doped substrates.

For Al films also a similar phenomenon is observed. Initial $\langle 111 \rangle + \langle 100 \rangle$ mixed archy structure transforms into a pure $\langle 100 \rangle$ orientation on doped substrates. On pure substrates, the change in orientation is very less. The important observation for Al is the parallel epitaxy on doped substrates at 250°C, which is an impossibility on pure alkali-halide crystals. The change in the substrate surface energy can alone be responsible for this novel observation.

The discontinuities in both Ag and Al films on doped substrates also speak of the influence of doping on the growth of the films. In otherwords, the tendency for agglomeration in the films is more on the doped substrates. This agglome-
ration increases with temperature which is characteristic of all metal films as discussed in chapter two. As discussed in chapter five, the doping must be causing non-uniform distribution of nuclei over the substrate surface which ultimately leaves gaps in the films in the final stages of the growth. This is evident from the studies on thin films of Ag on doped substrates at elevated temperatures.

The variation in the orientation of the deposits with substrate temperature and deposition rate can best be explained on the basis of Walton\textsuperscript{75,76} theory of epitaxial nucleation, briefly discussed in chapter two. Pashley\textsuperscript{188} has also suggested that the orientation of vapour deposits is connected with nucleation i.e. the orientation of the nuclei is to be considered.

Let us consider the nucleation of metal deposits from vapour. It is possible to have such a low substrate temperature such that the critical nucleus is a single atom. This is the low temperature limit, since the nucleus cannot be smaller than an atom.

At sufficiently high super saturation (low substrate temperature or high super saturation) nucleation of the deposit consists of formation of pairs. That is, each time a pair is formed, it does not on the average dissociate. Thus it grows and eventually becomes part of the deposit. Since we have assumed a pair to be stable, each time a single
atom strikes the cluster, it is captured and added to the growing cluster. However this is in fact a random process. Therefore, the cluster would not be expected to grow with a single orientation. If super saturation is lowered, a stage will be reached when a single bond in the cluster will be unstable. At super saturation below this, a double bond may still be stable. Thus an atom which joins the cluster in such a way that it is attached to two other atoms will alone be stable. Therefore an oriented structure can now be formed. Thus a single bond leads to non oriented growth and a multiple bond stability leads to oriented growth. Thus epitaxial temperature is that at which a single bond is not stable for the given deposition rate. The epitaxial temperature is given by the relation

\[ T_1 = \frac{U_1 + Q_{\text{ad}}}{K \log (R \alpha^2 / \nu^2)} \]

where
- \( U_1 \) = energy of single bond,
- \( Q_{\text{ad}} \) = Binding energy of single atom to substrate
- \( R \) = rate of incidence
- \( \nu \) = Frequency of vibration of adsorbed atom
- \( \alpha \) = Distance between adsorption sites

In the situation corresponding to two bonds per atom, there is more than one way of forming stable clusters. When there are four atoms, a square array serves this purpose. This will lead to a (100) plane parallel to the substrate (for f.c.c. deposits).
If there are three atoms it can be a triangle structure which will lead to a (111) plane parallel to substrate. Similarly for higher index planes to be produced, the cluster must contain even more atoms for a minimum of two bonds per atom. However, the nucleation rate decreases with increasing cluster size (chapter 2). However, if all other factors are equal, the \langle 111 \rangle orientation should be produced since the rate of formation of triangular configuration is much higher than any other. However, if a cluster is adsorbed on a surface, some configurations may be adsorbed more strongly than others and the balance may be upset in favour of a cluster which will lead to another orientation. The four atoms in a square array may be more strongly adsorbed and a \langle 100 \rangle orientation would result instead of \langle 111 \rangle orientation. Nevertheless, the preference should be for low index planes. Mayer\(^{189}\) has shown that the order of preference for different orientation is \langle 111 \rangle, \langle 100 \rangle and \langle 110 \rangle. Therefore, orientation will be such that a close packed plane is parallel to substrate and of all the stable configurations at a given super saturation, the one containing fewer atoms and hence most numerous will be favoured. The effect of doping is probably to favour one configuration over other and to control azimuthal orientation. A \langle 100 \rangle transformation from a \langle 111 \rangle orientation at higher substrate temperature may be explained as follows:

As the super saturation is lowered, a time will come when a cluster with a minimum of two bonds per atom will no
longer be stable. The next most stable cluster will have three bonds per atom. One way to achieve this is through a triangular based pyramid (Fig. 9.20 (ii)). However, in forming this cluster, it is necessary to remove the top atom from the surface. Thus, if the adsorption energy is greater than the single bond energy, the pyramid will be less probable than the planar configuration (Fig. 9.20(i)) which correspond to only two bonds per atom. It is possible to achieve a minimum of three bonds per atom with the five atom cluster shown Fig. 9.20(iv). Here the binding energy of a single atom to the substrate can be greater than that of a single bond in the cluster and this configuration will still be favoured since, the top atom has four bonds. This configuration will lead to a <100> orientation parallel to the substrate. Thus, if the initial orientation is <111>, and if the binding energy is greater than the energy of a single bond, but less than that of a double bond, the orientation can be expected to change over to <100>, when the super saturation becomes so low that a minimum of three bonds per atom is essential. Thus a change over to a <100> orientation in both Ag and Al at high substrate temperature can be explained. In fact in the case of Al, on doped substrates, both <111> and<100> orientations occur (Fig. 9.15a) together at 190°C, which means that both types of critical nuclei are equally favoured. At 250°C, <100> orientation completely overtakes.
The recurrence of \( \langle 110 \rangle \) orientation at higher deposition rates (Figs. 9.8 and 9.9) in Ag films on doped substrates can again be due to the increase in super saturation which again affects the stability of the bonds, modifying the orientation of critical cluster. However, on the pure substrate the film remains to be \( \langle 100 \rangle \) oriented (Fig. 9.7). This again stresses the importance of the nature of the substrate in deciding orientation, though we had earlier stated that it would control azimuthal rotation of nuclei.

9.4. Observations on Gold films:

Figs. 9.21 and 9.21a are the electron micrographs and the selected area diffraction pattern of Au films deposited on \( \text{AgSO}_4 \) doped substrate at 250°C. The film thickness is about 300Å. Fig. 9.21b is a dark field micrograph with (200) reflection contributing for image formation. Fig. 9.22 and 9.22a are illustrations of Au films deposited on pure substrates under identical conditions. Figs. 9.23 and 9.24 are Au films 100Å thick deposited on \( \text{AuAgSO}_4 \) doped substrates respectively, at 250°C. A close examination of Figs. 9.21 and 9.22 show that agglomeration is more in the film on doped substrate. The film consists of islands where as the film on pure substrate is continuous except that there are small channels. Figs. 9.21a and 9.22a reveal a contradictory behaviour of doped substrates with reference to Au films. On pure substrate it
has a sharp $\langle 100 \rangle$ orientation, whereas on doped substrate it shows incomplete $\langle 100 \rangle$ epitaxy. Fig. 9.21b reveals the crystallinity of the islands. The imperfection of orientation may be due to the fact that the second stage of coalescence (chapter two) during which recrystallisation also takes place has not set in. If we take this into account, then we have to conclude that the orientation of Au films on doped substrates is not much different from the one on pure substrates. But the difference in the nucleation and growth stages persists, as revealed by Figs. 9.21 and 9.22. Further, Figs. 9.23 and 9.24, show that the film is again non-uniformly nucleated with a larger average nuclei size on the doped substrate in contrast to a uniform nucleation on pure substrate (Fig. 9.23). This is in accordance with the observation made for Ag films on doped substrates at room temperature (Patel and Mohana$^{190}$). Thus the results of Au films fall in agreement with Ag films as far as growth stages are concerned, but do not keep with the same trend when film orientation is considered. Thus the effect of dopant remains limited only to vary the nucleation modes.

9.5. Conclusions:

At elevated substrate temperature, Ag grows more epitaxially on PbSO$_4$ doped substrates compared to AgSO$_4$ doped substrate. The orientation changes over from $\langle 110 \rangle$ to $\langle 100 \rangle$ on increasing the temperature to 200°C and later
It grows with a $\langle 100 \rangle$ parallel orientation on AgSO$_4$ doped substrate at 250°C. The films on both the doped substrates tend to be less continuous.

The AgSO$_4$ doped substrates seem to be good for Al epitaxy, whereas for Ag, PbSO$_4$ doped substrates serve better at elevated temperature.

Though higher agglomeration is observed on doped substrates for Au films, no marked variation is found in orientation.

Though, doping of the substrate considerably influences epitaxy in the case of Ag and Al films, it does not show any such tendency for Au films.

A number of experiments need to be done before drawing any quantitative conclusion.