CHAPTER FOUR

Experimental techniques & apparatus
4.1. INTRODUCTION:

A brief description of the various apparatus and experimental techniques employed in the present investigation is given in this chapter.

4.2. Thin film preparation:

Thin films of the various materials investigated were prepared by vacuum deposition in a coating unit (Fig. 4.1) similar in design to the Edwards high vacuum coating unit, 12EA (Fig. 4.2), fabricated in our workshop with necessary alterations such as introduction of additional terminals in the base plate, facilitation for the introduction of substrate heater cum holder, etc. A vacuum of the order of $10^{-6}$ torr was obtained in a belljar of 30 cms. diameter and of same height with the help of a silicone oil diffusion pump backed by a rotary pump, capable of giving a $10^{-2}$ torr vacuum in the jar independently. $\text{P}_2\text{O}_5$ was used as a moisture absorbant, inside the jar. The vacuum was measured by means of Pirani and Penning gauges (Hind Hivac) at rough and high vacuums respectively. Molybdenum boat and tungsten helix were used as evaporation sources (Fig. 4.3).

4.3. Substrate heating:

The substrate heater is a stainless steel structure with holes carved out to accommodate the substrates. It is so designed that the substrates will remain at the centre...
of the heater cum holder and will be heated from all sides to ensure uniform temperature throughout the substrate dimension. This is found to be more efficient than the one used by Patel and Das\textsuperscript{158} in which the substrate holder and heater were separate, placed one above the other. Arrangement was also made to accommodate a thermocouple (Cu-Constantan or Pt-Pt/Rh 10\%) so as to measure the substrate temperature accurately. The thermocouple function was fused into a dummy NaCl crystal which was kept at the centre of the heater. Figs. 4.4 and 4.5 show the side view of the heater and the schematic diagram of the inside where crystals are mounted for deposition. The thermocouple and the heater were connected to a microvoltmeter and a variac respectively. The thermocouple was calibrated with a mercury thermometer in high vacuum. After each run the crystal holder was thoroughly cleaned and dried.

4.3.1. Thickness measurement:

The thickness of the film was measured using the well known multiple beam interferometry technique of Tolansky the salient features of the technique are briefly described.

4.4.1. Silvering technique:

The thin film surfaces under study and the optical flats are to be coated with a highly reflecting layer of
silver for interferometric measurements of film thickness. For this purpose Edwards coating unit 12EA, mentioned earlier was used. The optical flats which were thoroughly cleaned with chromic acid, soap-solution and distilled water and subjected to breath test were used. They were further cleansed by ionic glow discharge inside the chamber. Spec. pure silver was used for deposition.

4.4.2. Multiple beam interferometry:

Multiple beam interferometry, a very sensitive technique for the topographical studies, was first developed by Tolanky\textsuperscript{159,160,169} and his coworkers. It combines microscopy with the testing of optical flats: a small reference flat is placed over the surface to be tested and the fringes are viewed with a microscope. If the surface studied is of an opaque specimen, as is the case for metal films, it is necessary to observe the fringes in reflection. In this case the silvering of the flat is more critical as any absorption in the silver reduces the visibility of the fringes.

Since multiple beam interferometry is quite a well established technique, only those points which have a special bearing on the investigation of crystal surfaces and thickness measurements are briefly discussed here.

When the two component surfaces of an interferometer (Fig. 4.6) are parallel to each other at a distance $t$ and
have transmission and reflection coefficients \( T \) and \( R \) respectively, the summation of the transmitted series of multiple reflected beams gives the intensity distribution,

\[
I_{\text{max}} = T^2(1 - R^2) \text{ at } n = 2t \cos \theta, \text{ and,}
\]

\[
I_{\text{min}} = T^2(1 + R^2) \text{ at } (n + 1/2) = 2t \cos \theta.
\]

If there is no absorption, \( R + T = 1 \) by definition. The fringe peak maxima without absorption have, then, the same intensity as that of the incident light. Therefore, the fringe shape is independent of \( T \) and is determined only by the reflectivity, \( R \). Even if we take into account the absorption, it can be seen that absorption merely influences the total intensity and not its shape. The optical arrangement of Fizeau fringes in the reflected system is shown in Fig. 4.7.

4.4.2.a. Optimum conditions:

The optimum conditions are those which lead to the production of the sharpest possible fringes with a reasonably good contrast. The contrast may be defined by the term \((I_{\text{max}} - I_{\text{min}})\) and the sharpness in terms of fringe half width, \( \delta \), which is given by the relation (Tolansky loc.cit) \( \delta = (1 - R)/R \) where \( R \) is the geometric mean, \( \sqrt{R_1 R_2} \) where \( R_1, R_2 \) are the reflectivities of two surfaces. \( \delta \) is a minimum when \( R \) is maximum. To achieve a maximum value of \( R \), it is essential to reduce the absorption coefficient as much as possible. The contrast or the visibility of the fringes also depends on absorption—
especially in the reflected system.

Although, Fabry and Perot\textsuperscript{162} used thin wedge silvered on both sides to produce sharp Fizeau fringes, Tolansky (loc.cit) was the first who investigated the critical conditions to be fulfilled for a doubly silvered wedge, so that a close approximation to the Airy\textsuperscript{163} summation can be achieved. He has formulated the following conditions:

(i) The surface must be coated with a highly reflecting film with minimum absorption.

(ii) The film should contour the surfaces exactly and be highly uniform in thickness.

(iii) Monochromatic light or at least a few widely separated or spaced monochromatic wave lengths must be used.

(iv) The interfering surfaces should be separated at the most, by a few wavelengths of light only.

(v) A parallel beam within 1-3° tolerance should be used.

(vi) The incidence should be preferably normal.

4.4.2.(b) Evaluation of step height:

Comparatively large step heights (100Å° or more) can be determined by the shift in the Fizeau fringes at
the steps. If 'S' is the shift of the fringes (Fig. 4.8) and X is the order separation (the distance between successive fringes) then the fraction of an order of the displaced fringes, \( dn = \frac{S}{X} \). The value of \( dn \) gives the height of the step, \( h \), as a function of \( \frac{\lambda}{2} \) as \( h = \left( \frac{\lambda}{2} \right) dn \). The shift and the order separation are always taken in a direction perpendicular to the fringes.

4.4.3. Determination of film thickness:

For the purpose of thickness determination of thin films by the above mentioned multiple beam interferometric technique, a dummy glass substrate (thoroughly cleaned) was introduced in the film preparation unit along with the NaCl substrates, such that the film of the material under investigation also formed on part of the dummy substrate. Well-defined edge of the film on the dummy glass substrate, necessary for obtaining an accurate value of the thickness by multiple beam interferometry, was obtained by introducing the sharp edge of a razor blade close to the glass substrate in the path of the beam of evaporating atoms of the material. On this dummy glass substrate, which was partly covered by the thin film of the material under investigation, a moderately thick layer of Ag was deposited such that the silver films covered the two sides of the step formed. An optical flat, which was thoroughly cleaned was also lightly silvered such that the thickness of the silver film was optimum. The step
height was now measured by obtaining an interferogram due to the silvered faces and measuring the shift and the order separation by means of a micrometer eyepiece. The monochromatic light used was Hg - green light of wave length 5461 Å. The measurements were made on the Vicker's projection microscope (Fig. 4.9) which is an inverted metallurgical microscope where the specimen to be studied is placed on a movable stage above the objective lens. The illuminating system which can be shifted from reflecting to transmitting settings, consists of a powerful mercury lamp, pointolite or carbon arc lamp, a condenser and an aperture, controlled by an iris diaphragm. The image can be focussed on the projection screen for photographic purposes.

4.5. Mounting the film for electron microscopic study:

The films formed on alkali-halide substrates could be easily detached by slowly dipping at an angle the film deposited surface of the crystal into double distilled water taken in a petridish. However, in the case of annealed films, the film was too much sticky to the crystal surface and hence the crystal was thinned by cleaving and floated on the water. The film would be free once the crystal is completely dissolved. The floating films were transferred on to copper grids and were dried before examination in the microscope.

In the case of very thin films and films with high
agglomeration (grown at high substrate temperature or annealed films), it was necessary to coat a thin film of carbon on to them to avoid collapsing when taken on the grids. Deposition of such carbon backing film was carried out using carbon arc deposition technique in Carl Zeiss Jena HBA/2 coating unit shown in Fig. 4.10 whose working principle is the same as that of the coating units mentioned earlier.

4.6. Examination of the film:

The films were examined in the electron optical plant EF-4 (Fig. 4.11) of Carl Zeiss Jena, West Germany. This plant is specially adopted for transmission reflection and emission microscopy (using bright field, dark field and stero transmission microscopy) as well as for electron diffraction employing various beam paths.

Fig. 4.12 shows the electron optical system of the microscope (using magnetic lenses) along with the microscope column. Electrons emitted from the tip of a hot tungsten filament (shaped like a hairpin) are accelerated towards the anode and focussed by a negative bias on the surrounding shield (Wehnelt cylinder to form a cross over at some distance below. In order to control the intensity of illumination and the aperture of illumination at the object, two condenser lenses have been used. The first condenser is used to produce a reduced
image of the source, the second is adjusted to give proper intensity of illumination.

The objects to be studied are inserted in front of the objective lens and can be displaced into two perpendicular directions to the optic axis and can also be tilted by ± 10° from the normal incident beam. The image formed by the objective lens is remagnified by the intermediate and the projective lenses to produce a final image on a fluorescent screen which can be observed at a higher magnification by means of an optical microscope. The lens system of the microscope also contains the contrast and the range diaphragms with the mechanisms for shifting and disengaging them.

The final image formed on the screen can be photographed by lifting the screen from the beam path manually. The photographic plate chamber consists of a magazine holding six photographic plates (6.5 cm x 9.0 cm) which can be exposed in any adjustable plate size during operation.

Besides the highly stabilized power supply being given out in three steps of 35kV, 50kV and 65kV, the plant consists of a pumping system for maintaining a vacuum of about 10⁻⁵torr. The practical resolving power and the maximum useful magnification available with the equipment are about 20Å° and 52,000X respectively.
4.6.1. Electron Microscopy:

Fig. 4.13 shows the schematic diagram of ray paths in a microscope employing three stages of magnification and a single condenser lens system for illuminating the specimen. The magnified image $I_1$ (Fig. 4.13a) produced by the objective is called the first intermediate. This serves as an object for the intermediate image, $I_2$, and this is magnified further by the projector lens to produce the final image on the fluorescent viewing screen.

4.7.1(a). Image formation and contrast:

Fig. 4.14 illustrates the mechanism of production of contrast on transmission micrographs. The almost parallel illuminating beam of electrons is scattered by the specimen. In the case of crystalline materials this scattering takes the form of one or more Bragg diffracted beams travelling at small angles (1 or 2 degrees) which are focussed by the objective to form a transmission diffraction pattern in its back focal plane. As in the work with metal foils the lowest order Bragg reflections encountered correspond to lattice spacing of about $2\text{Å}$ and so make the direct resolution of the lattice difficult because of spherical aberration of the objective lens and other defects. The image contrast in the micrographs is achieved by a mechanism described below which does not aim at the resolution of the atomic structure.
4.7.1(b). **Bright field image or diffraction contrast:**

This type of contrast is achieved by inserting an aperture - called the objective aperture - in the objective focal plane as shown in Fig. 4.15. This aperture prevents the diffracted beams from contributing to the final image which is therefore formed by the direct beam and any low angle inelastic scattering. The contrast is therefore produced by differences in intensities of electrons scattered into Bragg reflections from various parts of the specimen and is hence called "diffraction contrast".

**Dark field image:** If the objective aperture is displaced from its axial position, the central undeviated beam of electrons is intercepted by the aperture and a so called dark field image of the specimen can be obtained with the scattered electron beams which pass through the displaced aperture. The generally scattered beams will have lost energy in the scattering process, and hence, the image obtained is of poor quality because of the chromatic aberration of the objective lens.

When the specimen is crystalline, the objective aperture can be displaced so that an elastically scattered diffracted beam passes through the objective aperture to form a dark field image and, in this case there will be little energy loss and hence, the chromatic aberration effects will be much less. However, because of extra axial lens aberration effects, the quality of the image
will be poor.

The dark field imaging method applied to crystalline specimens is potentially powerful, because only those parts of the crystal giving rise to the selected reflection will appear with bright contrast in the image, and a close correlation can therefore be made between features on the specimen and corresponding effects on the diffraction pattern.

4.7.2. Electron diffraction:

4.7.2(a). Selected area diffraction:

A particular advantage of the selected area technique is that diffraction pattern from any selected region of the specimen can be obtained. Thus the identification or orientation determination of a small localised feature can be attempted. It is also very useful for identifying phases in an inhomogeneous specimen. However, the technique is subject to some errors - both systematic & random. This technique was first developed by Le Poole and the correct operational procedures can be found in the papers by Agar and Philips.

Under microscopy conditions, the intermediate plus projector system is focussed on the I₁ (first intermediate image) plane, and hence, produces a magnified image of this plane on the final screen. By reducing the strength
of the intermediate lens so that, the back focal plane of the objective is focussed on the final screen, transmission electron diffraction pattern of the illuminated area of the specimen can be obtained. If an aperture of diameter 'D' is placed in the I₁ plane and if the objective lens behaves as a perfect lens, only those electrons passing through an area of diameter \( \frac{D}{M} \) on the specimen will reach the final screen, here \( M \) is the magnification of the objective. Thus, diffraction from a limited area of the specimen — selected area diffraction — can be obtained.

To ensure that the diffraction pattern arises only from material within the aperture area, the correct operating procedure mentioned below must be followed:

(i) The intermediate lens excitation is first adjusted so that the selector aperture is in focus on the final screen.

(ii) The objective lens excitation is then adjusted so that the specimen is in focus. By doing so the image of the specimen is brought to the same plane as the intermediate aperture, and hence, the demagnified image of the latter will be in the plane of the specimen. (This is the correct setting for objective lens for diffraction).

(iii) The second condenser lens is then defocussed to obtain near-parallel illumination of the specimen.
(iv) Lastly, the excitation of intermediate lens is reduced so that the back focal plane of the objective lens is in focus on the final screen. (This position can be judged by making the central spot from the undeviated beam at small and round as possible).

These operations result in a correct setting for taking the selected area diffraction patterns. Fig. 4.13b shows the ray-paths through the lenses of a three stage microscope for the selected area diffraction condition.

4.7.2(b). General area or precision diffraction:

For precision diffraction patterns the specimen can either be mounted in the normal (microscopy) position (if the pole pieces have wide bores) or in a position immediately below the final projector lens. The latter method, which is generally used, has the advantage that the electron source can be greatly demagnified by all the imaging lenses so that exceedingly high resolving powers up to $10^4$ could be achieved, and the camera length, $L$, though short, can be accurately reproduced. In the former case all the imaging lenses have to be switched off and focussing of the electron source has to be done only by the condenser lenses. However, the objective lens can be used to form a low-magnification image of the specimen on the final screen without changing the condenser excitation thus enabling a rough estimate of the area contributing to the general diffraction pattern observed.
4.7.2(c). Reflection diffraction:

Reflection diffraction patterns can be obtained most conveniently by mounting the specimen on a diffraction stage beneath the final projector lens. Relatively, large specimens can be accommodated and the procedure is generally similar to that used in normal diffraction. It is to be noted that only a few top layers of the specimen contribute to the diffraction pattern and the camera length is subject to a considerable variation on account of the large thickness of the specimen in the direction of the beam, so that the resolving power is low. Reflection diffraction patterns can also be obtained by mounting the specimen in the normal (microscopy) position.