CHAPTER FIVE

Room temperature epitaxial growth of Ag on doped alkali halides.
INTRODUCTION:

The growth of thin metallic films on alkali halides in general and sodium chloride in particular by vacuum deposition, has been studied for a long time. Of these investigations, the oriented growth of a metal film on a substrate is of particular interest.

"Epitaxy" as it is known, is an important property of a thin solid film. The epitaxial nature of the film considerably influences its various properties. Right from the beginning, the field of thin film research has allotted a major portion of its space for the study of epitaxial films. The epitaxial study of thin film is in light not only due to its industrial usefulness, but also, for its understanding gives a new insight into the basic film growth processes.

Though high substrate temperature is a well known factor initiating epitaxy, attempts are being made to achieve lower epitaxial temperature, so that, the resulting film will be less fragile. Different investigators have reported, that under various growth conditions such films can be obtained at temperatures much lower than the usual epitaxial temperatures. Silver and Gold films have been the subject of such epitaxial studies of a number of investigators. Chopra \(^{114}\) has observed lowering of epitaxial temperature in vacuum deposited silver films by applying parallel electric field to the NaCl substrate. Ino et.al \(^{95}\)
have shown that by using vacuum cleaved NaCl substrate, epitaxial temperature comes down for a number of metals including silver and gold. Green et al.\textsuperscript{113} have observed that the presence of chlorine in minute quantity in the vacuum chamber enhances epitaxy in silver and gold films at room temperature. Sharma and Bahl\textsuperscript{167} have reported epitaxial growth of silver films on Cobalt doped NaCl substrates, contradicting the earlier reports of Toth and Cicotte\textsuperscript{168}. Distler et al.\textsuperscript{169} have carried out similar studies on silver and gold films grown on NaCl doped with a low concentration of PbCl\textsubscript{2}. They have reported that the electrical double layer formed on the substrate surface at the sites of inclusions enhances epitaxy. Stirland\textsuperscript{170} has shown the initiation of epitaxy in silver and gold films on electron irradiated crystals.

Of these, the favourable results on the doped crystal substrates seems to be interesting, because of simplicity. We have tried to investigate the role of dopants in enhancing epitaxy. In the following we describe the experiments done to grow silver films on doped NaCl and KBr substrate.

5.2. \textsc{experiment}:

Single crystals of sodium chloride doped with silver sulphate (2\% by weight) and also pure crystals were grown in the laboratory by the Bridgemann Stockbarger method using
Analar grade (BDH) NaCl. The dislocation density of the crystal was of the order of $10^6 \text{cm}^{-2}$.

Pure silver (99.99%) was evaporated from a molybdenum boat in the vacuum coating unit described in chapter 2, Fig. 4.1. at a pressure of $10^5 \text{torr}$ on to air cleaved faces of doped and undoped crystals kept side by side at a distance of 18cms from the source. The crystals were subjected to glow discharge cleaning prior to deposition. Films were grown, ranging from 30 to 250Å in thickness at room temperature (30°C). In all cases the evaporation rate was kept constant at 4Å/sec. In the case of very thin films (30Å), a carbon support film was deposited immediately after deposition of the silver film. Later the films were stripped off by gently dipping the substrates in distilled water. The films were then transferred to copper grids and studied in the electron microscope, Carl Zeiss Jena EF-4.

5.3. Results and discussion:

5.3(i) On doped NaCl substrates:

Figs. 5.1a and 5.1b show electron micrographs of silver films 30Å thick, deposited on to undoped and doped NaCl substrates, respectively. It is quite evident that there is uniform nucleation on the undoped crystal whereas nucleation has occurred at preferential sites on the doped one. It should also be noted that the nuclei on the doped
substrate appear to be bigger on average than those on the undoped substrate.

Electron micrographs of silver films 150Å thick, deposited on to undoped and doped substrates are shown in Figs. 5.2a and 5.2b, respectively. It is seen that coalescence of the nuclei appears to have occurred earlier in the case of the film grown on the doped substrate than for the film grown on the undoped substrate.

Figs. 5.3a and 5.3b show electron micrographs of films 250Å thick grown on undoped and doped substrates respectively. Attention is drawn to the fact that the film grown on the undoped substrate has a tendency to become continuous at a smaller thickness than that grown on the doped substrate. This may be due to the uniform nucleation on the undoped substrate. Also, the film seen in Fig.5.3a, which is on an undoped substrate, does not appear to have a uniform tint, suggesting that it consists of crystallites randomly oriented with respect to each other, whereas the film on the doped substrate has a uniform tint, indicating its mono oriented growth.

Films of different thickness have been studied and it has been observed that both series of films obey the mode of growth discussed by Pashley.

Birjega et al. have reported the epitaxial growth of gold films on Ag-doped NaCl crystals, electrolytically
coloured. They attributed the lowering of epitaxial temperature (200°C) for the (100) orientation of the gold films to the formation of Ag colloids, or to the defects or electrically heterogeneous surface created by these colloids, as reported by Distler et al.

In Distler's work the concentration of dopant was very low (7.5 x 10^{-3} mol %). In our work the concentration is as high as 2% (by weight). This may cause the dopant to concentrate in certain regions during the growth of the NaCl crystal and these sites may act as preferential sites for nucleation during deposition. Since the cleavage faces of pure and doped crystals responded in an identical way to etching, the nature and concentration of defects in the crystals may be conjectured to be the same. It therefore appears that the crystal defects have not played any role in differentiating the nucleation and growth of the film on the two types of substrates. Moreover there is little point in arguing that either dislocations or other lattice defects influence nucleation since there are no experimental proofs so far in this regard. Thus the only way out seems to hold the dopant, possibly nonuniformly distributed due to high concentration, responsible for the unusual deposition of the film or the doped crystal cleavages.

The electron diffraction patterns of the films were obtained by the usual selected area diffraction technique.
In the early stages of growth (30Å thickness) the film on the pure substrate gave rise to a ring pattern (Fig. 5.4a) indicating polycrystallinity, whereas the film on the doped substrate gave rise to a mixture of (100) and (111) preferential orientations (Fig. 5.4b), the former being predominant. In the case of a film 250Å thick grown on the undoped substrate the diffraction pattern consisted of sharp rings. However, the film grown on the doped substrate exhibited a (100) oriented spotty pattern (Fig. 5.4c). When the entire film was studied with a selected area aperture of 20μ, it was observed that about 80% of the film area exhibited a (100) oriented growth. In other regions either a (100) preferential orientation or a ring pattern was observed.

Figs. 5.5a and 5.5b indicate clearly that the growth on doped substrate proceeds with preferential deposition leading to clustering of nuclei whereas the nuclei are uniformly distributed over undoped substrates. Fig. 5.5c shows another case where selective deposition has lead to the growth of some islands faster than others. Fig. 5.6a is another striking illustration of selective deposition leading to nucleation free substrate regions surrounded by coalescing nuclei in contrast to the earlier observations (Fig. 5.5b). But in either case, the diffraction pattern obtained were essentially the same (Fig. 5.6b). Fig. 5.6c shows a dark field image formed with the (200) reflection which indicates that the crystallities are perfectly oriented.
5.3(ii) Results obtained on other substrates:

(a) AgSO₄ doped KBr substrates:

Doped KBr crystals were grown from the melt in an experimental set up similar to that used for the growth of doped NaCl crystals. The dopant concentration was maintained at 2% by weight. The films deposited on these substrates showed a similar tendency to form agglomerates. Fig. 5.7 shows such a case indicating highly selective nucleation and pronounced coalescence.

(b) BaBr₂ doped KBr substrates:

KBr crystals were grown from solution with a BaBr₂ dopant concentration of 2% by weight and used as substrates, the nucleation and growth on these substrates were confined to isolated star-like regions and coalescence was highly predominant (Fig. 5.8). It is probable that the dopant forms microcrystals, as suggested by Sharma et.al., which act as preferential nucleation sites. Further, the area of such preferential nucleation regions were very large compared to those observed on AgSO₄ doped crystals.

5.4. Contact angle considerations:

The peculiar growth of the film on the doped substrates and epitaxial enhancement in these films, as discussed earlier can be more clearly understood by considering the "contact angle" of the deposit nuclei on the doped substrate.
The contact angle of the nucleus with the substrate surface bears a considerable influence on the growth of the films. It depends on the interfacial energies of the vapour-condensate, condensate substrate system (as discussed in chapter 2) given by

\[ \sigma_{x-v} = \sigma_{c-x} + \sigma_{c-v} \cos \theta \]  

where \( \sigma_{x-v} \), \( \sigma_{c-x} \) and \( \sigma_{c-v} \) are energies of substrate-vapour, substrate-condensate, and condensate-vapour interfaces.

It can be seen that a change in the condensate substrate interfacial energy results in a change in the contact angle \( \theta \). As \( \theta \) decreases the catchment area of the nucleus becomes larger and hence the rate of growth will be faster leading to faster coalescence. It is observed that smaller the value of \( \theta \), better aligned will be the nuclei.

The growth of the nucleus takes place partly by the capture of atoms that diffuse across the substrate surface and strike its periphery and partly by the capture of atoms that land directly upon them. The relative importance of these two processes depends upon the fraction of the substrate surface covered by the deposit. The rate of growth by the capture of atoms at the periphery of a nucleus is proportional to its perimeter, and its growth rate by the impinging atoms is proportional to the solid angle it subtends at the source of film material. Thus, if we have--
a pair of nuclei of equal volume, but different contact angles, then, the one with the smaller contact angle will grow more rapidly. Fig. 5.9 shows how the growth rate is inversely proportional to the contact angle. As $\Theta_2 < \Theta_1$, $W_2 > W_1$ leads to faster growth by direct impingement and the periphery $2\pi r_2 > 2\pi r_1$, leads to faster growth by surface diffusion, thus making the nuclei of contact angle $\Theta_2$ grow faster.

Cabrera has treated the accommodation of misfit between a hemispherical nucleus and its substrate. He finds that the nucleus strains elastically to take up part of the lattice misfit between the condensate and the substrate. The magnitude of this strain is about 1% for a nucleus of 100Å diameter and is inversely proportional to the radius of the hemisphere.

According to capillarity theory of nucleation epitaxy will occur for that orientation which gives lower interfacial free-energy and hence a lower free energy of formation. Cabrera discusses interfacial energy using Frank and Vander Merwe's model and concludes that there will be a number of minimum free energy configurations corresponding to minimum number of misfit dislocations. These energy minima are cusps of various depths in the interfacial energy versus orientation relationship. All these arguments culminate into the fact that well alligned nuclei will have lower interfacial energy and hence a
smaller contact angle. Thus, smaller the value of $\theta$, better aligned will be the nuclei and faster will be their growth.

55. CONCLUSIONS:

It appears that nucleation on doped and undoped crystals takes place in a different manner. The dopant appears to become concentrated at certain regions in the parent crystal and these regions act as preferential sites for nucleation, whereas the nucleation is uniform on an undoped crystal.

It is observed that coalescence of nuclei occurs at an earlier stage on the doped crystal than on the pure crystal. A film 250Å thick grew as a $\langle 100 \rangle$ oriented monocristalline layer on the doped substrate but the film on the undoped crystal exhibited a ring pattern.

A $\langle 310 \rangle$ orientation, in the film grown on doped substrate is also observed, but very rarely.

Since the nuclei are non uniformly distributed, films on doped substrates tend to become continuous at a larger thickness, than those on undoped ones. This is because the distance between groups of nuclei is quite large compared with spaces between nuclei distributed uniformly on an undoped substrate.

It is likely that the change in surface energy at the
sites of dopant segregation is responsible for the better orientation and faster growth of nuclei at these sites, resulting in earlier coalescence and a monocrystalline film.