CHAPTER SEVEN

Annealing of Ag films deposited on pure and doped substrates
7.1. INTRODUCTION:

The growth, structure and physical properties of evaporated films have been and continue to be the subject of many recent investigations. All these investigations are leading to the same fact that structure of thin films is dependent on the conditions of formation and that the properties of thin films are influenced by their structural form. There has however been no comprehensive study of the effects of the formation conditions on the resultant film. If one can study these formation conditions and correlate them with the physical properties films of controlled characteristic can be prepared so that constant measurements may be made on various physical properties.

Though extensive work is done on these formation conditions in general, very little attention is paid to the thermal annealing of the films and preannealing of the substrates particularly. Bryne and Furubayashi et al. have observed little grain growth in annealed thin films. However, Mancini et al., Srivastava, Murr, and Singh et al. have shown grain growth and recrystallisation in metal films and rare earth oxides respectively. Also Mancini & Rimini have observed grain growth in annealed Ag and Au–Ag thin films deposited on amorphous substrates. Sloope and Tiller have studied the effect of preannealing of the alkalihalide substrate, on Ag films deposited upon them. They have also studied post annealing
effects on the deposited films. Johnson has studied post annealing of Ag films deposited on to NaCl cleavages.

In order to study the effect of similar treatments on Ag films deposited on pure and doped substrates, we carried out a number of experiments, the details of which are given below.

7.2. Experiment:

Pure silver (99.99%) was deposited on to pure, AgSO₄ doped and PbSO₄ doped NaCl crystals mounted in the substrate heater cum holder, mentioned in chapter 4, in high vacuum. In the same vacuum, they were annealed at different temperatures, for different intervals. The thickness of the film was kept constant in all the cases (≈450Å). The deposition rate was maintained at about 20Å/sec. Later the crystals were cooled to room temperature in the same vacuum.

In another set of experiments, the cleaved crystals placed in the substrate heater were annealed at different temperatures for different intervals in high vacuum. After cooling them to room temperature Ag was deposited on to them. Once again the film thickness (≈450Å) and the deposition rate (15Å/sec.) were kept constant in all the cases.

In the third set of experiments, the crystals were preannealed, silver was deposited and again they were annealed and cooled to room temperature.
The films were transferred to copper grids and observed in the electron microscope.

7.3. Observations and discussions:

7.3.1. Preannealing of the substrates:

Figs. 7.1, 7.1a and 7.2, 7.2a show the electron micrographs and selected area diffraction patterns of Ag films on pure and PbSO₄ doped substrates, preannealed to 120°C for one hour. It is evident that the grains are bigger on the doped substrates. Electron diffraction patterns show a higher degree of recrystallisation on the doped substrates.

Figs. 7.3, 7.3a and 7.4, 7.4a show the film regions and selected area diffraction patterns on pure and AgSO₄ doped substrates respectively, which are preannealed at 150°C for two hours. Once again better grain growth and orientation are observed in the films on doped substrates.

Figs. 7.5 and 7.6 show selected area diffraction patterns of the films on AgSO₄ doped and PbSO₄ doped substrates preannealed for three hours at 200°C, respectively. It is evident that 〈100〉 oriented growth is almost complete on both substrates. On pure substrates only a 〈100〉 preferential orientation was observed.

From these results it is clear that preannealing enhances epitaxy more strongly on doped substrates, at deposition rates as fast as 20Å/sec. in high vacuum.
This is in continuance of the trend for better epitaxy on doped substrates observed in chapters five and six. The preannealing of the substrates removes the adsorbed gas layer on the substrates, thus making the substrate surface forces more dominant on the depositing atoms. The cleaner the substrate surface, better oriented will be the film, as observed on vacuum cleaved substrates, by Ino et.al.\textsuperscript{95}. Thus the preannealing of the substrates, in a way, brings about the effect of vacuum cleaving.

The films on doped substrates (Figs. 7.2, 7.4) once again show a larger grain size, consistent with the observations made in chapter six.

Fig. 7.7 shows the electron micrograph of Ag film deposited on to AgSO\textsubscript{4} doped substrate preannealed at 300°C for 4 hours. It is clear that the film has preferentially deposited on square type-regions. It is possible that the substrate has selectively evaporated away leaving behind the rectangular hillocks on which the film has deposited. The film in between has lot of pinholes. The electron diffraction of the rectangular regions shows good epitaxy while as the area in between showed less oriented growth.

7.3.2. Post annealing of the films:

Figs. 7.8, 7.9 and 7.10 show electron micrographs and selected area diffraction patterns of the films deposited on (a) pure, (b) AgSO\textsubscript{4} doped and (c) PbSO\textsubscript{4} doped NaCl subs-
trates, annealed at 250°C for 15, 30 and 45 minutes respectively. Let us study the results one by one.

(a) Pure substrates:

As annealing time is increased, the orientation of the films improves from a spotty ring pattern (Fig. 7.8a) to a [100] preferred orientation (Fig. 7.9a). The grain size does not show much variation. With longer annealing the over growth shows a slight misorientation (Fig. 7.10a).

(b) AgSO$_4$ doped substrates:

In contrast to the films deposited on pure substrates a number of holes are present in the films deposited on AgSO$_4$ doped substrates. The orientation is improved from a [111] preferential (Fig. 7.8b) to a pure [100] orientation (Fig. 7.9b), when the annealing time is increased to 30 minutes. But the film has very big holes indicating a very high degree of agglomeration. With a higher annealing time (45 minutes), the films become lace like. The agglomerates are quite thick and the electron diffraction gives rise to non-uniform grainy rings (Fig. 7.10b).

(c) PbSO$_4$ doped substrates:

In this case also a similar trend is observed. Initially after a 15 minute annealing the films are having a [100] orientation (Fig. 7.8c) along with rings. With further annealing orientation is improved (Fig. 7.9c) with
less twinning and after 45 minutes annealing, the degree of orientation is considerably decreased (Fig. 7.10c) on increasing the duration of annealing to 60 minutes, the film on doped substrates became highly discontinuous (Fig. 7.11) and ultimately to isolated islands after 80 minutes annealing (Fig. 7.12). No electron diffraction was possible, because of the extraordinary thickness of the islands.

7.3.3. Prolonged annealing at low temperatures of thick films:

Prolonged annealing of thick films (600 Å) on doped substrates at 150°C for 120 minutes resulted in improved orientations. Figs. 7.13a and 7.13b show regions and selected area diffraction patterns of the films on AgSO₄ and PbSO₄ doped substrates respectively. A complete (100) epitaxy is achieved in the films on doped substrates. Once again it is seen that big holes appear in these films, though less numerous as observed earlier. The holes tend to have a regular geometric shape with edges parallel to each other. This suggests that they may be connected with the substrate surface directions. The films in between are continuous and very smooth.

As suggested by Johnson the difference in the thermal expansion of the film and the substrate (NaCl has greater thermal expansion) may be responsible for these parallel edged holes. The well-oriented silver film has the same orientation as NaCl and therefore lines of closest
packing are parallel to face diagonal of NaCl. These are the directions of greatest binding of silver atoms. During prolonged annealing, as a result of difference in thermal expansion, the films will break and this breaking will be along the line of closest packing, the process of failure will be one of shear. The surface tension forces further make the films contract. The holes were found to be somewhat parallel to \(\langle 110\rangle\) direction of the substrate, supporting the above argument. The failure to observe such holes in earlier cases for thinner films is due to the fact that surface tension forces which cause agglomeration are very large, dominating the differential thermal expansion effect.

Figs. 7.14a and 7.14b show electron micrographs and selected area diffraction pattern of the film annealed at 120°C for 3 hours on (a) AgSO\(_4\) doped and on (b) pure substrates respectively. It is found that the orientation improvement is achieved without much agglomeration as observed in all the previous cases (Fig. 7.9b, 7.13a, 7.13b). The orientation of the films on pure substrates also shows a good parallel epitaxy.

7.3.4. Very thin films:

Figs. 7.15 and 7.16 show the electron micrographs of very thin films (30Å) annealed for 10 minutes at 150°C on AgSO\(_4\) doped and pure substrates respectively. High agglomeration on doped substrates is quite evident from the micrographs. On further increasing the annealing time (40 min.),
agglomeration further increases in both the films (Figs. 7.17 and 7.18). The film on pure substrate shows $<100>$ preferred orientation (Fig. 7.17a), whereas the film on doped substrate shows $<100>$ orientation (Fig. 7.18a). Thus the tendency for better recrystallisation and agglomeration is observed on doped substrates in very thin films also.

7.4. Pre and post annealing:

When preannealing of the substrate was followed by annealing of the deposited film, the film was found to be of the best from both film continuity and orientation point of view. Fig. 7.19 and 7.19a show the region and selected area diff-pattern of the film deposited on to Ag$_2$O$_4$ doped substrate pre-annealed at 200°C for one hour and annealed after deposition at 150°C for one hour. Fig. 7.20 shows the film prepared in a similar way, on PbSO$_4$ doped substrate. It is observed that a $<211>$ orientation is also observed in these films rarely (Fig. 7.21).

Figs. 7.22 and 7.22a show the electron micrographs of Ag film deposited at 100°C on to Ag$_2$O$_4$ doped substrate and annealed at the same temperature for 60 minutes. Though the film is having typical channel structure, it is quite epitaxial.
7.5. Conclusions:

In the process of studying the effects of using doped substrates on the growth and orientation of the deposits and the influence of pre-annealing the substrate as well as the post annealing of the deposit-substrate composite, conditions have been arrived at for obtaining Ag films with the best orientation and surface structure under the given vacuum content. The results obtained indicate at the following implications:

(i) The use of doped substrates in place of pure substrates help in the improvement of the overgrowth orientation.

(ii) Pre-annealing of the substrates eliminates the effect of adsorbed air molecules which re-evaporate at a higher annealing temperature easily. Longer annealing times ensure the process of desorption and lead to a better substrate surface. Very high annealing temperatures result in the evaporation of the substrate surface thus affecting epitaxy and film morphology.

(iii) Post-annealing of the film-substrate composite, results in recrystallisation of the deposit. It has been observed that annealing at a lower temperature for a longer period gives a better results than the annealing at a higher temperature for a shorter period. At higher annealing temperatures agglomeration of the deposit will occur and longer annealing periods also increase agglomeration.