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IN SITU ULTRA HIGH VACUUM HIGH ENERGY
ELECTRON DIFFRACTION STUDIES

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Office of Sponsored Programs
Department of Chemical Engineering and Materials Science

Approved by:

Richard W. Vook
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I. INTRODUCTION

This project was initiated on June 1, 1966 and terminated on August 31, 1972. In that time a very sophisticated piece of research equipment was designed and constructed, an ultra high vacuum reflection high energy electron diffraction (UHV-RHEED) instrument. A total of twelve publications have been published or are expected to be published as a result of our work. Three students who worked on this project received M.S. degrees while a fourth student (part-time) is expected to receive his M.S. degree next January. One Ph.D. was produced. Two other students who have also worked on this project are expected to receive Ph.D.'s during the next two years. Thus the graduate education of seven students was facilitated by this research program.

The actual research results in terms of Master's Theses, Ph.D. Dissertations, Publications, and Talks are listed in a later section. Reprints of journal articles that have already been published have been sent to the AEC. The bulk of this report consists of research that has not been published yet, but has been either submitted for publication or is being prepared for publication. In addition, the first section, Section II, taken from F. A. Koch's Ph.D. Dissertation, describes the UHV-RHEED apparatus.

Publication number 12 in the list at the end of this report is being written at the present time. This article will review methods used for the microstructural characterization of thin films, using a

pedagogical point of view aimed at graduate students and scientists not directly involved in the field. An outline is given in Chapter VIII of this report.

II INSTRUMENTAL

II.1 Introduction:

Among the many techniques¹³ used to study surfaces and surface phenomena, the method of electron diffraction is especially well suited because of its relatively high sensitivity.¹⁴ Low and high energy electron diffraction, abbreviated as LEED and HEED respectively, are extensively used in surface research. In the LEED technique a collimated beam of electrons having energies of less than 1000 eV is backscattered from the face of the specimen. After passing through a set of suppressor and accelerating grids, the backscattered electrons strike a fluorescent screen and the resulting pattern is recorded. In the HEED technique, high energy electrons (10 to 100 keV or higher) are used in either the transmission (T mode) or the reflection mode (R mode). In the T mode the incident electrons penetrate the specimen and/or asperities on the surface of the specimen and the forward scattered electrons are recorded. The R mode is realized if the specimen surface is smooth enough so that the incident and scattered electrons enter and leave the specimen through the same surface. The scattered electrons are then displayed on the fluorescent screen. In both LEED and HEED studies, several authors have made use of Faraday cages to measure the intensities of the diffracted beams.

A critical discussion of LEED and RHEED was the subject of a recent review.¹⁴ It may perhaps be useful to emphasize that several authors^{15,16,17} have demonstrated the capability of RHEED to detect fractions of monolayers.

In section II.2, the UHV-RHEED camera constructed in our laboratory will be described. Special attention is given to the pumpdown procedure, the elec-

tron optics, the specimen manipulator, and extra components constructed, described in sections II.3, II.4, II.5, and II.6 respectively.

II.2 The UHV-RHEED camera:

In his masters thesis Mr. R. Portanova described¹⁸ the construction of the camera. Some improvements to the instrument were reported by Mr. M. Bujor.¹⁹ In order to achieve a higher pumping speed and to adapt the instrument to the experiments described in this report, it was convenient to rearrange the pumping system and to add several components to the camera.

An overall view of the camera is shown in Fig. 1. A schematic diagram showing some of the inner components is given in Fig. 2. The main components shown in Figs. 1 and 2 are: the pumping system P, the specimen manipulator M, the fluorescent screen F, the vapor source chamber V, the electron gun G, and the two beam limiting apertures A_1 and A_2 . The nude Bayard-Alpert vacuum gauge and quadrupole mass analyzer are indicated by RGA in Fig. 1. The system is supported on a table constructed from marenite sheet and slotted aluminum angle.

Standard UHV techniques were followed throughout the construction of the camera. Except for the glass components of the electron gun, the observation windows, and the fluorescent screen, the entire system was constructed from type 304 stainless steel and other UHV materials. All flanges are sealed by Cu or Au gaskets and the complete system is bakeable to 450°C . In practice the bake-out temperature was never allowed to exceed 250°C in order to increase the expected life of the components subjected to thermal cycling.

The pumping system consists of an 80 l/sec. ion pump, a 350 l/sec. watercooled Titanium sublimation pump (TSP), and two liquid nitrogen cooled

FIG. 1 THE UHV RHEED CAMERA.

FIG. 2 SCHEMATIC OF THE UHV RHEED CAMERA.

sorption pumps. The sorption pumps can be sealed off from each other by means of a neoprene gasket valve and both are isolated from the UHV section with an all metal UHV valve.

II.3 The pumpdown procedure:

Fast pumpdown to pressures of order 10^{-4} Torr was achieved by using a method due to Stern and DiPaola.²⁰ These authors suggested that cryosorption pumps should be used consecutively rather than simultaneously. When a vacuum system containing air at atmospheric pressure is opened to a sorption pump, the gases will start to flow towards the pump in a viscous manner. During the stage of viscous flow all the different types of gases flow into the pump. The gas composition in the system should not differ appreciably from the gas composition in air. However, He, Ne, and H_2 are not adsorbed on the refrigerated surfaces²⁰ and the gas composition inside the pump should become enriched in these three gases. If the residual gas pressure in the vacuum chamber is reduced, the gas molecules collide less often with each other. As a result appreciable amounts of He, Ne, and H_2 will be diffusing back into the system and the atmosphere of the vacuum system will become enriched by these three gases. This enrichment is undesirable and may be avoided by trapping the He, Ne, and H_2 gases in the sorption pump i.e. by simply isolating the sorption pump from the system before appreciable back diffusion occurred. gases. The optimum stage for isolation is found from a consideration of the ratio of the mean free path length (L) of the gas and the inner diameter (a) of the tube connecting the sorption pumps to the system. This ratio, the so called Knudsen number (K), is said to have a value of 0.01 at the lower limit of

viscous gas flow.²¹ The equipment used by Stern and DiPaola had an $a=2.54$ cm. At 25°C and a pressure of 20 Torr, $L \sim 2.5 \times 10^{-2}$ cm. and $K \sim 0.01$ cm.²¹ Experimentally, Stern and DiPaola found that an isolation pressure as low as 1 Torr was still sufficient to give rapid pumpdown. In our system $a=2.54$ cm. as well. Therefore the first sorption pump was isolated at a pressure of order 1 Torr. The second sorption pump was then opened; and it reduced the pressure of the system to 10^{-4} Torr, the starting pressure of the ion pump. Since the ion pump has a relatively low pumping rate for He, the manner of pumping described above resulted in a faster pumpdown rate in the UHV range as well.

At a pressure of order 10^{-4} Torr, the ion pump was started and the second sorption pump was isolated from the vacuum system. The system was allowed to pump overnight and a pressure of 2 to 5×10^{-8} Torr was attained after 5 to 8 hours of pumping. A 24 hour bake-out followed during which the pressure gauge, the evaporator, and the substrate holder were outgassed. By slowly increasing the bake-out temperature to 250°C , the pressure in the system could be kept in the 1 to 5×10^{-6} Torr range throughout the baking process.

At the end of the bake-out process and with the system pumped for an additional 10 to 12 hours at room temperature, a pressure in the 2 to 8×10^{-10} Torr range could be maintained. Bake-out of the specimen holder and evaporator was considered complete if subsequent heating of these components to 400 and about 2000°C respectively did not cause the background pressure to increase above 2×10^{-9} Torr.

The residual gas spectra of the atmosphere inside the system are shown in Figs. 3a and 3b. Fig. 3a was obtained before baking at a pressure of

FIG. 3. RESIDUAL GAS SPECTRA BEFORE AND AFTER BAKING.

2×10^{-8} Torr. Fig. 3b was obtained after bake-out and at a pressure of 6×10^{-10} Torr. Figs. 3a and 3b were obtained with a Varian quadrupole residual gas analyzer. The mass number m/e , characteristic of the gas which is ionized, is plotted along the abscissa. The ion current, detected with a Faraday cup and measured with a Keithley picoammeter, is plotted along the ordinate. From Figs. 3a and 3b one may find the main residual gas components present in the atmosphere of the vacuum system. The results are listed in Table I.

TABLE I

Residual Gas Analysis

Approximate mass number	m/e	Molecular species	Relative abundance (% of total)	
			Before baking	After baking
16		O_2^{++}	3	15
17		OH^+	9	5
18		HOH^+	36	9
28		CO^+, N_2^+	14	46
44		CO_2^+	17	15

Fig. 3a shows minor peaks in addition to those listed in Table I. Some of the molecular species which may contribute to these peaks are indicated in Fig. 3a. The results given above are qualitative i.e. the ionization probabilities of the various gasses were not taken into account.

II.4 The electron optics:

A block diagram of the electron gun power supply is given in Fig. 4. The battery for the filament current supply and the grid biasing circuit were housed in a box constructed from 1/2" thick plexiglass. This box is indicated by the dashed lines in Fig. 4. To prevent occurrence of electrical discharges between connecting points in the biasing circuit and ground, the biasing circuit was placed in a bath of transformer oil. Remote control of the filament current and bias voltage were made possible by connecting insulated gear drives to the rheostat R_1 and switch S_1 . These gears were manually operated via plexiglass rods. The high voltage and filament current were connected to the electron gun by means of an electron microscope (100 kV) cable.

A schematic diagram of the electron optical system is given in Fig. 5. Electrons emitted by a hot tungsten filament W, are accelerated to ground by a negative high voltage of up to 60 kV. They pass through two moveable water-cooled Mo apertures and strike the specimen at a glancing angle. The resulting pattern was observed on the fluorescent screen* and photographed with a portrait camera on 4x5 inch sheet film. A 35 mm. slide camera was used when high speed recording of the diffraction patterns was more desirable than the higher resolution afforded by the 4x5 inch negatives.

Initially an electron gun purchased from JEOLCO Inc. was used.¹⁸ That electron gun was identical to the guns used in the JEM-7A electron microscope. However, it was found that the body of this gun was manufactured from Ni coated

*For processing see Appendix.

FIG. 4 BLOCK DIAGRAM OF ELECTRON GUN POWER SUPPLY.

FIG.5 THE ELECTRON OPTICAL SYSTEM

brass and thus was not suitable for use in UHV. Another gun body was constructed from type 304 stainless steel. Two 3/8" holes were drilled in this gun to prevent virtual leaks from the filament cavity.

A Mo aperture, A_3 , was inserted between the two beam limiting apertures, A_1 and A_2 , to prevent illumination of the fluorescent screen by light generated by the hot filament. The set of electromagnetic solenoids* shown in Fig. 5 was used to deflect the electron beam during alignment of the electron optics. These solenoids were energized by two independent power supplies.** The outputs of these supplies were regulated to 0.01%. The solenoids were found to be useful in correcting for small deviations from correct alignment of the electron beam.

Alignment of the electron optics was achieved by retracting apertures A_1 and A_2 and observing the full beam on the fluorescent screen. Care was taken at this stage to keep the accelerating voltage below 20 kV in order to avoid burning of the fluorescent material or cracking of the glass screen by local overheating. The filament current and bias voltage were then adjusted to obtain a high intensity beam of about 1/3 cm. in diameter. The beam was then centered with the deflection coils. Next, the rear aperture A_2 was inserted and adjusted to transmit the highest intensity portion of the beam. Finally, the 50 micron front aperture was aligned to maximize the beam intensity.

At 60 kV accelerating voltage the total beam current was about 1 ma

*Phillips Advance Control Company, Joliet, Illinois. Catalogue # 39C11560-AX.

**KINTEL model 50B-50 power supply; Lambda model C280 power supply.

under optimum conditions. The final beam current falling on the specimen was about 1 μ a. A selfbias resistance (R_1) of 0.05 to 1.17 megaohm was used. See Fig. 4. The focussing action of the bias voltage on the electron beam was studied in detail by Haine and Einstein.²² The gun used in the present camera gave a total beam with a spot size of 1/3 to 1/4 cm^2 . The high energy density of the beam caused a heat dissipation problem. For example, in an earlier version of the camera a 1/4" thick stainless steel (SS) plate was used to support the front Mo aperture A_1 . This SS plate became red hot after prolonged exposure to the electron beam. The resulting outgassing of the SS plate caused an increase of the background pressure from 10^{-10} Torr to the high 10^{-7} Torr range. Heating of the Mo aperture support was prevented by attaching the front beam limiting aperture to a watercooled support. The rear aperture was replaced by a watercooled aperture as well. The two watercooled apertures were machined from type 304 stainless steel. The design permitted a continuous flow of cold water through the aperture supports, see Fig. 5. The SS supports were prevented from melting by protecting them with 0.020 inch Mo sheets. The Mo sheets were pressed against the watercooled supports by means of SS screws. The approach described above was only partially successful and the pressure during electron irradiation still increased to 5 to 8×10^{-8} Torr at full beam current for a 60 kV accelerating voltage. During deposition of the films the pressure was kept between 0.6 to 9×10^{-9} Torr. The relatively high pressure during electron diffraction thus limited the instrument to in situ RHEED examinations of UHV deposits only after completion of growth. However, recent changes in the camera were made by C.T. Horng²³ and a pressure of 1 to 3×10^{-8} Torr can now be

maintained during RHEED examinations.

II.5 Specimen manipulator and connecting piece:

In order to scan the reciprocal lattice during RHEED examinations it is necessary to manipulate the specimen in situ. A bakeable UHV manipulator was manufactured by Cooke Vacuum Products and improved by the author for this purpose. A sectional view of the manipulator is shown in Fig. 6.

The specimen was attached to the stainless steel rod R shown in Fig. 6. The specimen manipulator provides three motions to the specimen. These motions are:

- 1) 360° rotation around rod R,
- 2) a translation of 5 cm. along R, and
- 3) a tilting of $\pm 6^\circ$ of rod R about an axis perpendicular to the paper in Fig. 6.

These motions were made possible through the use of a set of thin walled stainless steel bellows. The graduated disc on top of the manipulator was used to record the azimuthal orientation of the specimen during rotation. Rod R was connected via a rotary electrical couple, to the specimen heater. This rotary couple is described in section II.6 i.

Power feedthroughs to the specimen heater were supplied by an extension to the specimen manipulator, which is also shown in Fig. 6. The extension piece contained six electrical feedthroughs, two each for the heater and thermocouple, one for the thickness monitor (section II.6 v), and one extra for possible future use. Provision was also made in the extension piece for two liquid feedthroughs for use in cooling the crystal thickness monitor.

FIG. 6 SPECIMEN MANIPULATOR AND EXTENSION PIECE.

II.6 Other components:

In order to perform the experiments described in this report it was necessary to construct various extra attachments and devices to the camera. These components are described in this section.

II.6 i Rotatable electrical couple:

A couple between electrical feedthroughs inside the UHV chamber and the specimen was developed. This device allows unlimited positive and negative rotation of the specimen heater about an axis. Its main virtue is that it avoids twisting of the electrical leads regardless of the amount of rotation. Several units may be stacked on top of each other so that in principle a large number of electrical connections may be maintained. The construction of this device was reported earlier²⁴ and it operates on a principle similar to that of a more recently reported couple.²⁵

A scale diagram of the device and one particular specimen heater is shown in Fig. 7. The specimen holder consisted of an OFHC Cu block and Mo clamps for a flat specimen. A Ta heating element was pressed to the Cu block by means of an OFHC Cu plate C. The specimen holder was attached to the electrical couple via a thin walled stainless steel (SS) tube having low thermal conductivity.

The actual electrical couple was a compound body consisting of two SS ball bearings, other SS machined parts, and mica spacers. The various components were held together by the SS screw S. The ball bearings are electrically insulated from each other as well as from A, B, and S, by means of mica spacers and Al_2O_3 tubing.

FIG. 7 ROTATABLE ELECTRICAL COUPLE AND SPECIMEN HOLDER

The outer races J of each bearing were rigidly attached with ring clamps and heavy Cu wire (not shown), to current feedthroughs in the vacuum chamber. The inner races, I_1 and I_2 , of each bearing made electrical contact with SS discs D_1 and D_2 respectively. These discs were then connected to the heater element with partially threaded 1.6 mm. diameter SS wire. The upper disc D_1 was slotted so that it did not touch the SS wire making connection with D_2 . Fixture B was attached, via SS rod R, to the specimen manipulator described in II.5. Thus by rotating R, the outer races J of each bearing remained stationary while the rest of the device was free to rotate and electrical current was conducted via the bearings to the heating element.

Many pumpout holes P were provided to eliminate virtual leaks from the screw holes and cavities in the fixture.

This device has been used repeatedly and satisfactorily for the past three years to conduct an alternating current of 8 amperes in UHV, for periods of up to 10 hours at a time.

II.6 ii. Shutter, cleavage device and evaporator:

These components are shown in Fig. 8. Two thin walled SS bellows were heliarc welded to a 6" UHV flange that was mounted directly opposite the observation window O of Fig. 1. One of the bellows was attached to a stainless steel cleavage blade and a Mo shutter. The other bellows was attached to a SS rod R_2 . This rod was used to operate the clamping screw for the repeated vacuum cleavage device, see II.6 iii, and to turn the substrate holder in the two-specimen holder for the NaCl/mica studies; see II.6 iv. The Mo shutter was used to shield the substrates during outgassing of the evaporator, to catch portions

FIG. 8 SHUTTER, CLEAVAGE DEVICE, AND EVAPORATOR.

of the NaCl crystals cleaved off, and to selectively shield portions of the specimen during evaporation.

A third bellows was welded to a 2 3/4" flange. This bellows was connected to a Cu wire via a SS rod. The Cu wire was used to push the evaporant chips into the evaporator, see Fig. 8.

The evaporator consisted of resistance heated helical 0.020" Ta or W wire baskets. The evaporant holder was almost directly above the baskets. Before an evaporation was performed, the evaporator was outgassed at a high temperature (2000°C) for many hours. The evaporator was loaded with evaporant chips of predetermined mass by pushing individual chips so that they would drop from the holder into the basket. As a consequence of this improvement the pressure during deposition could be kept in the 0.6 to 5×10^{-9} Torr range.

II.6 iii Substrate holder for repeated vacuum cleavage:

This holder was used primarily for the deposition on two air cleaved and up to three vacuum cleaved faces of NaCl in a single run.

The construction of this holder is shown in Fig. 9. An OFHC Cu block containing a Ta heater element, the substrates to be used, a thermocouple, and a specimen release mechanism were attached to rod R (see Fig. 6.) of the specimen manipulator. Connection to R was made via the electrical connecting device described above.

A large crystal, X, shown in Fig. 9 yielded one of the air cleaved and, through multiple cleavage, all of the vacuum cleaved substrates. Crystal X was clamped between two V-shaped Cu grips V. One of these grips was semi-permanently fastened to C while the other could be adjusted by means of the

FIG. 9 SUBSTRATE HOLDER FOR REPEATED VACUUM CLEAVAGE.

clamping mechanism. This mechanism consisted of a winged SS screw that could be turned from outside the vacuum system by the moveable SS rod, R_2 , shown in Fig. 8. Upon releasing the winged screw, crystal X dropped a short distance ($1/4$ to $1/8$ ") onto the cleavage blade shown in Fig. 9. Thereafter the clamping screw was retightened and the exposed portion of the crystal was cleaved off. During cleavage the specimen holder was supported by a SS rod that was rigidly attached to the wall of the vacuum chamber.

This procedure of generating UHV cleaved NaCl faces could be repeated three times on the average before a typical crystal was used up. The cleaved portions of the initial crystal were caught by the shutter described above. The shutter also was used to shield the substrates from evaporant whenever necessary.

A second air cleaved specimen was clamped to C and was used for reference purposes. The films formed on the surfaces of the crystal X were used in the RHEED examinations. The additional air cleaved surface was used, along with one of the vacuum cleaved surfaces, in simultaneous depositions to compare the epitaxy on air and vacuum cleaved substrates. On the other hand, in cases where in situ RHEED studies may influence the epitaxy, the additional air cleaved substrate may be used to compare unirradiated with irradiated films. The extra air cleaved substrate was clamped on the block C in a position out of the line of sight of the electron beam and is not shown in Fig. 9.

II.6 iv Two specimen holder for NaCl/mica studies:

This specimen holder was constructed to allow two depositions of NaCl on mica to be carried out in the same run. The construction is shown in Fig. 10.

FIG. 10 TWO SPECIMEN HOLDER FOR NaCl/MICA STUDIES.

The holder consisted of an OFHC Cu block A which was heated by a Ta heating element. Block A was attached to the electrical couple described in section II.6 i via a thin walled SS tube. Another OFHC Cu block B, on which the air cleaved mica substrates were clamped, was fitted over the Cu rod R_3 . R_3 was tightly pressed into the block A. By means of the moveable rod R_2 of Fig. 8 block B could be rotated around R_3 . Thus the two mica substrates could be successively exposed to the vapor stream. The mica substrates were pressed to block B by means of Mo clamps M.

This device may be used to form NaCl films on more than two mica substrates during a single run. The original design used a square block as substrate carrier and a masking shutter. The masking shutter was simply a Mo plate with a rectangular hole in it. It was found that this method worked well but unfortunately complicated the experimental procedure for this operator. Accidental contamination of the substrates during masking was avoided by using only two substrates mounted directly opposite each other on a rectangular substrate holder.

II.6 v. UHV quartz crystal thickness monitor:

The principle of operation of this kind of thickness measuring device has been described in the literature.⁵ A quartz crystal in the tank circuit of a frequency oscillator is exposed to the vapor stream. The mass added to the crystal by vapor condensation results in a shift of the crystal's natural oscillating frequency. By measuring the frequency shift, and assuming the bulk density to apply to the thin film, one can calculate the average film thickness.

FIG.II UHV QUARTZ CRYSTAL THICKNESS MONITOR

An inexpensive UHV thickness monitor was designed and constructed in our laboratory. A schematic diagram of the device is shown in Fig. 11. The oscillator circuit and quartz crystals were supplied by Inficon Inc., Syracuse, N.Y. A Hewlett Packard model 5248 frequency counter was used to measure the frequency shift.

The watercooled crystal holder consisted of a thin walled SS tube onto which a SS seat S was heliarc welded. Care was taken to polish the crystal seat to a high finish in order to obtain a firm support. Electrical contact to the crystal was made through three points connected to the UHV feedthrough F. The three-point contact was made from a 0.010" Mo sheet and three 0 -80 SS screws. By means of a shielded Cu wire, F was connected to another feedthrough F_1 that was welded into the extension piece described in II.5. The Cu wire was shielded by means of Cu mesh. The Cu conductor was electrically insulated from the Cu mesh with fibre-glass sleeving.

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III. EPITAXY OF NaCl ON MUSCOVITE

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SUMMARY

NaCl films (1500 to 2500 Å thick) were formed in an ultra high vacuum reflection high energy electron diffraction (UHV-RHEED) camera at pressures below 9×10^{-9} Torr on air cleaved muscovite at 25, 100, 200, 250, 300, and 380°C by vapor deposition. In situ RHEED studies showed that all films were (111) oriented monocrystals containing twins. In situ surface replicas of these films were prepared and examined by transmission electron microscopy (TEM). The RHEED patterns showed structural features that were correlated with the type of facets observed from the surface replicas. The results of these studies were compared with earlier work carried out in a technical vacuum (TV) of the order of 10^{-6} Torr. It was shown that there were relatively minor differences between UHV and TV films. Surface replicas of 25 to 1000 Å thick NaCl films formed in TV also were made. In the TV case, the surface microstructures of films formed at 25°C on unbaked and vacuum baked muscovite were compared. Vacuum baking consisted of in situ heating of the muscovite inside the vacuum chamber before cooling to the deposition temperature (25°C). The surface microstructure of films formed on baked substrates depended upon the details of the baking process. Relatively large tetrahedral growth features with side faces parallel to {100} were observed on the surfaces of some of the films formed on the baked substrates. Two plausible explanations

were considered to explain the formation of these tetrahedral growth features. The first is based on the dehydroxylation stages of muscovite that occur during heating. The other explanation involves a carbon layer that forms on air cleaved mica during vacuum baking. The latter explanation is preferred since it was consistent with both the TV and UHV results obtained in the present study.

1. INTRODUCTION

The epitaxy of ionic compounds on various substrates has been widely studied in the past under vacuum conditions that were poor by present capabilities.⁽¹⁾ Contrary to the case of metals on alkali halide substrates, investigations of the epitaxy of alkali halides were not extended to UHV conditions.

Three studies^(2,3,4) of the epitaxy of NaCl on muscovite at pressures of about 10^{-6} Torr have been reported. Schulz⁽²⁾ deposited several alkali halides on mica at room temperature in a vacuum of about 10^{-5} Torr and investigated these films in situ with reflection high energy electron diffraction (RHEED), giving major emphasis to films less than 10A thick. The alkali halide films studied by Schulz were all {111} oriented monocrystals. Alkali halide deposits with a lattice parameter $a_0 > 5.32\text{\AA}$ (a_0 for NaCl = 5.63A) contained {111} twins. The $\langle 111 \rangle$ twinning axis was normal to the plane of the film, i.e. the films were double positioned. Schulz did not report on twinning about $\langle 111 \rangle$ directions that were not normal to the plane of the film.⁽²⁾

Ogura⁽³⁾ emphasized the surface structure of NaCl films, 1000 to 2000A thick, grown on muscovite at 100 to 400°C in a vacuum of about 5×10^{-6} Torr. His replicas showed pronounced triangular and square features on the surfaces of these films. Ogura gave a qualitative explanation of the triangular features by using Schulz's suggestion that nucleation occurs at the edges of potassium atom patches that remain on the mica after cleavage.

Shimaoka and Herold⁽⁴⁾ studied NaCl films of about 600A in average thickness formed at temperatures between 24 and 500°C on air cleaved

mica at about 10^{-4} Torr. The films were studied by RHEED, transmission electron microscopy (TEM), transmission electron diffraction (TED), and surface replication techniques. The epitaxial orientation of the films was (111) NaCl // (001) mica and $[\bar{1}10]$ NaCl // [100] mica over the entire temperature range studied. Twinning on all the {111} planes was observed. However, it should be noted that these authors did not study the epitaxy in situ. The NaCl films were exposed to moist air before electron optical studies were carried out. (5)

Some of the structural aspects of thick (1500 to 2500Å) NaCl films formed in UHV on air cleaved muscovite were reported in a previous communication. (6) The purpose of the present paper is to give a more detailed account of these experiments, to report on additional results obtained, and to compare these results with those of earlier workers.

2. EXPERIMENTAL

The experimental procedure that was followed will be described under three topics, namely: 1) the RHEED camera, 2) deposition of UHV films and 3) films formed in a technical vacuum (TV) of 10^{-5} to 10^{-7} Torr.

2.1 THE RHEED CAMERA

The first UHV camera was reported by Siegel⁽⁷⁾ and work resulting from it by Siegel and Patterson⁽⁸⁾ in 1959. Subsequently several other such instruments were built, many of which used at least one electromagnetic or electrostatic lens to focus the electron beam.^(9,10,11) However, such a lens is not essential.^(12,13,14) The instrument used in the present study had no lens but employed two beam limiting apertures. Various improvements and modifications were made in an earlier version of this instrument reported in reference 15. A schematic diagram showing the main vacuum chamber, the substrate manipulator and the electron optics is given in Fig. 1. The oil-free pumping system consisted of two sorption pumps, an ion pump, and a titanium sublimation pump. The complete system is bakeable to 250°C. After baking, a base pressure in the low 10^{-10} Torr range is regularly obtained. Electrons, emitted by a hot W filament, are accelerated by a high voltage of up to 60 kV. They pass through two moveable watercooled Mo-apertures and strike the specimen surface at a glancing angle. The resulting diffraction patterns are observed and recorded by photographing the fluorescent screen.

The muscovite* substrate was clamped to a heatable OFHC Cu block by means of Mo strips. These strips also were used to press a thermocouple against the Cu block. All the required substrate motions could

* Muscovite mica of African origin purchased from Asheville-Schoonmaker Mica Co., Virginia, in the form of sheets ~ 0.02 mm thick.

be carried out by means of a specially constructed specimen manipulator. During rotation of the specimen, one avoids twisting of the electrical leads (connecting the feedthroughs to the specimen heater) by using the device shown in Fig. 2. Its construction was reported earlier⁽¹⁶⁾ and it operates on the same principle as a more recently reported device.⁽¹⁷⁾ The outer races (J) of each stainless steel ball bearing were connected to power feedthroughs in the chamber walls while the inner races (I) were connected to the specimen heater. An ample supply of pumpout holes (P) was provided to eliminate virtual leaks from the many screw holes and cavities in the device. The device has operated satisfactorily under UHV conditions for over two years. No galling or sintering problems of the bearings were experienced when currents of up to 8 amperes were conducted for several hours in UHV.

2.2 DEPOSITION OF UHV FILMS

The vapor sources consisted of coiled W wire baskets charged with measured masses of NaCl and replicating materials. After bakeout the substrate was heated to 400°C in UHV for a period of at least 12 hours before being cooled to the deposition temperature. Then the NaCl was outgassed, the substrate being shielded from the source by means of a shutter. Film thicknesses were estimated from the mass of NaCl evaporated and the source to substrate distance (~10 cm). The thicknesses varied from 1500 to 2500 Å for films formed at 25, 100, 200, 250, 300, and 380°C. The residual gas pressure was kept below a maximum of 9×10^{-9} Torr during deposition. The average deposition rate was about 10 Å/sec. Two thin films (100 Å thick) were also formed in UHV at 25°C.

No electron bombardment of the substrate or growing film was permitted prior to the completion of evaporation in order to avoid unknown

irradiation effects. After the in situ RHEED studies were completed the films were replicated, also in situ. The system was then opened and the SiO-Ge replica floated off by dissolving the NaCl in water. It was then examined in a conventional transmission electron microscope.

2.3 FILMS FORMED IN A TECHNICAL VACUUM (TV)

Replicas of NaCl films formed at 25°C on air cleaved muscovite in a commercial belljar system operating at 10^{-5} , 10^{-6} , and 10^{-7} Torr also were examined. These experiments were performed to study the effect of prior heat treatment of the air cleaved muscovite substrates on the epitaxy of NaCl films. The heat treatment consisted of heating the mica to various temperatures between 300 and 500°C for various periods of time in vacuum. The substrates were then cooled to 25°C, the temperature at which the NaCl was deposited. Henceforth all substrates treated in this fashion will be called "baked". A total of 80 films were examined. Fifteen of these films were formed on unbaked substrates while the remainder were formed on baked substrates.

A thickness range between 25 and 1000Å was covered, but in most cases films of about 100Å were studied. Usually, deposition rates between 1 and 10Å/sec. were employed. The substrate to source distance was 12 cm, and the substrates were placed perpendicular to the vapor stream. In many cases films were prepared simultaneously on baked and unbaked substrates.

A few depositions were carried out on air cleaved muscovite in which the substrate surfaces and certain deposition conditions were varied in order to find out what effect such variations would have on the epitaxy. These variations in substrate and deposition conditions

consisted of the following:

1. variations in deposition rate from 1 to 40A/sec.
2. intentional scratching and severe cold working of the substrates before and after cleavage.
3. deviations of up to 30° from perpendicular incidence of the vapor stream on the substrate.
4. enhancing the formation of a carbon contamination layer on the substrates. The enhanced carbon contamination was achieved by dipping freshly air cleaved substrates in acetone for about five minutes before inserting the substrates in the deposition chamber. Vacuum baking of air cleaved muscovite was shown⁽¹⁸⁾ to cause the formation of a carbon contamination layer on the surface of the mica. Dipping air cleaved mica into acetone enhances the formation of such a carbon contamination layer.⁽¹⁸⁾

In addition, five films ranging in thickness from 60 to 650A were formed on muscovite substrates cleaved in situ in a vacuum of about 10^{-5} Torr, 1 to 3 seconds before deposition commenced. These depositions were performed at a substrate temperature of 25°C . In these cases the mica was unbaked and deposition rates between 1 and 2A/sec. were used.

3. RESULTS

The results obtained in this study may conveniently be described in four sections: 1) diffraction results for thick UHV films, 2) surface replicas of thick UHV films, 3) thin UHV films, and 4) thin films formed in a TV of 10^{-5} to 10^{-7} Torr at 25°C .

3.1 DIFFRACTION RESULTS FOR THICK UHV FILMS

The in situ RHEED patterns obtained in the $[110]$, $[211]$, and $[321]$ azimuths showed that all the thick NaCl films formed on baked air cleaved mica between 25 and 380°C were $(\bar{1}11)$ oriented monocrystals. Prominent diffraction spots due to the parent, twins, and double diffraction between the twins and parent matrix were observed in the $[110]$ and $[321]$ azimuths. Typical examples of RHEED patterns for the $[110]$ and $[321]$ azimuths are shown in Figs. 3a and 3c. The corresponding interpretations are given in Figs. 3b and 3d respectively. A diffraction pattern in the $[211]$ azimuth is not shown because neither twinning nor double diffraction between parent and twins gives additional spots besides those that arise from the parent.

The diffraction pattern for the $[110]$ azimuth shown in Fig. 3a is identical to the pattern reported by Schulz.⁽²⁾ It shows that double positioning $(\bar{1}11)$ twins are present and that twins on the $(1\bar{1}1)$ planes are either absent or present in very low densities. Twins on (111) and $(11\bar{1})$ would not give extra spots. The crystallographic information about the epitaxy that is given by Fig. 3a is not sufficient to explain several additional features in many of the RHEED patterns that were obtained in the present study. In the remainder of this section these additional features are described.

In the [321] azimuth, spots due to the parent, double positioning ($\bar{1}11$) twins, (111) twins, and double diffraction between the parent and the (111) twins are present. Twins on ($\bar{1}11$) and ($11\bar{1}$) would not give extra spots. See Figs. 3c and 3d. The intensities of the beams diffracted by the parent matrix and its double positioned twins (dpt) were higher than those from beams diffracted by the (111) twins. However, double diffraction between the matrix and its dpt was not detected, while it was observed between the matrix and the (111) twins. Double diffraction between the matrix and its dpt, for the [321] azimuth, would involve the use of relatively weak high order diffracted beams. It is perhaps for this reason that this particular double diffraction effect was not detected. For double diffraction between the parent and the (111) twins, much lower order reflections are involved. Spots arising from double diffraction among the variously oriented twinned regions were not observed, suggesting that these regions did not overlap each other in the films.

In summary then, these NaCl films contained double positioning ($\bar{1}11$) twins in relatively high concentrations as well as low concentrations of other twins. Some RHEED patterns obtained only from specific areas of films formed at 25 and 100°C also showed all the allowed powder diffraction rings in addition to the strong spot pattern. Portions of these films were thus randomly oriented. Ring patterns also were observed from small areas of films formed at 250 and 300°C. However, because of the relatively low intensity of these rings, no conclusive evidence about the presence of a possible preferred orientation could be obtained.

Extra diffraction spots were observed in the $\langle 110 \rangle$ azimuth of some

portions of the film formed at 200°C. The diffraction pattern containing the extra spots and its interpretation are shown in Figs. 3e and 3f respectively. The extra spots arose from the presence of some {001} oriented NaCl. The [110] azimuth of the (001) oriented NaCl coincided with the [110] azimuth of the dominant ($\bar{1}11$) matrix. The [001] direction of the (001) oriented NaCl did not coincide exactly with the film normal, but was rotated clockwise about the [110] azimuth by approximately 4° from the normal. As discussed in 3.2, additional evidence for {001} oriented NaCl was obtained from the surface replicas.

3.2 SURFACE REPLICAS OF THICK UHV FILM

Replicas of NaCl films formed at various substrate temperatures are shown in Figs. 4a. to 4f. At all temperatures facets of various sizes and distributions were observed to coexist. The replicas all contained a fine structure that appeared to be identical in shape (but not in size) at all temperatures. Large facets were observed also at all temperatures; however, the crystallographic shapes of the large facets varied with the substrate temperature. Since all films were entirely or primarily ($\bar{1}11$) oriented monocrystals, it is reasonable to suggest that the fine structure was ($\bar{1}11$) oriented and that the larger facets contributed to the other orientations that were observed.

The size of the fine structure increased with increasing deposition temperature. The same temperature dependence occurred for the large facets in films formed at 100°C and above. However, the 25°C depositions resulted in films with facets as large as those formed at 380°C. Specifically: 1) the larger facets were mostly irregularly shaped at 25°C and about 1100Å in size. These irregularly shaped facets are indicated

by I in Fig. 4a. 2) At 100°C the large facets were about 300A in size and still irregularly shaped. However, there was tendency for some of the larger facets to assume square or parallelogram shapes. See S and P in Fig. 4b. The large irregularly shaped facets at 25 and 100°C were probably randomly oriented, thus perhaps contributing or causing the ring patterns observed in some of the RHEED examinations. 3) At 200°C and above, well developed rectangular and square features could be recognized among the larger facets. The dimensions of the larger facets attained sizes of 500 and 600A at 200 and 250°C respectively. At both 300 and 380°C they attained a size of about 1100A.

Replicas of the thick films formed in UHV showed some differences from those reported by Ogura⁽³⁾ for films formed in a TV. In both cases the large facets had the same general shapes. However, the large facets reported in the present work were smaller so that the replicas had an overall smoother appearance. The same conclusion holds for the fine structure consisting of many small tetrahedra, which in this study, were observed at all temperatures.

A higher magnification image of a surface replica of a film formed at 300°C is shown in Fig. 5. The typical tetrahedral shape of the fine structure is well displayed.

At a particular place on the film formed at 380°C and shown in Fig. 4f, the larger facets were concentrated along straight lines which made angles of approximately 60° and 120° with each other. Since the cleavage face of muscovite has six fold symmetry, the growth of large facets would appear to occur preferentially at the cleavage steps. Preferential growth of large facets at steps is shown also in Figs. 4a (25°C) and 4c (200°C).

A particular kind of facet growth appeared preferentially at cleavage steps and is marked A in Figs. 4a, 4c, and 4f. This "corrugated" kind of growth may have resulted from the intergrowth of {110} oriented crystallites. However, no corresponding diffraction evidence was obtained.

3.3 THIN UHV FILMS

Replicas also were obtained for two thin films (thicknesses of about 100A) formed at 25°C in UHV. Large areas of these replicas (several microns in size) contained small tetrahedra and truncated tetrahedra of about 50A in size. At irregular intervals across the replicas many well developed larger tetrahedral features of various sizes and densities were observed. An example of such an area is shown in Fig. 6. Low shadowing angle replicas showed that the tetrahedral features projected out from the film surface. Of special interest is the fact that the apices of all the larger tetrahedral features are truncated at approximately the same height. Thus all the tetrahedral features appear to have become truncated during growth when a certain height above the level of the main portion of the film was attained.

Two double positioned tetrahedral features are indicated by 1 and 2 in Fig. 6 and their projections are indicated by a_{i+} and a_{i-} respectively. An additional type of contrast, indicated by E in Fig. 6b was observed after tilting the specimen. Its origin is not clear at present.

In order to determine the Miller indices of the side faces of the tetrahedral features, one must know the height h of the truncated tetrahedron and the angle θ that the side faces make with the plane of the film. Approximate values of h and θ can be obtained by viewing images of the replicated tetrahedral features as a function of the angle of tilt. Let ϕ_i be the angle between the incident beam and the normal to the film; see Fig. 7. The projection,

a_i , of the side faces (onto the plane of the thin NaCl film) is a function of θ , h , and ϕ_i . From a series of micrographs one can measure a_{i+} and a_{i-} as a function of ϕ_i . Fig. 6a was obtained under apparently normal incidence of the electron beam. It is clear, however, that an initial angle of tilt, ϵ , was present over at least portions of the specimen because of local buckling of the replica. Thus the effective angle of tilt is $\phi_i = \psi_i + \epsilon$, where ψ_i is the goniometer angle of tilt on the electron microscope stage. The electron microscope used in the present study allowed a maximum goniometer angle of tilt of 28° .

The projection of the side faces of the tetrahedral features under tilted or untilted illumination is:

$$a_o = 1/2 (a_{i+} + a_{i-}).$$

Define:

$$\Delta a_{i+} \equiv a_{i+} - a_o = 1/2 (a_{i+} - a_{i-}),$$

$$\Delta a_{i-} \equiv a_o - a_{i-} = 1/2 (a_{i+} - a_{i-}).$$

These quantities are indicated in Figs. 7a and 7b.

Let $\phi_{\max}$ be the beam tilt angle for which $a_{i-} = 0$, i.e. $a_{i+} = 2a_o$.

$$\Delta a_{i+} = \Delta a_{i-} = h \tan \phi_i = h \tan (\psi_i + \epsilon) = \begin{cases} a_o & \text{if } \phi_i = \phi_{\max} \\ 0 & \text{if } \phi_i = 0 \end{cases} \quad (1)$$

The value of ϵ was obtained by employing equation (1) in the following way. For $\phi_i = (\psi_i + \epsilon) \leq 20^\circ$, $\tan \phi_i \approx \phi_i$; i.e. $\Delta a_{i+} \approx h (\psi_i + \epsilon)$ to within 4%. For $(\psi_i + \epsilon) > 20^\circ$ this approximation rapidly breaks down. A least squares

plot of $\Delta a_{i\pm}$ vs. ψ_i was made for the data points obtained with $\phi_i < 20^\circ$. The approximation used above permits a linear extrapolation to $\Delta a_{i\pm} = 0$. Such an extrapolation yielded $\epsilon = 2.5 \pm 1$ degree. A least squares plot of $\Delta a_{i\pm}$ vs. $\tan(\psi_i + \epsilon)$ was then made using this value of ϵ . The latter plot yielded a value of $\phi_{\max} = 41 \pm 7^\circ$ upon extrapolation to $\Delta a_{i\pm} = a_o$, and a value of $h = 220 \pm 70\text{\AA}$. From Fig. 7, $\theta = 90^\circ - \phi_{\max}$. Using the value of $\phi_{\max}$ given above one finds $\theta = 49 \pm 7^\circ$.

tetrahedral features,
For / with {111} basal planes and all side faces parallel to either {100} or {111} planes, θ would be 54.7 or 70.5° respectively. Our observation of $\theta = 49 \pm 7^\circ$ suggests that the side faces were not parallel to {111} but more likely parallel to {100}. Higher order planes, such as {221} and {321} would give θ values that fall within the experimental error. NaCl tends to expose {100} faces in nature indicating that the latter are the low energy faces. This fact, together with tetrahedral features, our measured value of θ suggests that the side faces of the / are parallel to {100} rather than {221}, {321} or still higher order planes.

3.4 FILMS FORMED IN TV AT 25°C

A typical surface replica of a film formed on unbaked air cleaved muscovite is shown in Fig. 8a. tetrahedral features, No / were observed on any of the 15 films that were formed on unbaked air cleaved substrates. These films had surfaces which were smoother than those of all the other kinds of NaCl films made in this study. Also they did not appear to contain any tetrahedra, small or large. Thin NaCl films ($\sim 100 \text{\AA}$) formed on unbaked mica were used, in situ, as substrates to form extremely smooth {111} oriented monocrystalline films of Ag, Au, and Cu. (19,20)

tetrahedral features,
Large / , apparently identical to those found on thin UHV films, were observed only in TV films formed on vacuum baked air cleaved (ac)

substrates. It was found that the occurrence of these tetrahedral features depended upon the details of the prior baking process.

Thus, tetrahedral features were observed in 14 out of 18 films formed on air cleaved substrates baked in vacuum at 450°C for 1/4 to 2 hours prior to 25°C deposition but not on air cleaved substrates that were baked for shorter or longer periods. Similarly, 14 out of 25 films formed on air cleaved mica baked at 400°C for 1/2 to 4-3/4 hours yielded tetrahedral features, while none were obtained for shorter baking times. Baking the substrate at 300 or 500°C for 1/4 to one hour was again not sufficient to yield tetrahedral features. The data thus shows that there exist intermediate temperature ranges and baking times for which tetrahedral features grew in (or on) the NaCl films formed on air cleaved muscovite. The tetrahedral features did not grow on unbaked or extensively baked air cleaved muscovite in TV.

Ogura⁽³⁾ observed tetrahedral features in NaCl films grown in TV. He used exclusively air cleaved substrates baked at 450°C for 1/2 hour in his study. Zouckermann⁽²¹⁾ observed tetrahedral features in KI films formed on air cleaved muscovite. The growth of tetrahedral features was recently reported by Egerton for KCl⁽²²⁾ and PbTe⁽²³⁾ films formed on air cleaved muscovite heated to 450 and 300°C respectively during deposition. An ingenious suggestion was made by Green⁽²⁴⁾ to explain the growth of the tetrahedral features reported by Egerton. He made two suppositions about the mica surface. The first was that the potassium ions on the muscovite surface are arranged in such a fashion that the surface is "grooved" on an atomic scale. The grooved surface is obtained by removing alternate rows of K ions from the K monolayer on the mica surface. The second assumption was that previously reported electric dipoles⁽²⁵⁾ detected on vacuum cleaved muscovite are also present on heated air cleaved muscovite. These

dipoles would be expected to influence the alignment of ionic molecules deposited on the mica surface. Using these two assumptions Green concluded that ionic deposits on mica may grow in the tetrahedral fashion that was reported by Egerton.

It was often observed in the present work that repetition of apparently similar deposition conditions did not consistently result in the growth of tetrahedral features. Certain variations in the deposition conditions were carried out in an attempt to shed some light on this problem. The results obtained from these latter depositions were as follows:

- 1) Films formed on vacuum cleaved unbaked mica showed no tetrahedral features. This result implies that the electric dipoles present on mica⁽²⁵⁾ are not responsible for the formation of tetrahedral features in the growth of NaCl on mica.
- 2) Films formed on acetone dipped unbaked mica showed no tetrahedral features. Acetone dipped and baked mica gave tetrahedral features, but these were no different from those obtained from simultaneously formed films on baked substrates not treated by acetone.
- 3) Variation of deposition rate from 1 to 40A/sec., scratching and cold working of the substrates, and variation of the angle of incidence of the vapor stream had no effect on the occurrence of tetrahedral features. When tetrahedral features were observed, they did so only on vacuum baked mica.

Several replicas showed macrosteps on the mica cleavage face. In some cases the tetrahedral features were concentrated along macrosteps. An example is shown in Fig. 8b. Many small tetrahedral features formed at the macrosteps while a few larger ones formed elsewhere. Double positioned tetrahedral features occurred in both places.

Films of thicknesses up to 900A formed in TV on baked muscovite also contained tetrahedral features, most of which were not truncated. However, in films thicker than 375A, square facets and corrugated growth became more prominent, see Fig. 8c.

4. DISCUSSION

The results may be discussed under two topics, namely thick UHV films and the influence of substrate baking on the growth of tetrahedral features in thin TV films.

4.1 THICK UHV FILMS

The structural aspects of the epitaxy of NaCl on air cleaved muscovite were only slightly influenced by improving the background pressure from 10^{-5} to 9×10^{-9} Torr during deposition. The RHEED patterns from thick UHV films showed that all the films were (111) oriented and contained double positioning twins. This result is the same as that reported by Schulz⁽²⁾ for thin films formed on unbaked air cleaved muscovite at room temperature in a TV of about 10^{-5} Torr. Schulz did not report on twinning about $\langle 111 \rangle$ directions that were not normal to the plane of the film. In the present study several deviations from the main double positioned ($\bar{1}11$) orientation were observed in thick UHV films. These deviations consisted of the following:

- 1) In the [321] azimuth, twinning on (111) also was observed. Thus twins formed on at least one of the three {111} planes that are not parallel to the surface of the film. Symmetry arguments suggest, therefore, that all {111} planes not parallel to the film contained twins. If so, then one can conclude that twinning occurred on all possible {111} planes in NaCl films formed between 25°C and 380°C.
- 2) Randomly oriented NaCl was occasionally observed.
- 3) In rare instances {001} oriented NaCl formed at 200°C together with the main ($\bar{1}11$) double positioned orientation.

A comparison of the diffraction patterns with the surface replicas suggests that the fine structure in the replicas was $(\bar{1}11)$ oriented, the irregularly shaped large facets at 25 and 100°C were randomly oriented, and the square facets at 200°C were $\{001\}$ oriented.

(TETRAHEDRAL FEATURES)

4.2 INFLUENCE OF SUBSTRATE BAKING ON THE FORMATION OF / IN THIN TV FILMS

A model for the epitaxy of NaCl on mica must take into account the relation between the tetrahedral growth features occurring in thin films and the baking of the substrate. Construction of a complete model for the epitaxy of NaCl is complicated by the uncertainty regarding the arrangement of the K ions on muscovite cleavage faces. Auger electron analysis of vacuum cleaved muscovite has shown that the K ions are shared evenly by the opposite cleaved faces.⁽²⁶⁾ Since no ordering of the surface K ions was detected in LEED studies^(25,27) of vacuum cleaved mica, these K ions are thought to be randomly arranged.⁽²⁵⁾ Au decoration replicas of heated muscovite surfaces⁽²⁸⁾ failed to give a clue to the occurrence of the tetrahedral features, of the / observed in the present study. Two plausible explanations relating the different growth modes and the baking of the substrates are given below.

It is known that during heating muscovite at 600°C, water molecules form in the mica lattice by a local reversible reaction of structural OH⁻ groups.⁽²⁹⁾ There is indirect evidence that dehydroxylation of muscovite occurs already at 400°C.^(30,31,32) Thus it is reasonable to assume that water molecules are present in the lattice of muscovite heated to 400 or 450°C. Diffusion of water molecules through the mica lattice was shown to be relatively slow below 550°C.⁽³¹⁾ Consequently, cooling mica from 400-500°C would tend to trap water molecules in the lattice. It is well

known that water molecules have an asymmetric charge distribution that gives rise to an electric dipole moment.⁽³³⁾ Also, NaCl is known to evaporate predominantly as monomeric molecules,⁽³⁴⁾ each monomer thus having an electric dipole associated with it. Interactions between the water dipoles near the mica substrate surface and the NaCl dipoles deposited on the mica would be expected to occur. Such interactions might play important roles in determining the alignment of the NaCl monomers during the nucleation stage of film formation. In the early stages of dehydroxylation (that is, after short baking times or after low temperature baking) and on unbaked substrates, no significant number of water dipoles would be expected to be present. In addition, they may accumulate at defect sites and participate in the formation of lenticular flaws observed in heated phlogopite⁽³⁵⁾ and muscovite.^(36,37) The resultant electric multipole moment, if any, of the accumulated water in the flaw would be expected to be small and probably would not influence the NaCl epitaxy. With other factors equal, the epitaxy of NaCl on substrates in which either very little or extensive dehydroxylation occurred should be the same. Thus tetrahedral features, form on moderately baked air cleaved mica under circumstances similar to those required for the formation of water molecules in the mica substrates.

An alternative explanation for the occurrence of different growth mechanisms is suggested by the findings of Poppa and Elliot.⁽¹⁸⁾ These authors found a C contamination on the surface of air cleaved mica that was baked in vacuum. It is possible that the C layer would influence the epitaxy of the NaCl. Suppose organic contamination occurs on the surface of air cleaved mica. A moderate baking (at 400 to 450°C, 1/4 to several hours) may result in decomposition of the organic layer and

precipitation of elemental C on the muscovite. This elemental carbon may be responsible for the growth of tetrahedral features in the NaCl film. At high temperatures ($\sim 500^\circ\text{C}$) and long baking times, the C may be oxidized (to CO and/or CO_2) and thermally desorbed from the mica surface. For low baking temperatures ($\sim 300^\circ\text{C}$) and short baking times (less than 15 min.) the changes in the organic layer described above may not occur. Thus elemental C would be expected to occur only on moderately vacuum-baked mica, a process that was shown to be essential for the occurrence of the tetrahedral features.

The explanation in terms of C contamination also fits the observation of tetrahedral features in UHV NaCl films formed on air cleaved mica that was baked in UHV at 400° for 12 hours. The latter observation would be difficult to explain ⁱⁿ / terms of the dehydroxylation picture discussed above. The explanation in terms of C contamination would be as follows: Poppa and Elliot,⁽¹⁸⁾ using an ion pumped vacuum system at 10^{-6} Torr, found that high temperature vacuum baking alone was not sufficient to remove the C layer. However, the C layer could be removed by heating (500°C for 3 hours) the air cleaved mica in an oxygen residual gas pressure of 10^{-6} Torr. A relatively high oxygen pressure usually is present in the atmosphere of oil diffusion pumped systems such as the one used for the formation of technical vacuum films in the present work. It is reasonable to expect the oxidation of the C and desorption of the oxide would occur upon heating the mica at 500°C in the technical vacuum of the diffusion pumped system. Thus tetrahedral features would not be expected to occur on such surfaces. In the UHV case the carbon layer would be present even after prolonged heating since the oxygen residual gas pressure is very low. If elemental

C is indeed needed for the growth of tetrahedral features on mica, the above explanation in terms of C contamination is in agreement with both the UHV and TV results presented in this work.

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Figure Captions

Figure 1: Schematic diagram of the UHV RHEED camera.

Figure 2: Rotable electrical couple and specimen holder.

Figure 3a: UHV RHEED pattern from 1500 Å NaCl deposited at 100°C on mica in UHV. Beam in $\langle 110 \rangle$ of NaCl.

Figure 3b: Interpretation of Fig. 3a.

- ⊗ - ($\bar{1}11$) oriented parent matrix spots,
- - spots due to double positioning ($\bar{1}11$) twins,
- ⊠ - spots due to double diffraction between parent matrix and ($\bar{1}11$) twins,
- ▲ - spots due to ($1\bar{1}1$) twins.

Figure 3c: UHV RHEED pattern from 1500 Å NaCl deposited at 100°C on mica in UHV. Beam in $\langle 321 \rangle$ of NaCl.

Figure 3d: Interpretation of Fig. 3c.

- ⊗, ○, ⊠ - Same as Fig. 3b
- + - weak spots due to (111) twins,
- - weak spots due to double diffraction between parent matrix and (111) twins.

Figure 3e: UHV RHEED pattern from a 1500 Å thick NaCl film formed on mica at 200°C in UHV. Beam in $\langle 110 \rangle$ of NaCl.

Figure 3f: Interpretation of Fig. 3e.

- X - extra spots due to $\{001\}$ oriented NaCl. Beam in $\langle 110 \rangle$ of NaCl.

Figure 4 : Surface replicas of 1500 Å thick NaCl films formed on baked mica in UHV at various temperatures, (a) 25°C, (b) 100°C, (c) 200°C, (d) 250°C, (e) 300°C, and (f) 380°C.

Figure Captions (Cont'd.)

Figure 5: High magnification image of the surface replica of a NaCl film formed at 300°C in UHV.

Figure 6: Surface replicas of a 100 Å NaCl film formed at 25°C on baked mica in UHV.

(a) Electron beam approximately perpendicular to the replica.

(b) Same area as (a) but obtained with the electron beam tilted by 28° from the replica normal.

Figure 7: Schematic of two double positioned tetrahedral features, 1 and 2 of Fig. 6.

(a) Sectional and top views of 1 and 2 under normal incident electrons.

(b) Sectional view defining the decrease and increase of the projection of a side face of 1 and 2 respectively when viewed under effectively tilted electron illumination.

Figure 8: Surface replicas of NaCl films formed at 25°C in a technical vacuum; (a) 100 Å thick film on unbaked mica, (b) 200 Å thick film formed on baked mica, (c) 875 Å thick film formed on baked mica.

FAKoch & Pohl, 1971

Fig. 2.

3a

3c

3e

3f

(a)

(b)

(c)

(d)

(e)

(f)

FAKoch 1 RW 100k
Figs 4a-f

Figs

FPKoch, RW Koch

Fig 6a

Fig 6b

FAKoch & RW Vook

SECTIONAL VIEW

SECTIONAL VIEW

8a

8b

8c

Black & White Figs 8 a-c

IV. THE VAPOR EPITAXY OF CaF_2 ON NaCl

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ABSTRACT

CaF_2 films, 30 to 1500 Å thick, were vapor deposited at 25 to 380°C onto air cleaved and vacuum cleaved NaCl in residual gas pressures of order 10^{-5} , 10^{-7} , and 10^{-9} Torr. The structures of the films were examined by in situ ultra high vacuum reflection high energy electron diffraction, conventional transmission electron microscopy, transmission electron diffraction, and surface replication techniques. The films consisted of many crystallites, the complex $\{110\}$ and $\{001\}$ orientations of which depended on the deposition parameters. The transition from the complex $\{110\}$ orientation to the $\{001\}$ orientation is described in detail in terms of its dependence on the deposition temperature, film thickness, vacuum, and substrate conditions. The $\{001\}$ orientation was identified with two sets of thin needle-shaped crystallites oriented at 90° to each other. The $\{110\}$ orientation was identified with two sets of larger crystals also oriented at 90° to each other. At higher deposition temperatures the larger crystals formed predominantly at cleavage steps on the NaCl substrate, while the needle-like crystals tended to form on the surface of the films.

IV. THE VAPOR EPITAXY OF CaF_2 ON NaCl

I. INTRODUCTION

Four previous studies of the microstructure of CaF_2 films formed by vapor deposition on NaCl substrates have been reported^{1,2,3,4}. Bauer¹ formed films of some alkali and alkali earth fluorides on air cleaved NaCl and mica substrates. The substrates were heated, in situ, at 400 to 600°C for several hours before cooling to the deposition temperature. Substrates which were given in situ heat treatments will be referred to as "baked" substrates. During deposition the residual gas pressure was kept at 1 to 8×10^{-5} Torr and the substrate temperatures were varied between 25 and 500°C. CaF_2 films less than 100 Å in thickness and formed at room temperature on baked NaCl consisted of many small crystallites aligned predominantly in the parallel orientation, i.e. $\{100\} \text{CaF}_2 // \{100\} \text{NaCl}$ and $\langle 001 \rangle \text{CaF}_2 // \langle 001 \rangle \text{NaCl}$. At greater thicknesses the parallel orientation was lost and crystallites with $\{110\} \text{CaF}_2 // \{100\} \text{NaCl}$ and $\langle 001 \rangle \text{CaF}_2 // \langle 011 \rangle \text{NaCl}$ were observed. The $\langle 001 \rangle$ directions of the $\{110\}$ oriented crystallites were not exactly parallel to $\langle 011 \rangle$ of the NaCl substrate but varied by $\pm 5^\circ$ about it. Films formed at higher substrate temperatures were in parallel orientation and contained $\{111\}$ twins.

Shigeta² formed 60 Å thick CaF_2 films on air cleaved unbaked NaCl . During the depositions the residual gas pressure was of order 5×10^{-5} Torr. Substrate temperatures were varied between 15 and 400°C. Shigeta found randomly oriented films only.

In a recent study, Bujor and Vook³, formed CaF_2 films on baked (500°C, 30 min.) air cleaved NaCl in a residual gas pressure of $6 - 8 \times 10^{-7}$ Torr. CaF_2 films 1000 Å thick formed on NaCl at 25°C were randomly oriented. At substrate temperatures of 150 to 250°C the films had a {110} preferred orientation. The latter films were polycrystalline and consisted of at least two sets of {110} oriented crystallites. The two sets of crystallites were observed to be rotated by 90° with respect to each other such that, for example [001] of set I was parallel to $[\bar{1}\bar{1}0]$ of set II. The resulting epitaxy was characterized by (110) CaF_2 // (001) NaCl and average $\langle 111 \rangle \text{CaF}_2$ // $\langle 100 \rangle \text{NaCl}$.

At 350°C {100} oriented monocrystalline films were obtained.³ Transmission electron micrographs of these films exhibited crystallographic streaks which were interpreted as due to thin platelets or rods in the films. Further evidence for this interpretation came from the selected area transmission electron diffraction (TED) pattern. It showed spikes perpendicular to the streaks through all the spots.

A comparison of the work outlined above reveals several differences among the reported results. For this reason a more detailed experimental study of the epitaxy of CaF_2 on NaCl was undertaken. The epitaxy on baked and unbaked air and vacuum cleaved NaCl was studied as a function of film thickness and substrate temperature. Films were formed in three different residual gas pressure ranges: technical vacuum (TV) of 1 to 5×10^{-5} Torr, high vacuum (HV) of 0.2 to 5×10^{-6} Torr, and ultra high vacuum (UHV) of 0.6 to 5×10^{-9} Torr. A preliminary report of the results obtained from these studies was given earlier.⁵

II. EXPERIMENTAL PROCEDURE

UHV films were formed in the ultra high vacuum reflection high energy electron diffraction (UHV RHEED) camera constructed in our laboratory and reported elsewhere.⁶ As a rule films were formed simultaneously on air cleaved (ac) and vacuum cleaved (vc) NaCl. CaF_2 chips of known mass were placed in the camera on a platform that was located almost directly above a helical Ta wire evaporator. The CaF_2 chips could be pushed into the Ta evaporator by means of a Cu wire that was attached to a thin walled stainless steel bellows⁶. Thus the Ta basket could be outgassed in UHV before loading it with evaporant.

The thickness of each film was estimated from the mass of CaF_2 evaporated and the source to substrate distance (10 to 12 cm.). The evaporation rate was varied from 5 to 10 A/sec. Before evaporation each CaF_2 chip that was pushed into the Ta basket was heated to 1000 - 1200°C for 15 minutes in order to remove volatile surface contaminants and occluded gases. During this time the substrate was shielded by a shutter. During deposition the residual gas pressure in the vacuum chamber was kept in the 0.6 to 5×10^{-9} Torr range.

The UHV CaF_2 films were examined in situ with the RHEED technique. Electron irradiation of the NaCl substrates and growing CaF_2 films was not permitted prior to completion of evaporation in order to prevent unknown electron irradiation effects on the epitaxial growth.

The single crystal NaCl substrates used in the present study were purchased from Harshaw Chemical Company. The NaCl crystals used for the vacuum cleaved surfaces were in the form of rectangular parallelepipeds 1 cm. x 1 cm. x 2 cm. long. Crystals of this size could be

aligned easily by eye (through an observation window in the vacuum chamber) to have a cube edge perpendicular to the electron beam. A rotation indicator on the specimen manipulator permitted alignment of the NaCl cleavage face relative to the electron beam within $\pm 3^\circ$ of the desired direction.

After the in situ RHEED examination was completed the vacuum system was opened to air. The films were then removed, floated off the NaCl in water, and picked up on Cu grids for electron microscopy. The microstructure was then examined by conventional transmission electron microscopy and TED methods.

TV and HV films were formed in a commercial glass bell jar system utilizing oil diffusion and rotary mechanical pumps. HV and TV were achieved by respectively using or not using a liquid N_2 trap on the diffusion pump. Evaporation occurred from previously outgassed Ta wire baskets. Film thicknesses were measured by a quartz crystal film thickness monitor*. Films were formed on baked (500°C for 30 min.) and unbaked air cleaved and baked and unbaked vacuum cleaved NaCl. After the films were cooled to room temperature, they were removed from the vacuum chamber and examined in a conventional transmission electron microscope.

Films of thickness less than 500 Å were found to shatter when they were floated off their substrates in water. For this reason these films were covered, in situ, with a 200 to 300 Å thick layer of SiO_2 .

*Purchased from Inficon Incorporated, Syracuse, New York.

III. RESULTS

A. Diffraction Data Obtained From the CaF_2 Films

1. Interpretation of Certain Complex TED and RHEED Patterns:

Complex electron diffraction patterns were observed often from polycrystalline CaF_2 films that contained two sets of $\{110\}$ oriented crystallites. Such a complex TED pattern is shown in Fig. 1a. The interpretation of Fig. 1a is given in Fig. 1b where the open circles indicate electron diffraction spots formed by one set of $\{110\}$ oriented crystallites (set 1). The solid circles resulted from the second set of $\{110\}$ oriented crystallites (set 2). The $\{110\}$ planes of the two sets of crystallites are rotated by 90° with respect to each other about an axis normal to the plane of the film. The orientation shown in Fig. 1a will be called the $2x\{110\}$ orientation.³

The pure $2x\{110\}$ orientation shown in Fig. 1a was obtained only for some thin films formed at 25°C on vc NaCl. See Table I. With increasing film thickness additional diffraction spots were observed; see Fig. 2a. The interpretation of Fig. 2a is given in Fig. 2b. The basic orientation is again $2x\{110\}$. The open and solid circles shown in Fig. 2b refer to crystallite sets 1 and 2, as was the case in Fig. 1b. All the spots and streaks present in Fig. 2a (except for the four short streaks marked S_1) that are not present in Fig. 1a, may be caused by double diffraction between the two different sets of crystallites³. Double diffraction occurs when a portion of a relatively strong diffracted beam from crystallite set 1 is re-diffracted by crystallite set 2 (or vice versa). The solid triangles in Fig. 2b indicate the method used to identify all the doubly diffracted spots. Re-diffraction

of the $\bar{1}11$ spot of set 1 (the large solid triangle) by crystallite set 2 contributes to the spots marked by small solid triangles. The positions of the small triangles were found by translating the diffraction pattern of set 2 (the solid circles in Fig. 2b) and centering it on the large solid triangle. The relative orientations of the two lattices were maintained. By successively using the four 111 spots, two 002 spots, and two 220 spots of set 1 as incident beams for set 2, and vice versa, all the double diffraction spots present in Fig. 2a were obtained. Double diffraction between crystallites belonging to the same set could contribute to the short streaks marked S_1 in Figs. 2a and 2b. These streaks would then result from the approximately $\pm 10^\circ$ arcing of the diffraction spots of the basic $2x\{110\}$ orientation. See for example spot S in Fig. 2a. In addition such streaks also could arise from the presence of thin (001) oriented needles in the film. This possibility will be discussed more fully in a subsequent section.

Double diffraction spots were not observed for $2x\{110\}$ oriented films with thicknesses less than about 300 Å. Films 300 to 1000 Å thick that were in the $2x\{110\}$ orientation gave prominent double diffraction spots. The occurrence of double diffraction in thicker films was interpreted as meaning that in these films the two sets of $\{110\}$ oriented crystallites overlapped, at least at their boundaries.

Not all the films were in the pure $2x\{110\}$ orientation. See Table I. Most thin films (<100 Å thick) formed at 25 to 350°C gave diffraction patterns such as is shown in Fig. 3a. The interpretation of Fig. 3a is given in Fig. 3b. Fig. 3b is identical to Fig. 1a except for the set of spots marked S_2 and S_3 in Fig. 3b. These spots were

TABLE I: LIST OF DIFFRACTION DATA

DEPOSITION CONDITIONS	Temperature °C	Pressure	Substrate	FILM THICKNESS (Angstroms)							
				30	50 - 60	150	300 - 330	500 - 600	750	1000	1500
25	HV	ac	1	<u>A+B(r)</u>	<u>A+B</u>	*	<u>A+B+R(vf)+D</u>	<u>A+B+R(f)+D</u>	*	<u>A+B(r)+R(f)+D</u>	*
				<u>A+B(r)</u>	<u>A</u>		<u>A+R(vf)+D+B(?)</u>	<u>A+B+R(vf)+D</u>		<u>A+R(r)+D+B(?)</u>	
		vc			<u>A+R</u>			<u>A+R</u>		<u>A+R</u>	*
				*	<u>A</u>			<u>A+D</u>		<u>A+B(r)+D</u>	
	UHV	ac				*		<u>A+B(f)+R</u>			
				*	*	*	*		*	*	*
		vc						<u>A+D</u>			
											<u>A+B(f)+R</u>
	UHV	ac		*	*	*	*	*	*	*	
											<u>A+B+D</u>
		vc									
100	HV	ac		<u>A+B(r)</u>	<u>A+B</u>	*	*	<u>A+B+D</u>	*	<u>A+B+D</u>	*
				<u>A+B</u>	<u>A+B</u>			<u>A+B+D</u>		<u>A+B+D</u>	
		vc			<u>A+B+R</u>	*	*	<u>A+B+D+R(f)</u>	*	<u>A+B+R(f)</u>	*
				*	<u>A+B</u>			<u>A+B+D</u>		<u>A+B+R(vf)</u>	
	UHV	ac									
				*	*	*	*	*	*	<u>A(r)+B</u>	*
		vc									
200	HV	ac						<u>A(r)+B+R(f)</u>	<u>A(r)+B+R(f)</u>	*	*
				*	*	*	*	<u>A(r)+B</u>	<u>A(r)+B</u>		
		vc						<u>A(r)+B+R(f)</u>	<u>A(r)+B+R</u>	*	*
				*	*	*	*				
	UHV	ac						<u>A(r)+B</u>	<u>A(r)+B</u>		
								<u>A(r)+B</u>	<u>A(r)+B</u>		
		vc		<u>A+B</u>	<u>A+B+R(f)</u>	<u>A(f)+B</u>	<u>A(vf)+B</u>			<u>A(r)+B</u>	*
				<u>A+B</u>	<u>A+B</u>	<u>A(r)+B</u>	<u>A(r)+B</u>	<u>A(r)+B</u>		<u>A(r)+B</u>	*
300	HV	ac		*	*	*	*	<u>B+R(f)</u>	*	*	*
		vc									
	UHV	ac									
		vc									
350	HV	ac									
		vc									
	UHV	ac									
		vc									
380	HV	ac									
		vc									
	UHV	ac									
		vc									

Notation for orientation: * - no data; A - 2x{110}; B - {001}; D - double diffraction; R - random. Intensities: f-faint; vf-very faint.

Relative abundance of orientation: Dominant orientation is underlined; r - rare.

interpreted as due to diffraction by $\{001\}$ oriented CaF_2 crystallites. Films that gave patterns such as shown in Fig. 3b were thus in the $2x\{110\} + \{001\}$ orientation. This interpretation of Fig. 3a was verified by tilting the specimen during TED and analyzing the different diffraction patterns that appeared.

Note that in Fig. 2a, of the spots of types S_2 and S_3 , only the latter are clearly present. Spots S_2 cannot arise by double diffraction and therefore when they are detected, $\{001\}$ oriented CaF_2 crystallites are present. Spots S_3 , however, may arise by double diffraction as well as from the presence of $\{001\}$ oriented crystallites. Since the structure factor for spots S_2 (200 type reflections) is much less than for S_3 (400 type reflections), it is possible for spots S_2 to be too weak to detect even in cases where S_3 are clearly present. Thus the film of Fig. 2a may have a weak concentration of $\{001\}$ oriented crystallites in addition to the dominant $2x\{110\}$ orientation.

TED patterns for thick films in the $2x\{110\} + \{001\}$ orientation showed additional double diffraction spots due to the presence of the $\{001\}$ orientation. See Fig. 4a. The $2x\{110\}$ orientation and its double diffraction spots are marked in Fig. 4b in a way similar to that used in Fig. 2b. Figs. 4a and 4b contain additional spots not present in Figs. 2a and 2b. The additional spots are marked by the large open squares and small solid squares in Fig. 4b. The large open squares indicate the $\{001\}$ orientation. The small solid squares (which include the four marked S_1) are due to double diffraction between the $2x\{110\}$ spots and the $\{001\}$ oriented CaF_2 . The intensities of the spots marked S_1 (contrary to the case discussed for Fig. 2) are directly related to the concentration of

{001} crystallites, as indicated by the intensities of the spots in the normal {001} diffraction pattern.

Complex UHV RHEED patterns also were observed. A typical pattern obtained for films formed on vacuum cleaved NaCl at 25 and 100°C in UHV is shown in Fig. 5a. Different patterns were observed for other azimuths, showing that the pattern of Fig. 5a was not due only to a simple fiber axis perpendicular to the film. The broadness of the spots is due partially to electrostatic charging. The interpretation of Fig. 5a is given in Fig. 5b. This diffraction pattern was the result of diffraction from two sets of {110} oriented crystallites. Set 1 has $[1\bar{1}0]$ parallel to the electron beam and set 2 has $[00\bar{1}]$ parallel to the electron beam. The separate diffraction patterns from sets 1 and 2 are indicated by open and solid circles, respectively, in Fig. 5b. The spots common to both patterns are indicated by solid triangles. The epitaxy of films that gave the diffraction pattern shown in Fig. 5a may be characterized as follows: for set 1, $\{110\} \text{ CaF}_2 // \{001\} \text{ NaCl}$ with $\langle 011 \rangle \text{ CaF}_2 // \langle 011 \rangle \text{ NaCl}$ and for set 2, $\{110\} \text{ CaF}_2 // \{001\} \text{ NaCl}$ with $\langle 001 \rangle \text{ CaF}_2 // \langle 011 \rangle \text{ NaCl}$. The interpretation of Fig. 5a is consistent with that given for Fig. 1a. It is thus equivalent to the $2x\{110\}$ orientation. The two superimposed {110} reciprocal lattice nets that are parallel to the {001} NaCl substrate may be constructed from the interpretation given to Fig. 5a. This construction has already been shown in Fig. 1b. The azimuthal epitaxy of the CaF_2 films relative to the NaCl substrate, as inferred from the RHEED data, is indicated in Fig. 1b. It is clear that the epitaxy of the combined pattern may be indicated by $\{110\} \text{ CaF}_2 // \{001\} \text{ NaCl}$ with average $\langle 111 \rangle \text{ CaF}_2 // \langle 100 \rangle \text{ NaCl}$ ³.

UHV RHEED patterns for films formed at 200 to 300°C on ac NaCl were of the type shown in Fig. 5c. The corresponding interpretation is given in Fig. 5d. This diffraction pattern is made up of the superposition of 1) a net due to prominent diffraction from {001} oriented monocrystalline CaF_2 in parallel aximuthal orientation with the NaCl substrate, 2) arcs due to diffraction from crystallites with a fiber texture consisting of {110} parallel to the surface of the substrate, and 3) rings due to some randomly oriente' crystallites.

Films formed on vc NaCl at 200°C in UHV gave RHEED patterns similar to Fig. 5c. However, the diffracted intensities due to {110} oriented and randomly oriented crystallites were reduced. The majority of the crystallites (sampled by the RHEED beam) in UHV films formed at 200°C on vc NaCl were thus in the parallel orientation, i.e. {001} CaF_2 // {001} NaCl and $\langle 100 \rangle \text{CaF}_2$ // $\langle 100 \rangle \text{NaCl}$.

The RHEED data for UHV films formed on vc NaCl at 300°C suggested that these films contained mainly {001} oriented monocrystals in parallel orientation with the NaCl substrate. A typical UHV RHEED pattern obtained from such films is shown in Fig. 5e.

2. Diffraction Evidence for the Epitaxy of CaF_2 on {001} NaCl:

The specific diffraction data obtained for CaF_2 films are listed in Table I. All the substrates were baked prior to deposition. HV films formed on baked and unbaked vc NaCl gave essentially identical TED patterns. The crystalline orientation that occurred was found to be a function of the deposition temperature, film thickness, the substrate condition (ac or vc), and the residual gas pressure during deposition. The effect of deposition temperature was as follows: at

25°C the $2x\{110\}$ orientation dominated the $\{001\}$ orientation. At 200°C both $2x\{110\}$ and $\{001\}$ oriented CaF_2 were present in roughly equal amounts. At temperatures above 200°C the $\{001\}$ orientation dominated the $\{110\}$ orientation.

The effect of film thickness on the structure of the films varied with the deposition temperature. See Table I. At 25°C the amount of $\{001\}$ oriented CaF_2 varied in a somewhat complex manner with film thickness, vacuum, and substrate condition (ac or vc). At 200°C and above an increase in film thickness resulted in an increase in the amount of $\{001\}$ oriented CaF_2 . Thus the $\{001\}$ orientation dominated the $2x\{110\}$ orientation in 1000 Å thick films formed at 200°C. At 350°C (HV films), the amount of $2x\{110\}$ oriented CaF_2 decreased with increasing film thickness while the amount of $\{001\}$ oriented material increased. The $2x\{110\}$ orientation was very rarely observed for 350°C films of thickness above 1) 500 Å on ac NaCl and 2) 150 Å on vc NaCl. These films were predominantly $\{001\}$ oriented monocrystals.

Films formed on air cleaved NaCl generally contained more randomly oriented CaF_2 than films formed on vacuum cleaved NaCl. The random orientation was often more pronounced in UHV films formed on vacuum baked ac NaCl than in the corresponding HV films.

Four HV and five TV runs were made in which 1000 Å thick films were formed simultaneously on baked and unbaked ac NaCl and on baked vc NaCl, respectively. The diffraction results for films formed on unbaked ac NaCl were not consistent from run to run. Some of these films were randomly oriented while others were highly oriented. Consistent results were obtained, however, for the films formed on baked ac and vc NaCl.

The latter films were always highly oriented. The inconsistent results for films formed on unbaked ac NaCl may be due to different levels of impurity in the NaCl and CaF_2 used. This possibility was not explored in detail. The CaF_2 used in the present study as well as in the earlier work^{3,4} was purchased from Harshaw Chemical Company in batches of chips that remained after cutting operations at the factory. The batches were originally made of at least two varieties⁷ of CaF_2 , namely "rare earth free" and natural CaF_2 (containing traces of rare earth impurities).

B. Microstructure of CaF_2 Films Formed on {001} NaCl

The results obtained by transmission electron microscopy and surface replication techniques are presented in Table II. It was found that the 30 Å thick films were generally composed of islands (Fig. 6a) and that continuity was complete when the thickness reached 60 Å (Fig. 6b). A few holes remained in the latter. Some of the films exhibited fine cracks (Fig. 6b). Because films without a SiO overlayer shattered into fine pieces when the film and substrate were immersed in water, it is believed that strains induced by the SiO layer were not the prime causes of the cracks. These cracks were possibly caused by stresses originating in the CaF_2 films during deposition and/or brittle fractures formed during handling, most likely the former.

Thick films formed at 25 to 100°C on ac and vc NaCl contained many small crystallites; see Fig. 6c. A typical surface replica for thick CaF_2 films formed in the range 25 to 100°C in HV on ac and vc NaCl is shown in Fig. 6d. While the orientations of the crystallites making up these ac and vc films varied substantially (Table I), the micrographs

TABLE II

			Microstructure (Transmission Electron Micrographs and Surface Replicas)					
DEPOSITION CONDITIONS	Temperature °C	Pressure	Substrate	FILM THICKNESS (Angstroms)				
				30	50 - 60	150	300 - 330	500 - 1500
25	{ HV	{ ac	DC		C+H(r)+K		C+K(r)	C,N(pd)
			DC		C+H(r)+K		C+K(r)	C,N(pd)
		{ vc		C+H(r)+K			C,N(pd)	
				C+K			C,N(pd)	
	{ UHV	{ ac	*		*	*		
				C			C,N(pd)	
		{ vc					C,E,N(pd)	
							C,E,N(pd)	
	{ 100	{ UHV	{ ac	*	*	*	*	
								C,E,N(pd)
		{ vc					C,E,N(pd)	
							C,E,N(pd)	
150	{ UHV	{ ac	*	*	*	*		
							C,E,N(wd)	
		{ vc					C,E,N(wd)	
							C,E,N(wd)	
	{ 200	{ HV	{ ac	DC	C+H(r)	*	*	
				C+H	C+H(r)			C,E,N(wd)
		{ vc		C			C,E,N(wd)	
							C,E,N(wd)	
	{ UHV	{ ac	*		*	*		
				C			C,E,N(wd)	
		{ vc					C,E,N(wd)	
							C,E,N(wd)	
250	{ UHV	{ vc	*	*	*	*		
							C,E,N(wd)	
		{ ac					C,E,N(wd)	
							C,E,N(wd)	
	{ 300	{ HV	{ ac	*	*	*	*	
								C,E,N(wd)
		{ vc					C,E,N(wd)	
							C,E,N(wd)	
	{ UHV	{ ac	*	*	*	*		
							C,E,N(wd)	
		{ vc					C,E,N(wd)	
							C,E,N(wd)	
350	{ HV	{ ac	DC	C	C	C+N		
							C,E,N(wd)	
		{ vc	DC	C	C	C+N		
							C,E,N(wd)	
	{ UHV	{ ac	*	*	*	*		
							C, no E or N	
		{ vc					C, no E or N	
							C, no E or N	

Notation: C - continuous films; DC - discontinuous films; H - holey film; N - needle-shaped crystals, see Fig. 7a; E - large crystals of type E, see Fig. 7a; K - small cracks, see Fig. 6b; * - no data; pd - poorly developed; wd - well developed.

all showed microstructures and topographies that were very similar to those shown in Figs. 6c and 6d.

Characteristic crystallographic streaks were observed by Bujor and Vook³ in the transmission electron micrographs of films formed between 150 and 350°C. Such streaks were observed in all thick films formed between 25 and 350°C in the present study. Generally they were very poorly developed and much more difficult to detect at lower deposition temperatures (see Fig. 6c, where very few such streaks can be seen). A high resolution micrograph illustrating these streaks at higher temperatures is shown in Fig. 7. Transmission electron micrographs obtained from broken edges of the films showed that the streaks were due to a layer of needle-like shaped CaF_2 crystallites. See the dark lines N in Fig. 7a. Surface replicas of the films showed that the needles formed the major part of the upper surface structure; see Fig. 7b. A somewhat similar replica was reported by Bauer¹ for a 3000 Å thick CaF_2 film formed at 400°C in TV on {001} NaCl. Fig. 7a shows that the long axes of the needles are perpendicular to each other. They are parallel also to the mutually perpendicular $\langle 110 \rangle$ directions of the {001} oriented CaF_2 (or equivalently parallel to the two mutually perpendicular $\langle 001 \rangle$ directions of the $2 \times \{110\}$ oriented CaF_2). See Fig. 8. The average diameter of the needles was approximately 50 Å and was independent of the deposition temperature. However, needle diameters as low as 25 Å and as high as 120 Å were measured in some micrographs. One potential application for films containing such needles might be for determining resolution in scanning electron microscopy.

It was mentioned in the Introduction that the previous authors³ observed reciprocal lattice spikes in TED patterns of thick films formed at 350°C. These spikes were interpreted as due to line broadening of thin (~ 20 Å thick) crystallographic rods or platelets which were parallel to $\langle 110 \rangle$ directions in the $\{001\}$ oriented films. Similar spikes and needle-shaped crystallites were observed in the present study. Moreover, diffraction patterns taken in different azimuths showed that the spikes through the major spots did not disappear, strongly suggesting that the spikes were in reality due to "discs" in reciprocal space perpendicular to the needle axes. The discs, which are not necessarily circular, are presumed to arise from the small cross-section of the needle-shaped crystallites. The density of the needle-shaped crystallites increased with deposition temperature up to 350°C where they also were most highly developed. The intensities of the diffraction spikes increased with increasing deposition temperature. When one set of needle crystallites dominated the micrograph, the corresponding $\{001\}$ diffraction pattern showed only one set of spikes through all the spots.

Transmission electron micrographs of broken edges showed that large crystals of the type marked E in Fig. 7a occurred in thick films. Two sets oriented at 90° to each other can be observed in the insert in Fig. 7a. These large crystals were irregularly shaped at lower temperatures but became crystallographically well developed at and above 250°C deposition temperatures. In this latter temperature range surface replicas showed that these large crystals occurred less often and were especially concentrated at cleavage steps (see Fig. 7b).

The results from dark field transmission electron microscopy are given in Figs. 8. Spots that were due solely to crystallites in the

{001} orientation (such as those numbered 1 in Fig. 8a) gave electron micrographs as shown in Fig. 8b. Spots due to the $2x\{110\}$ orientation (such as those numbered 2 in Fig. 8a) gave electron micrographs as shown in Fig. 8c. Note that the needle-shaped crystallites are present in Fig. 8b but that none appear in Fig. 8c. The latter figure shows only larger crystals that were similar to those marked E in Fig. 7a. In most of the dark field micrographs from the {001} diffraction pattern, one set of needles predominated. However, it was usually possible to see a few needle-shaped crystallites from a second set oriented at 90° to the first. It was thus concluded that in general two sets of needle-shaped crystallites oriented at 90° to each other were responsible for the {001} orientation, while two sets of the larger crystals also oriented at 90° to each other, were responsible for the $2x\{110\}$ orientation. This conclusion is consistent with the following experimental facts: (1) the {001} orientation became more pronounced at higher temperatures (see Table I; (2) RHEED patterns, indicative of the upper part of the film, showed a dominant {001} orientation at higher deposition temperatures, while transmission patterns showed both {001} and the $2x\{110\}$ orientations (see Fig. 5e and Table I); (3) Surface replicas of high temperature CaF_2 films showed that their surfaces consisted predominantly of needles (see Fig. 7b) except in regions corresponding to cleavage steps on the NaCl substrate; (4) Transmission electron micrographs taken at broken edges of the high temperature films showed that a layer consisting predominantly of needles lay on top of a layer consisting mainly of larger crystallites (see Fig. 7a).

IV. DISCUSSION

In the present work the epitaxy of CaF_2 films formed in HV and UHV on ac and vc NaCl substrates was studied as a function of substrate temperature, film thickness, and substrate conditions. The microstructure was characterized by UHV RHEED, transmission electron microscopy and diffraction, and surface replication techniques.

The main results of the present study were similar to those reported by Bujor and Vook.^{3,4} These authors found that $2\times\{110\}$ oriented polycrystalline films were formed on $\{001\}$ NaCl below 250°C . These films consisted of two sets of epitaxial $\{110\}$ oriented crystallites rotated by 90° relative to each other. In the present work the presence of some parallel $\{001\}$ oriented CaF_2 , coexisting with the $2\times\{110\}$ oriented crystals, was detected in this temperature range. It was found that the films were $2\times\{110\} + \{001\}$ oriented and that the parallel $\{001\}$ orientation was favored at higher substrate temperatures. The azimuthal orientation of the $2\times\{110\}$ oriented CaF_2 , as reported before,³ was verified with RHEED examinations. Bauer¹ reported a dominant parallel orientation for films less than 100 Å thick formed at room temperature. At greater thicknesses the parallel orientation was lost and $\{110\}$ oriented CaF_2 developed.¹ In the present investigation films of thicknesses less than 100 Å formed at 25°C were predominantly $2\times\{110\}$ oriented and the parallel orientation occurred only in small portions of these films.

In the present study the $\{001\}$ oriented CaF_2 was always in parallel orientation with respect to the NaCl substrate. This result is in agreement with that given by Bauer.¹ Bujor and Vook³, however, reported

that {001} oriented CaF_2 was rotated by 45° from the parallel orientation relative to the NaCl substrate. Their conclusion was based on the observation of fractures in the film which they assumed were parallel to large $\langle 100 \rangle$ oriented cleavage steps on the {001} NaCl surface. In the present work, however, it was found that the parallel oriented {001} CaF_2 films often tended to fracture along the $\langle 110 \rangle$ directions in the plane of the films. This latter observation is consistent with the view that the {001} oriented CaF_2 film tended to fracture by cleavage along its {111} cleavage face. The intersection of this face with the {001} surface of the film is along $\langle 110 \rangle$.

Direct evidence was obtained for the presence of two sets of mutually perpendicular {001} oriented thin needle-shaped crystallites. The axes of the needles lay along $\langle 110 \rangle$ directions of the NaCl substrate. These crystallites appeared to be responsible for the reciprocal lattice discs that gave rise to the spikes observed in the corresponding selected area TED patterns³. It was shown that the upper part of the films, that is, that portion of the CaF_2 film farthest from the substrate, consisted largely of these needle-shaped crystallites. Underneath the needle structure, and sometimes protruding above the film surface, were larger crystals. Dark field microscopy showed that these larger crystals were $2x\{110\}$ oriented. In analogy with this latter notation, the {001} orientation of CaF_2 crystallites could be designated as $2x\{001\}$. Thus one of the most interesting aspects of these CaF_2 films is that they are polycrystalline and epitaxial. An important problem for future study would be an investigation of the interfaces between the $2x\{110\}$ and $2x\{001\}$ sets of crystallites which compose these films.

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FIGURE CAPTIONS

FIG. 1a: COMPLEX TED PATTERN FOR A 30 Å THICK CaF_2 FILM FORMED AT 25°C ON vc NaCl IN HV ILLUSTRATING THE $2\times\{110\}_2$ ORIENTATION.

FIG. 1b: INTERPRETATION OF FIG. 1a.

○ - SET 1 } $\{110\}$ ORIENTED CaF_2
 ⊗ - SET 2 }

FIG. 2a: COMPLEX TED PATTERN FOR A 1000 Å THICK CaF_2 FILM FORMED AT 25°C ON BAKED vc NaCl IN HV.

FIG. 2b: INTERPRETATION OF 2a.

△, ○ - SET 1 } $\{110\}$ ORIENTED CaF_2
 ⊗ - SET 2 }
 ○, —, AND △ : DOUBLE DIFFRACTION BETWEEN SETS 1 AND 2 AND VICE VERSA.

FIG. 3a: COMPLEX TED PATTERN FOR A 60 Å THICK CaF_2 FILM FORMED AT 200°C ON ac NaCl IN HV ILLUSTRATING THE $2\times\{110\}_2 + \{001\}$ ORIENTATION.

FIG. 3b: INTERPRETATION OF FIG. 3a.

○ - SET 1 } $\{110\}$ ORIENTED CaF_2
 ⊗ - SET 2 }
 ▣ - $\{001\}$ ORIENTED CaF_2 .

FIG. 4a: COMPLEX TED PATTERN FOR A 500 Å THICK CaF_2 FILM FORMED AT 200°C ON vc NaCl IN HV.

FIG. 4b: INTERPRETATION OF FIG. 4a.

○, ⊗, ○, —, AND △ : SAME AS FIG. 2b.
 ▣ - $\{001\}$ ORIENTED CaF_2
 ▣ - DOUBLE DIFFRACTION BETWEEN ○ OR ⊗ ACTING AS INCIDENT BEAMS ON ▣ AND VICE VERSA.

FIG. 5a: UHV RHEED PATTERN FOR A 500 Å THICK CaF_2 FILM FORMED IN UHV AT 100°C ON vc NaCl. ELECTRON BEAM PARALLEL TO $\langle 011 \rangle$ NaCl.

FIG. 5b: INTERPRETATION OF 30a.

○ - SET 1 } $\{110\}$ ORIENTED CaF_2
 ⊗ - SET 2 }
 △ - SPOTS COMMON TO BOTH SETS.

FIG. 5c: UHV RHEED PATTERN FOR A 500 Å THICK FILM FORMED ON ac NaCl AT 200°C IN UHV. ELECTRON BEAM PARALLEL TO $\langle 110 \rangle$ NaCl.

FIG. 5d: INTERPRETATION OF 30c.

⊗ - $\{001\}$ ORIENTED CaF_2 .
 △ - ARCS DUE TO $\{110\}$ ORIENTED CRYSTALLITES.

FIGURE CAPTIONS (CONT.)

- FIG. 5e: UHV RHEED PATTERN FOR A 750 Å THICK FILM FORMED ON vc NaCl AT 300°C IN UHV. ELECTRON BEAM PARALLEL TO $\langle 100 \rangle$ NaCl AND $\langle 100 \rangle$ CaF_2 .
- FIG. 6: MICROGRAPHS OF CaF_2 FILMS FORMED IN HV ON {001} NaCl. (a) 30 Å THICK FILM FORMED ON ac NaCl AT 200°C, (b) 60 Å THICK FILM FORMED ON vc NaCl AT 25°C, (c) 1000 Å THICK FILM FORMED ON vc NaCl AT 25°C, AND (d) SURFACE REPLICA OF A 1000 Å THICK FILM FORMED ON ac NaCl AT 25°C.
- FIG. 7: TRANSMISSION ELECTRON MICROGRAPHS AND SURFACE REPLICA OF A 1000 Å THICK FILM FORMED AT 250°C IN UHV. (a) TWO EXAMPLES OF BROKEN EDGES IN THE FILM, (b) SURFACE REPLICA OF FILM SHOWN IN (a).
- FIG. 8: TED PATTERN AND DARK FIELD TRANSMISSION ELECTRON MICROGRAPHS FOR A 500 Å THICK CaF_2 FILM FORMED AT 200°C IN UHV ON ac NaCl. (a) TED PATTERN, (b) MICROGRAPH OBTAINED WITH A DIFFRACTION SPOT OF THE TYPE NUMBERED 1 IN 8a, (c) MICROGRAPH OBTAINED WITH A DIFFRACTION SPOT OF THE TYPE NUMBERED 2 IN 8a.

1a

1b

FA Rock + RW Rock

Figs 1a & 1b

F.H. Koss & R.W. Koss

Figs 2a & 2b

2a

2b

3a

3b

FA Koch + RW Vook

Figs 3a & 3b

4a

4b

F A Koch & R W Vook

Figs 4a & 4b

5a

5b

5c

5d

5e

FAKoch & RW Vook

Figs 5a-e

Figs 6a-d

F. Alcock & R. M. Wood

6d

6b

6a

7a

7b

Alcock + RLV book Figs 7a, 7b

8a

8b

8c

F.A. Koch & R.W. Vook

Figs 8a-c

V. ELECTRON IRRADIATION EFFECTS ON THIN CaF_2 FILMS

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ABSTRACT

CaF_2 films, 30 to 1000 Å in average thickness, were formed at 25 to 380°C on {001} NaCl under ultra high vacuum conditions. Transmission electron diffraction and microscopy showed that these films consisted of many {110} oriented crystallites coexisting with {001} oriented crystallites. It was found that high intensity 50 kV, 80 kV, and 100 kV electron beams in the electron microscope altered the structure of these films. The electron beams had a randomizing effect on the CaF_2 films. Extra diffraction rings were observed that could not be explained in terms of CaF_2 or double diffraction reflections. These extra rings were due to CaO. No diffraction evidence for free Ca metal was obtained. Previous work by T. Evans suggested that CaF_2 decomposes to form free Ca under the action of an electron beam. In the present work it is believed that electron irradiation first produces free Ca metal which then oxidizes to CaO in the relatively high oxygen partial pressure in the electron microscope.

INTRODUCTION

It is known that the structural state of oriented thin crystals of CaF_2 may be altered by electron beam irradiation in an electron microscope.^{1,2} Evans¹ reported the formation of free Ca metal during electron irradiation of {001} and {111} oriented CaF_2 . Parallel Moire fringe patterns were observed to form during electron microscope examination. Values of the d-spacings calculated by Evans¹ from the fringe spacings were in good agreement with those of Ca.

Vook and Bujor² pointed out that great care was needed in order to prevent the effect of electron beam irradiation during transmission electron microscopy of vacuum deposited {110} oriented CaF_2 films.³ They found that transmission electron diffraction patterns for these CaF_2 films taken at 100 kV were converted to diffraction patterns that contained rings with non-uniform intensity distributions. The rings observed in that work were due to polycrystalline CaF_2 and double diffraction among the various CaF_2 crystallites. No powder diffraction rings due to free Ca-metal were detected.

A detailed study of the structural aspects of the epitaxy of vapor deposited CaF_2 films formed on {001} NaCl was recently carried out in this laboratory.^{4,5} The purpose of this paper is to report on the effect of electron beam irradiation on the structure and composition of these CaF_2 films.

EXPERIMENTAL

CaF_2 films, 30 to 1000 Å in average thickness, were formed at 25 to 380°C on {001} NaCl under residual gas pressures of order 10^{-5} , 10^{-7} , and 10^{-9} Torr. The CaF_2 was evaporated from helical Ta wire baskets onto air cleaved and vacuum cleaved NaCl at rates from 5 to 10 Å/sec. The films were examined by UHV RHEED, transmission electron diffraction, and transmission electron microscopy.

RESULTS

The CaF_2 films consisted of many small epitaxial crystallites. The film structure varied from a complex {110} orientation at lower deposition temperatures to a simple {001} orientation at higher temperatures.^{3,4} Films containing both {110} and {001} oriented crystallites gave transmission electron diffraction patterns similar to the one shown in Fig. 1a. Its interpretation is given in Fig. 1b. Fig. 1a is made up of the superposition of two {110} reciprocal lattice planes and an {001} reciprocal lattice plane. The two {110} planes are rotated by 90° with respect to each other. The extra spots and streaks present in Fig. 1a are the result of double diffraction among the various CaF_2 crystallites.^{3,4} Films giving diffraction patterns such as Fig. 1a are said to be in the $2\times\{110\} + \{001\}$ orientation. Thick films formed at deposition temperatures above 300°C were predominantly {001} oriented, although the $2\times\{110\}$ orientation occurred in small areas of these films.

The structure of some areas of $2\times\{110\} + \{001\}$ and {001} oriented films was altered in the electron microscope by high intensity 50, 80, and 100 kV electron beams. The electron beam effect was most prominent

for 500 Å thick films formed at 200°C in UHV. The changes produced in the transmission electron diffraction patterns of $2x\{110\} + \{001\}$ oriented films are illustrated in Figs. 2a and 2b. Diffraction patterns of the type shown in Fig. 1a were changed by electron irradiation first to the type shown in 2a and, after more extensive electron bombardment, to the type shown in Fig. 2b.

Similar to the case reported by Vook and Bujor², it was found that the electron beam tended to randomize the CaF_2 film, resulting in the formation of Debye diffraction rings of CaF_2 and double diffraction among the various overlapping CaF_2 crystallites, see Fig. 2b. However, extra rings are present in Fig. 2b that do not belong to CaF_2 or double diffraction reflections. The calculated interplanar spacings d from rings 2, 4, 7, 10, 11, 15, 17, 18 and 20 in Fig. 2b and from the corresponding arcs in Fig. 2a are in excellent agreement with the first nine allowed reflections of CaO. See Table 1. Fig. 2a shows that the CaO is initially in parallel orientation with both the $2x\{110\}$ and the $\{001\}$ oriented CaF_2 , present in Fig. 2a. At a somewhat later stage during irradiation, both the CaF_2 and CaO become randomized. See the continuous diffraction rings in Fig. 2b.

Transmission electron micrographs obtained before and after extensive electron bombardment are shown in Figs. 3a and 3b respectively. The two sets of mutually perpendicular crystallographic streaks as well as the darker areas (such as the one marked D), that are present in Fig. 3a, were typical of the thick (500 to 1000 Å thick) films formed at substrate temperatures above 150°C in UHV. It was shown elsewhere⁴ that the streaks

in the electron micrographs were due to a layer of thin needle-shaped crystallites having {001} parallel to the NaCl substrate, thus giving rise to the {001} orientation in the diffraction patterns from the $2x\{110\} + \{001\}$ oriented films. It was also shown that the dark areas D were caused in part by diffraction contrast from the {110} oriented crystallites.

Fig. 3b shows that some of the needle-shaped crystallites remain after extensive electron bombardment. The main effect of the electron bombardment, as detected in some micrographs, was the formation of more or less circular shaped diffuse areas of the kind marked L in Fig. 3b.

DISCUSSION

An electron beam induced alteration of the structure of CaF_2 films containing {110} and {001} oriented crystallites was observed. It was shown that CaO was formed under the action of a high intensity electron beam. Similar to previous studies^{1,2}, no diffraction rings from free Ca-metal were observed. However, in view of Evans' results¹, it is believed that under the action of the electron beam, some CaF_2 is converted to free Ca that forms in parallel orientation with respect to both the {110} and the {001} oriented CaF_2 crystallites. In the relatively high oxygen partial pressure of the electron microscope, this free Ca is then oxidized to form CaO, the latter being also in parallel orientation with respect to both the {110} and {001} oriented CaF_2 . The final stage of the electron beam irradiation effect was the randomizing of most of both the CaF_2 and the CaO crystallites.

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TABLE I-Indexing of Fig. 2b

Ring #	Measured d(A)	CaF ₂		CaF ₂ double dif- fraction (Fig. 1a) d(A)	CaO	
		hkl	dhkl		hkl	dhkl
1	3.15	111	3.153	2.38		
2	2.78				111	2.778
3	2.70	200	2.732		200	2.405
4	2.40					
5	2.38					
6	1.93	220	1.931		220	1.701
7	1.70					
8	1.65	311	1.647			
9	1.58	222	1.577		311	1.451
10	1.45				222	1.390
11	1.39					
12	1.36	400	1.366			
13	1.25	331	1.253			
14	1.24	420	1.226			
15	1.19				400	1.203
16	1.11	422	1.115			
17	1.09				331	1.104
18	1.07				420	1.076
19	1.03	333,511	1.051		422	0.982
20	0.98					
21	0.96	440	0.966			

FIGURE CAPTIONS

Fig. 1a Typical transmission electron diffraction pattern for a 500 Å thick $2\times\{110\} + \{001\}$ oriented CaF_2 film formed at 200°C in UHV.

Fig. 1b Interpretation of Fig. 1a.

- : set 1
- : set 2
- : spots due to $\{001\}$ oriented CaF_2
- — □ : spots due to double diffraction between ○ or ● acting as incident beams on □ or vice versa.

Fig. 2 Electron diffraction patterns from an irradiated CaF_2 film (a) initial appearance of CaO in parallel orientation with the $2\times\{110\}$ and the $\{001\}$ oriented CaF_2 , (b) final randomizing of the CaF_2 and CaO crystallites in the film.

Fig. 3 Transmission electron micrographs taken from the same area of a 500 Å thick CaF_2 film formed at 200°C in UHV, a) before extensive electron bombardment, b) after extensive electron bombardment.

Figs 1a and 1b

F.H. Koenig and R.W. Vook

2a

2b

3a

3b.

FA Rock + RW look

Figs 3a and 3b.

VI. DETACHABLE (111) Cu FILMS FORMED IN

ULTRA-HIGH VACUUM

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ABSTRACT

Epitaxial Cu films 1200Å thick were formed on evaporated (111) NaCl films in an ultra-high vacuum RHEED camera. Information on the surface structure, microstructure, and surface smoothness was obtained by in-situ RHEED techniques. The microstructure of the Cu films was also studied by transmission electron microscopy. (111) Cu films were doubly positioned. The smoothness of the films increased with increasing Cu deposition rate. The microstructure of the as-deposited Cu films also depended upon the deposition rate. Annealing the Cu films improved their perfection. However, the final microstructure of the annealed films was independent of the initial deposition rate. These annealed Cu layers were used as substrates for the epitaxial growth of Ag films several monolayers thick.

INTRODUCTION

Single crystal (001) oriented Cu films prepared either in high vacuum (HV), or ultra-high vacuum (UHV) have been studied by several authors.¹⁻¹⁰ Relatively little work has been reported on (111) oriented monocrystalline Cu films,¹¹⁻¹⁷ and there have been almost no investigations of their microstructure.¹⁸ The reasons most likely are due to the difficulties experienced in removing (111) Cu films from their

substrates, usually cleaved mica, molybdenite, or (111) surfaces of metals, as well as to interdiffusion in the latter case.¹³ A technique which avoids these problems was recently developed.¹⁸⁻²⁰ In this method monocrystalline Au, Ag, and Cu are grown on a thin (111) NaCl film formed on mica at approximately 1×10^{-6} torr.

In the present work epitaxial monocrystalline (111) Cu films were grown on (111) NaCl/mica in UHV. This result is important since previous reports indicated that in UHV polycrystalline films tended to grow on clean (001) NaCl.^{9,10} In addition, the surface microstructure, and surface smoothness of these films was investigated as a function of deposition rate and annealing. A preliminary investigation of the epitaxy of thin Ag films grown on these monocrystalline (111) Cu films was also carried out.

EXPERIMENTAL

All specimens described in this paper were grown in a UHV reflection high energy electron diffraction (RHEED) camera.²¹ The system is evacuated by a titanium sublimation pump and a vac-ion pump following pre-evacuation by two liquid nitrogen cooled sorption pumps. Without baking the system, pressures of around 5×10^{-9} torr were obtained after 24 hours of pumping. At such pressures, a 100Å thick NaCl film was evaporated onto a thin air-cleaved mica substrate at room temperature. This epitaxial NaCl film served as a substrate for subsequent deposition of 99.9999% Cu, previously degassed in a tungsten basket (2 baskets were used for high deposition rates) under a shutter while the NaCl/mica substrate was heated slowly to 400°C. This temperature was held for 15 minutes prior to depositing a 1200Å thick film of Cu at a desired rate onto the NaCl/mica substrate to form a completely continuous film. The thickness and

deposition rate were controlled by a thickness monitor (minimum resolution 1A). Deposition rates ranged from 0.2A/sec to 13A/sec. The pressure in the system during Cu evaporation never exceeded 5×10^{-8} torr. Both the Cu films deposited at 400°C and similar films annealed at 525°C for 10 minutes were investigated. In the following, the former will be called "as-deposited" and the latter "annealed". Annealing at a higher temperature or for longer times tended to deplete the thin NaCl film from the sandwich. This depletion resulted in strong adhesion of the Cu film to the mica substrate. As a result the Cu film could not be detached from its substrate. Both the as-deposited and annealed Cu films were studied, in situ, by RHEED for surface microstructure and smoothness. However, in general, RHEED was not carried out prior to or during film growth in order to prevent unknown irradiation effects on the nucleation and growth stages. When RHEED work was completed, the films were removed from the UHV-RHEED system and detached from their substrates by dissolving the sandwiched NaCl in distilled water. The detached film was examined immediately by 100 KV transmission electron microscopy (TEM).

Thin Ag films also were evaporated on some of the annealed monocrystalline Cu films. In this case, Ag was deposited on Cu at 300°C and was followed by a 10 minutes 400°C anneal. Ag film thicknesses ranged up to 20A.

RESULTS AND CONCLUSIONS

A. Cu Films

Monocrystalline (111) Cu films were grown in UHV (i.e. at residual gas pressures less than 5×10^{-8} torr) on freshly deposited (111) NaCl

films. However, the process of growing single crystal Cu in UHV was much more difficult than in HV. Only 8 of 15 evaporation runs made in UHV resulted in (111) single crystals. In the other 7 runs the films were polycrystalline, i.e. they showed spot and ring RHEED patterns. By contrast, (111) Cu films grown in a HV of 0.5 to 1.0×10^{-6} torr, under otherwise similar evaporation conditions, were consistently monocrystalline.²⁰

The smoothness of the surface of the Cu films was studied by RHEED as a function of annealing and deposition rate. Smoothness was judged by the elongation of the diffraction spots perpendicular to the specimen surface, the film being smoother when streaks rather than spots are observed. It was found that annealing had no detectable effect on smoothening the as-deposited Cu films. The smoothness of the surface, however, was observed to increase with increasing deposition rate. This result is illustrated in Fig. 1 which shows RHEED patterns of annealed (111) Cu films deposited at various rates. Figs. 1a and 1b also show that the films contained double positioning twins.²²

When the RHEED work was completed and the Cu specimen was removed from the system, some of the Cu films partially peeled-off their substrates upon exposure to air. The same phenomenon was never observed on Cu films evaporated in HV under otherwise similar evaporation conditions. This result suggests the adhesion of Cu to NaCl is poorer for films formed in UHV than in HV.

Transmission electron microscopy (TEM) showed that single crystal (111) Cu films deposited at different rates were completely continuous at a thickness of 1200 Å. Occasionally, a few holes were observed in

certain areas. Polycrystalline films, however, contained considerably more holes for the same average film thickness. Typical micrographs are shown in Fig. 2. The as-deposited (111) Cu films contained a high density of dislocations and the density increased with increasing deposition rate. Fig. 2 also shows some of the double positioning boundaries (indicated by D). These boundaries can be shown more clearly by dark-field techniques.²² See Fig. 3a where the $\frac{1}{3}\{\bar{2}\bar{2}4\}$ spot, circled in the transmission electron diffraction (TED) pattern, was used. The double positioning boundaries lie along $\langle 110 \rangle$ directions in the (111) plane and appear as bright lines on an otherwise dark background. The domain size bounded by the double positioning boundaries was estimated to be about 0.9, 0.45, 0.3 μ (in diameter) respectively for the as-deposited (111) Cu films evaporated at 0.2, 1.6 and 10 A/sec. Micro-twins and stacking faults were not observed in the as-deposited (111) Cu films. Transgranular twins, however, were always observed in the polycrystalline films, that is in those films that failed to grow as monocrystals.

Annealing the as-deposited (111) Cu films improved their microstructure. Greater improvement occurred for the Cu films deposited at higher rates. It was found also that Cu films deposited at different rates were about equivalent in microstructure after annealing. A typical micrograph of an annealed (111) Cu film is shown in Fig. 3b. Comparing Fig. 3b to Fig. 2c, which was deposited at an equivalent rate, shows the improvement in microstructure due to annealing. Generally speaking, annealing resulted in an increase in the double positioning domain size. The domain size of the annealed Cu films was estimated to range from 1.1 μ to 1.5 μ , being independent of the initial deposition rate. Large domains

more than $10\ \mu$ across were frequently observed. A large number of the grown-in dislocations disappeared during annealing, although the dislocation density of the annealed Cu films was still high ($10^9 \sim 10^{10}/\text{cm}^2$). Stacking faults and dislocation networks also were present in the annealed films.

B. Ag-Cu Films

UHV-RHEED patterns of Ag films ranging in thickness from 1 Å to 20 Å on annealed (111) Cu films were also obtained. See Fig. 4a. This $[1\bar{1}0]$ pattern was obtained from a 3 Å thick Ag film on a rough (111) Cu film. The spot pattern arises from the Cu substrate while the streaks are due to the Ag overgrowth. Faint double diffraction streaks, due to diffracted Cu beams acting as incident beams for the Ag film, may be seen around the central line above the transmitted beam. It is interesting to note that the Ag overgrowth is very smooth despite the roughness of its substrate. Since 3 Å of Ag is less than two (111) monolayers, we may conclude that the growth of Ag on Cu is two dimensional. When more Ag was deposited the Cu diffraction spots became fainter while the Ag diffraction streaks became brighter. At a Ag thickness of around 16 Å the diffraction pattern was due to Ag alone. Thus the elastically scattered electrons in this RHEED experiment arose from a surface layer less than 16 Å thick. A similar growth was observed for Ag on the smoother (111) Cu films evaporated at about 1 Å/sec. No diffraction pattern as observed by Gradmann^{16,17} and Krause²³ was found.

Fig. 4b shows a typical bright-field micrograph obtained from a

Ag-Cu film. Patches of misfit dislocations, as the one indicated by "M", are typical for the bi-layers. Micrographs showing misfit dislocation networks have also been obtained. The spacing between the misfit dislocations in Fig. 4b is around 48A. However, the spacing of the parallel (220) moire fringes would be 11A. A rotation moire between Ag and Cu would give a smaller spacing. Thus an interpretation of M in terms of a moire pattern is ruled out. The corresponding TED pattern showing Ag, Cu, and double diffraction spots as well as faint Kikuchi lines is also given.

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CAPTIONS

- Fig. 1 RHEED patterns of monocrystalline (111) Cu films evaporated at (a) 0.2 A/sec., (b) 1.2 A/sec., (c) 13 A/sec.
- Fig 2 Microstructure of as-deposited monocrystalline (111) Cu films evaporated at (a) 0.2 A/sec., (b) 1.6 A/sec., (c) 10 A/sec.
- Fig. 3 Microstructure of annealed monocrystalline (111) Cu films;
(a) Dark-field of $\frac{1}{3} \{2\bar{2}4\}$ reflection from a 1.2 A/sec. film,
(b) Bright-field of Cu film evaporated at 13 A/sec.
- Fig. 4 (a) RHEED pattern of a 3 A Ag overgrowth on a monocrystalline (111) Cu film evaporated at 0.2 A/sec. on NaCl/mica, (b) Microstructure of a Ag-Cu bilayer; C-Cu, S-Ag, and D-double diffraction.

1a

1b

1c

Fig. 1, a. b. c

2a

2b

2c

3a

3b

Fig. 3. a, b.

4a

4b

Fig. 4. a, b.

VII. EPITAXIAL Cu FILMS ON (111) AND (100) NaCl

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When one grows oriented or single crystal films on a substrate of different material the process is called "heteroepitaxy". Cleaved NaCl single crystal substrates usually are used for growing (100) single crystal. However, the same substrates could not be used for growing (111) single crystals. It would be very meaningful, in studying heteroepitaxy, to be able to grow single crystal films of different orientations on a common substrate material from which it may subsequently be removed.

Detachable single crystal Cu films of (111) and (100) orientations were deposited simultaneously on monocrystalline NaCl substrates. The substrates, which are (111) and (100) monocrystalline films, were prepared by depositing 100 $\text{\AA}$ of NaCl respectively onto a cleaved mica and a cleaved NaCl crystal at room temperature. Cu, 1100 $\text{\AA}$ thick, was then deposited on these substrates at the desired conditions. For comparison purposes, we also incorporated a vacuum cleaved and an air cleaved single crystal NaCl substrates in the runs.

The experimental variable in this work were the substrate temperature and Cu deposition rate. The temperature was measured directly on the substrate. The deposition rate and film thickness were controlled by a thickness monitor, and the total residual gas pressure in all of the runs was around 5×10^{-7} Torr.

Transmission electron microscope and electron diffraction were then used to determine the films' microstructure and crystal orientations. When log. rate was plotted vs. $1/T_{\text{empt.}}$ for all the deposited Cu films, the line separating the polycrystalline and monocrystalline regions was a straight line. This is shown in the first slide (1). An Arrhenius-type relationship was obtained. The next slide (2) shows the Arrhenius-type of plot for three types of Cu films on NaCl. The lines here indicate the critical epitaxial conditions. The activation energy for the polycrystalline-monocrystalline transition, as calculated from the plot, is 1.45 eV for (111) Cu films, 1.27 eV for (100) Cu films on air cleaved NaCl, and 1.24 eV for (100) Cu films on the evaporated (100) NaCl. It is obvious that for a constant deposition rate, the critical substrate temperature for epitaxial (111) Cu films is higher than that of (100) Cu films. Between (100) oriented Cu films, the critical epitaxial temperature for the air-cleaved NaCl is significantly higher than for the evaporated NaCl. Except in the case of very slow deposition rates, $\sim 0.1 \text{ A/sec.}$, we did not obtain single crystal Cu films on the vacuum cleaved NaCl. This result indicates that contamination by the residual gases is also a critical parameter in affecting the epitaxy of Cu on NaCl.

Cu films in the (111) orientation become continuous at a lower thickness than Cu films with (100) orientation. This result is shown in the next slide (3). This is a simultaneous deposition of Cu on (111) and (100) NaCl. The deposition variables are well within the single crystal region of both (111) and (100) Cu films. The (111) Cu film, at 900 Å thick, has already become continuous and is a single crystal. However, the (100) Cu film at the same thickness shows discontinuities and is slightly

mis-oriented from a single crystal. The same experimental conditions would result in a single crystal if it were thicker and continuous. This indicates that crystal reorientation occurs during coalescence of the Cu deposits.

The micro-structure of the (111) Cu single crystal films is different from that of (100) single crystal films. (111) epitaxial films are smoother and frequently twin-oriented. The next slide (4), on the left, shows a very smooth (111) Cu film deposited at a high deposition rate. The smoothness is indicated by the elongation of the diffraction spots. The Cu film on the right, which was deposited at a very slow deposition rate, is rougher. This RHEED pattern also reveals that the Cu film is twin-oriented. The twin-axis is along the [111] direction which is perpendicular to the surface. A typical micro-structure of (111) Cu epitaxial films is shown in the next slide (5). In (111) Cu films, double-positioning boundaries and high densities of dislocations are the only detectable lattice imperfections. Double-positioning boundaries lie in $\langle 110 \rangle$ directions. However, on the next slide (6), we will find transgranular twins in the highly oriented (111) polycrystalline film. These twins also lie along $\langle 110 \rangle$ directions. The micro-structure of mono-crystalline (100) Cu films is shown in the last slide (7). (100) single crystal films usually show uneven textures as revealed on the left picture. The film is continuous. However, it shows thick regions about $2000\text{\AA}$ wide separated by thinner regions. The thick regions probably correspond to the island structure that existed prior to coalescence. Note that faults extend across several of these thick regions indicating film continuity. The micrograph in the middle shows stacking faults and

dislocations, while the one on the right shows twins in dark field taken from a twin spot.

For both orientations, (111) and (100), the densities of the above mentioned lattice imperfections in Cu are strongly dependent on the deposition variables. A slower deposition rate together with a higher substrate temperature, in general, would grow Cu single crystal with a better micro-structure.

In conclusion, Cu films have been deposited simultaneously on (111) and (100) NaCl substrates. The critical epitaxial temperature and activation energy for the polycrystalline-monocrystalline transition for (111) Cu films on NaCl is higher than that for (100) Cu films. (111) Cu films become continuous at a thinner stage in film growth, and are smoother than (100) Cu films. The lattice imperfections that were observed in (111) Cu single crystal films are dislocations and double-positioning boundaries. However, in (100) Cu single crystal films micro-twins, stacking faults, and dislocations were observed.

FIG. I. (III) Cu on (III) NaCl on MICA

ARRHENIUS-TYPE PLOTS for Cu FILMS on (111) & (100) NaCl

FIG. 2

(111) Cu on (111) NaCl MICA

(100) Cu on (100)_e NaCl

SIMULTANEOUS DEPOSITION of Cu FILMS on NaCl: $T=345\text{ }^{\circ}\text{C}$
 $R=1.6\text{ A/SEC}$
 Thickness = 900 Å

$R = 15 \text{ A/SEC}$ $T = 400^\circ\text{C}$

$R = 0.2 \text{ A/SEC}$ $T = 400^\circ\text{C}$

AZIMUTH $\langle 110 \rangle$

(111) Cu FILMS on (111) NaCl/MICA
EFFECT of DEPOSITION RATE

MONOCRYSTALLINE (111) Cu on (111) NaCl/MICA: $T = 395^{\circ}\text{C}$ $R = 0.22 \text{ A/SEC}$

FIG. 5

HIGHLY ORIENTED (111) POLYCRYSTALLINE Cu FILM on
(111) NaCl/MICA $T=295^{\circ}\text{C}$, $R=1.8\text{A/SEC}$

FIG. 6

MICROSTRUCTURE of MONOCRYSTALLINE (100) Cu FILMS on (100) NaCl

VIII. MICROSTRUCTURAL CHARACTERIZATION OF THIN FILMS

I. INTRODUCTION

II. MACROSTRUCTURE: X-RAY DIFFRACTION

A. Peak Positions

1. Crystal structure
2. Uniform strains
3. Stacking faults in fcc materials
4. Thermally induced substrate stains

B. Line Profiles

1. Theoretical and experimental interference function
2. Crystallite size and microstrain
3. Twin faults in fcc materials

C. Integrated Intensity

1. Preferred orientation
2. Grain growth

D. Radial Distribution Function Analyses

III. MICROSTRUCTURES

A. High Energy Electron Diffraction (HEED)

1. Theory

- a. Reciprocal space
- b. Kinematic theory
- c. Ewald construction
- d. Typical reciprocal lattices
 - 1) Single crystal
 - 2) Randomly oriented polycrystalline material
 - 3) Polycrystalline material with a fiber axis

III. MICROSTRUCTURE (Cont.)

e. Kikuchi lines

1. Origin and use in structure analysis
2. Orientation of crystals
3. Kikuchi line maps

2. Transmission electron diffraction (TED)

a. Diffraction pattern analysis

1. Perfect crystal
2. Imperfect crystal
3. Polycrystalline material

b. Multiple scattering

3. Scanning electron diffraction (SED)

4. Low angle scattering electron diffraction (LASED)

B.. Transmission Electron Microscopy (TEM)

1. Perfect crystals

- a. Resolution of lattice planes
- b. Diffraction contrast and selected area TED
- c. Bright and dark field microscopy

2. Imperfect crystals

- a. Stacking faults
- b. Twins
- c. Dislocations
- d. Precipitates

3. Magnetic domain contrast

IV. SURFACE CHARACTERIZATION

A. Topography

1. Reflection electron microscopy (REM)
2. Scanning electron microscopy (SEM)
3. Replication TEM

B. Structure

1. Low energy electron diffraction (LEED)
2. Reflection high energy electron diffraction (RHEED)

V. COMPOSITION ANALYSIS

A. X-ray Fluorescence

B. Electron Spectroscopy

SUMMARY

A review of the research accomplished on this project will now be given. In the early years, most of our efforts were spent on developing the UHV-RHEED instrument. Simultaneously we investigated the possible substrates that were to be used in future work. Thus our first two publications were concerned with (110) and (001) CaF_2 films. More work was reported recently on these films (publications 8 and 9). We planned to investigate epitaxy on different faces of the same crystalline substrate. Along with the (110) and (001) CaF_2 films we considered use of the (111) CaF_2 face and investigated surface structures on this face that formed during thermal vaporization (publication 6).

We were also interested in using NaCl substrates and investigated NaCl films (publications 3 and 7). As a result we developed a method for forming detachable (111) oriented Cu, Ag, and Au films using thin (111) layers of NaCl vapor deposited on mica (publications 4, 5, 10, and 11). This latter development was extremely important in that now it was possible to form thin films in ultra high vacuum on NaCl/mica, carry out in-situ surface studies using RHEED, and finally be able to detach the film easily from the substrate for subsequent transmission electron microscopy studies. We are presently using this technique for correlating RHEED patterns of adsorbed monolayers with TEM studies. We hope to be able to detect the formation of interfacial dislocations in bilayers by RHEED and to confirm this conclusion with TEM.

Similar techniques are applicable to studies of the formation of

surface phases and transformations. We believe we are presently in the most productive phase of our research efforts using the UHV-RHEED camera.

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TECHNICAL PERSONNEL INVOLVED IN PROJECT

The following persons participated in the research efforts supported by this project:

1. Dr. Richard W. Vook, Principal Investigator
2. Mr. R. J. Portanova, Graduate Research Assistant
3. Mr. M. Bujor, Graduate Research Assistant
4. Mr. N. Bezerianos, Graduate Research Assistant
5. Mr. F. A. Koch, Graduate Research Assistant
6. Mr. C. T. Horng, Graduate Research Assistant
7. Mr. John Macur, Graduate Research Asssitant
8. Mr. John Siefken, part time student employed by General Electric Co.
9. Mr. Rolf Ziemer, Electron Microscope Technician

RESEARCH RESULTS

Masters Theses:

1. R. J. Portanova: "An Ultra High Vacuum High Energy Electron Diffraction Camera". July 1968.
2. M. Bujor: "A Study of the Epitaxial Deposition of CaF_2 on the (100) Cleavage Face of NaCl". May 1969.
3. N. Bezerianos: "Photo and Electron Optical Studies of the Etched and Thermally Evaporated (111) CaF_2 Cleavage Face". September 1971.
4. J. Siefken: "X-Ray Study of CaF_2 Layers". Expected completion date: January 1973.

Ph.D. Dissertations (completed or in progress)

1. F. A. Koch: "In Situ Ultra High Vacuum RHEED Studies of Thin Films and Surfaces". May 1972.
2. C. T. Horng: "Interfacial Dislocations Studied by RHEED and Transmission Electron Microscopy". Expected completion date: February 1973.
3. J. Macur: "UHV-RHEED Surface Studies". Title not definite. Expected completion date: September 1974.

Publications:

1. Bujor, Marc and Vook, R. W., "Epitaxial Poly and Monocrystalline CaF_2 Films". J. Appl. Physics 40, 5373 (1969).
2. Vook, R. W. and Bujor, Marc, "Epitaxial Polycrystalline CaF_2 Films". J. Vacuum Science and Technology 7, 115 (1970).
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4. Koch, F. A. and Vook, R. W. "Smooth Detachable (111) Monocrystalline Ag Films". J. Appl. Physics 42, 4510 (1971).
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7. Koch, F. A. and Vook, R. W., "Epitaxy of NaCl on Muscovite". Accepted for publication in Thin Solid Films.
8. Koch, F. A., and Vook, R. W., "The Vapor Epitaxy of CaF_2 on NaCl". Submitted to J. Appl. Physics.
9. Koch, F. A., and Vook, R. W., "Electron Irradiation Effects on Thin CaF_2 Films". Submitted to J. Vacuum Science and Technology.
10. Horng, C. T., and Vook, R. W., "Detachable (111) Cu Films Formed in Ultra High Vacuum". Submitted to J. Vacuum Science and Technology.
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12. Vook, R. W., "Microstructural Characterization of Thin Films". To be published as a chapter in Treatise on Materials Science and Technology, Vol. 3 (H. Herman, ed.), Academic Press, N. Y. (1973).

TALKS

1. October 31, 1969 American Vacuum Society Meeting, Seattle, Washington, "Epitaxial Polycrystalline CaF_2 Films".
2. March 31, 1971 American Physical Society Meeting, Cleveland, Ohio, "Epitaxy of CaF_2 on NaCl ".
3. August 9, 1971 Twenty Ninth Annual Electron Microscope Society of American Meeting, Boston, Mass., "UHV RHEED and Replica Studies of NaCl Films Formed on Mica".
4. October 11, 1971 Fifth International Vacuum Congress, Boston, Mass., "Atomically Smooth (111) Monocrystalline Metal Films Formed on NaCl ".
5. March 30, 1972 American Physical Society Meeting, Atlantic City, New Jersey, "Epitaxial Cu Films on (111) and (100) NaCl ".
6. August 18, 1972 Materials Science Seminar, Sandia Corporation, Albuquerque, New Mexico, "Surface Relaxation and Thin Film Studies".
7. October 4, 1972 American Vacuum Society Meeting, Chicago, Ill., "Detachable (111) Cu Films Formed in Ultra High Vacuum".