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VACUUM EVAPORATED AND CATHODIC SPUTTERED THIN FILMS

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RESEARCH AND TECHNOLOGY DIVISION
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

PROJECT NO. 4150, TASK NO. 415003

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FOREWORD

This report was prepared by the Physics and Infrared Section of General Dynamics/Pomona under Contract AF 33(657)-8728, Project No. 4150, Task No. 415003.

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The authors wish to thank their fellow scientists and assistants of the Physics and Infrared Section of General Dynamics/Pomona for their contributions to the success of this program. Specifically they acknowledge the contributions of Dr. Kronenberg and Miss P. Whipp (electron diffraction), Messrs. J. Tramontana (electrical measurements), J. Pinto and L. Kress (experimental assistance).

The valuable assistance of the personnel of the General Dynamics/ Pomona Chemistry Laboratory, in particular Messrs. D. Wilson and J. Maurits for x-ray diffraction data and spectroscopic analyses is also gratefully acknowledged.

ABSTRACT

The effects of formation conditions on the epitaxial growth of thin films deposited by cathodic sputtering and vacuum evaporation are reported. The primary condition parameters considered are substrate temperature and rate of deposition. Trends have also been established for the effect of thickness, annealing and residual gas pressure. The results of a detailed investigation of Ge sputtered onto single crystal Ge, both [111] and [100], and [111] CaF_2, are presented. Less detailed, but consistent results were obtained for identical film-substrate systems obtained by vacuum deposition. Data are also included for Ge deposited on single crystal Si, mica, amorphous quartz and glass. Other film-substrate systems considered include gold on rock salt and glass, silver on rock salt, and Si on Si.

The systematic dependence of the epitaxial temperatures and amorphous-crystalline transition temperatures of Ge films on the primary formation conditions is shown.

A qualitative, theoretical model describing the epitaxial process is suggested.

Initial data on the electrical properties of films produced both by sputtering and vacuum evaporation are presented.

Noteworthy is the random occurrence of N-type films. Deposition conditions for their formation are as yet undefined.

This technical documentary report has been reviewed and is approved.

Robert D. Larson
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Chief, Electronic Research Branch
Electronic Technology Division

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I. INTRODUCTION

The work reported here pertains to a research study on the epitaxial growth of single crystal films by vacuum evaporation and cathode sputtering.

Observations on the growth and properties of thin films have been made by many researchers. The results of these studies have shown that the properties of thin films depend on their formation conditions such as rate of deposition, substrate temperature, etc. Only recently, have systematic studies of the effects of formation conditions on the epitaxial growth of thin films been carried out. These studies, however, have involved only vacuum evaporated films.[1][2][3] No comprehensive study has apparently been made on cathodic sputtered films. The work reported here pertains to the effects of formation conditions on the epitaxial growth of thin films deposited by cathodic sputtering as well as vacuum evaporation.[4][5] However, the initial emphasis in this study was on sputtering. The condition parameters which are primarily considered are substrate temperature and rate of deposition. Other parameters for which some trends have been established are film thickness and post-growth annealing treatments.

While the current investigations cover a wide variety of film-substrate systems, this report emphasizes the epitaxial growth of germanium since the most systematic data have been obtained, to date, on this material. Germanium, as a function of the condition parameters, was sputtered on substrates of single crystal germanium, both [100] and [111] orientations and on cleaved surface of CaF_2 [111]. Single crystal mica, single crystal silicon [100], and amorphous quartz were also used as substrate materials for sputtered germanium. The results from the latter experiments will only

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be briefly indicated. Germanium was also evaporated, as a function of condition parameters, on substrates of the same materials used in sputtering. However, more detailed studies were performed for the case of sputtering. Studies on the evapcration of gold and silver **on rock salt** and glass as a function of formation conditions were initiated in this study. The results of this work will also be discussed briefly.

The ultimate objective of this work is to derive a theoretical description of the epitaxial growth processes as a function of the condition parameters. The consistency of the data on sputtered germanium promise to lend themselves readily for this purpose. The data obtained on identical film-substrate systems produced by vacuum evaporation show identical trends. This seems to indicate that a generalized treatment is feasible which is applicable to all epitaxial growth techniques.

Thus far, structural characterization of the films deposited was mainly considered in the determination of film quality. However, electrical characterization is necessary to determine what relations exist between films of equal structural quality produced by different techniques or under different conditions. Consequently, preliminary investigations of electrical properties have been undertaken for the purpose of correlating electrical properties with film structure.

Phases of the work reported here have been presented at the "Conference on Single Crystal Films" in Philadelphia, May, 1963 and at the American Vacuum Society Symposium in Boston, October, 1963. Two publications of this work will appear in the Proceedings of the Conference on Single Crystal Films and in the 1963 Transactions of The American Vacuum Society.

II. EXPERIMENTAL

A. FILM DEPOSITION TECHNIQUES

1. Sputtering System

The equipment comprising the sputtering system is shown in Figure 1. Several control features have been incorporated into this sputtering system for the purpose of maintaining a controlled sputtering rate and environment. Provisions are made to accurately measure and control gas pressure, cathode temperature, anode temperature and, therefore, substrate temperature. In addition, the sputtering system is equipped with the following features: (a) the operating voltage can be varied from 0-5000 Volts; (b) a mixture of two different gases (e.g., inert-inert, inert-reducing or reactive mixtures) can be used; (c) the inert and reducing gases are passed through an automatic gas purification system; (d) the deposition time is monitored and the deposition can be "turned" off and on automatically at pre-determined intervals.

A close-up of the cathode-anode arrangement in the sputtering chamber is shown in Figure 2. The cathode consists of a disk of intrinsic germanium, 3 1/2" in diameter and 5 mm thick, held by an aluminum block. The aluminum cathode holder has provision for circulating a liquid coolant through a cavity to control the cathode temperature. The anode consists of an alumina block with an imbedded tantalum strip heater. The alumina block is placed in contact with a tantalum disk which accommodates as many as seven substrates. The substrates are held in thermal contact with the tantalum disk by means of a second disk which also serves as a multiple mask. The substrate temperature is monitored by thermocouples mounted between the mask and the tantalum disk, and between the substrate surface and the mask. It

Figure 1. Sputtering Apparatus.

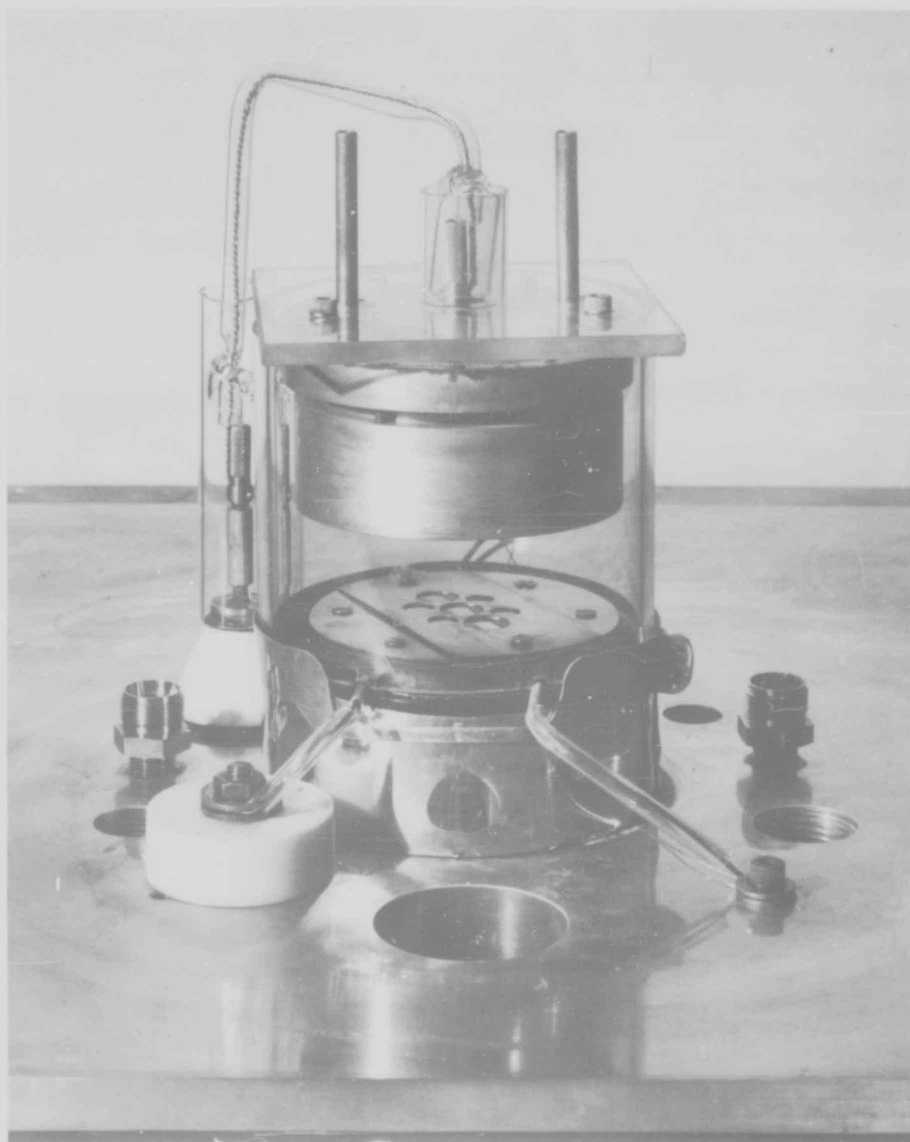


Figure 2. Cathode-Anode Arrangement of the Sputtering System.

should be noted that a difference in temperature is always observed between these two thermocouple measurements. We feel that these temperature measurements indicate the actual substrate temperatures perhaps more accurately than in most other reported studies.

2. Evaporation Systems

Two vacuum systems were used. The majority of the results reported here were obtained from a six-inch, oil diffusion pump CVC LC1-18B vacuum system. For some preliminary work and for the calibration of resistance and rate control monitors, a VEECO six-inch oil diffusion pump vacuum system was used. Both systems have an 18" x 30" glass bell jar. However, the CVC system has no gate valve, uses gold and viton seals and is equipped with liquid nitrogen baffle, heating blankets, etc. Its ultimate pressure falls in the low to medium 10^{-9} torr range. However, its ultimate working pressure falls in the middle to low 10^{-8} torr range. Figure 3 shows the CVC system along with the resistivity monitor, ultra clean bench, vacuum dry box, etc. The VEECO system has a gate valve, uses neoprene seals, and is not bakeable. Its ultimate pressure is in the 10^{-7} torr region. For the evaporation of metals and semiconductors, two heating techniques were used: resistive heating and electron bombardment. The resistive heater used was made of tantalum, molybdenum or tungsten in the form of boat or cup or coil. For example, aluminum was evaporated from a three-strand 25-mil tungsten coil and gold was evaporated from a tantalum boat. The arrangement used in electron beam heating is shown in Figure 4. The filament of the electron gun used is of the annular work-accelerated type, 5/8-inch diameter. It is made of 20-mil tantalum wire or 25-mil tungsten wire. Half an inch above and below the annular filament are two circular electron

Figure 3. Ultra-High Vacuum Deposition System, Resistivity Monitor, Clean Bench and Dry Box.

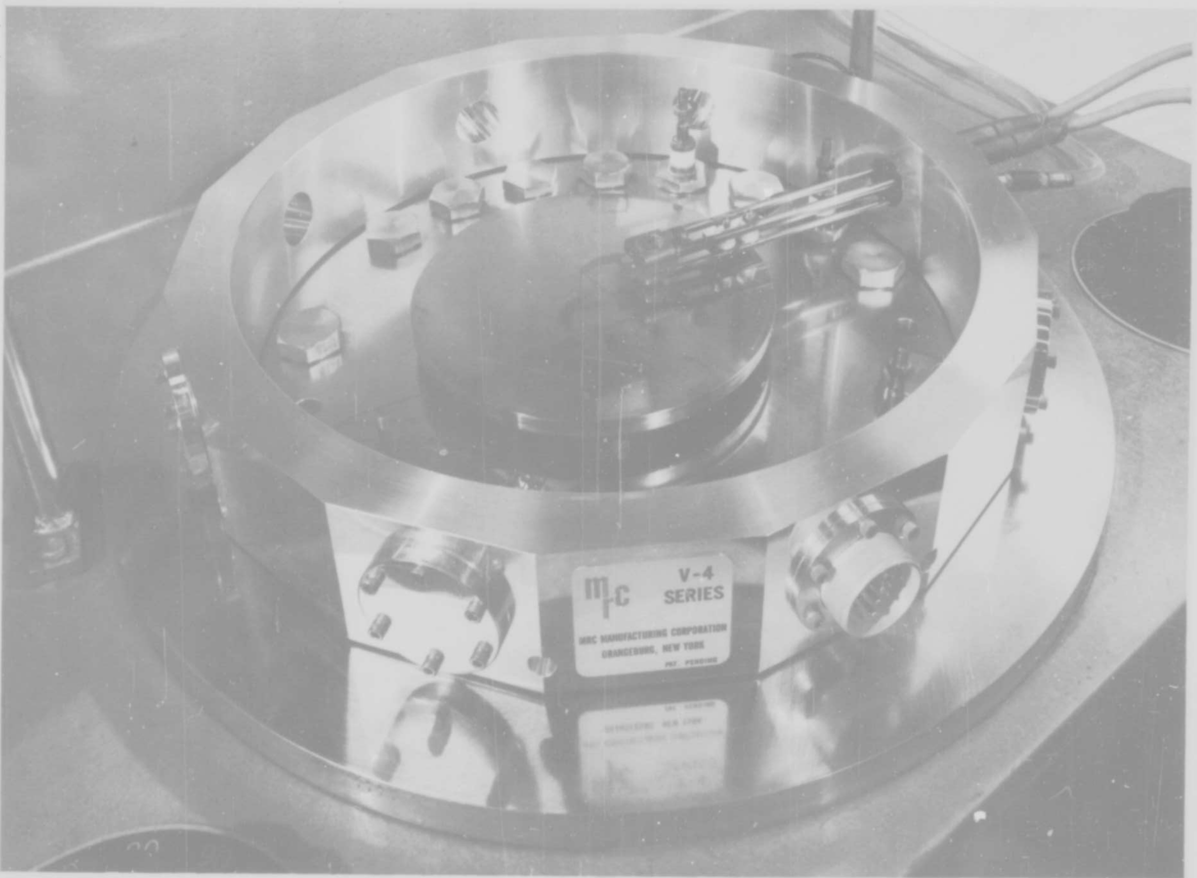


Figure 4. MRC V4-200 Electron Beam Vapor Deposition Assembly.

shields. In operation, these two shields are biased at the same negative potential as the filament. The source material to be evaporated is placed on a water-cooled pedestal and is at ground potential. The power supply used for electron beam generation is of the high reactance type so that no sparking is possible. Thus far, electron beam heating has been used only for the evaporation of germanium.

Several oven-type heaters were used to bring the substrate to the proper temperature. For high substrate temperatures, bare nichrome resistance coil was used as heating element. Nichrome wires insulated with magnesium oxide powder and stuffed in 321 stainless steel tubing were used for moderate substrate temperatures. Substrate temperature was measured with a chromel alumel thermocouple placed in the close proximity of the substrate as illustrated in Figure 4. The effect of the heat radiated from the source is minimized by the shutter and also by the fact that the source-to-substrate distance was kept as large as possible, 6-10 inches.

The substrate holder has a number of openings around its center. Above each opening, there was placed a mask and a substrate as shown in Figure 4. Although the positions of substrate are all slightly off center, because the source-to-substrate distance was kept large, the impingement of atomic beam onto the surface of substrate can be considered to have normal incidence for all practical purposes. The shutter used was of the rotary type. It has the same number of openings as the substrate holder and in corresponding positions. The closing or opening of the shutter is done by operating manually a rotary magnetic clutch from one predetermined position to another. This type of shutter is not satisfactory for very

high substrate temperatures. Currently we are experimenting with shutters of somewhat different types.

The evaporation rate was controlled by the power supply to the source heater. This controlling technique worked fairly satisfactorily for the case of gold, because the desired evaporation temperature of gold is only slightly above its melting point.

For the case of resistive heating, the total amount of material evaporated can be controlled by the use of a predetermined amount of the source material. In vacuum evaporation, the rate of deposition is not only controlled by the rate of evaporation but also by the distance between the source and the substrate. In most of the experiments reported here, the distance between the source and the substrate is controlled by placing a pyrex cylinder of the proper length below the substrate holder and shutter. By adjusting the power supplied the amount of source material, the distance between source and substrate, the time of evaporation, it is possible to control the rate of deposition and the thickness of the films.

3. Substrate Preparation

The germanium substrates are dislocation-free single crystals of both [100] and [111] orientation and non-dislocation-free single crystals of [111] orientation. The substrates are in the form of slices having a diameter of .499" and a thickness of .070". The surfaces of the substrates are mechanically polished and then etched with a CP-4 solution.

In the case of insulating substrates, cleavage surfaces are used for single crystals (e.g., CaF_2); the amorphous substrates are mechanically

polished. All substrates are cleaned with ultrasonic techniques and given a final wash in de-ionized ultra-pure water prior to placement in the sputtering chamber. In addition, the germanium substrates are given a final cleaning with HF solution.

The substrates are partially masked both for thickness determination and for direct comparison of the substrate and film after deposition. During each sputtering experiment, the sputtering system is first evacuated to a pressure in the 10^{-5} to 10^{-6} Torr region. The substrates are then heated and degassed until no degassing is observed.

In each evaporation experiment, after pumpdown and before admitting the liquid nitrogen to the cooling baffle, the source and substrate heaters are both turned on for half an hour for degassing purposes. The source temperature is kept well below the evaporation temperature, while the substrates are degassed at a temperature equal to or higher than the predetermined substrate temperature. In order to further decrease the residual gas pressure in the bell jar after the cooling baffle reaches the liquid nitrogen temperature, a liquid nitrogen cold trap was placed inside the bell jar in the working area. This technique has not shown any improvement due to several technical difficulties.

4. Deposition Conditions

In the study reported here, several sets of deposition conditions (corresponding to cathode voltage, sputtering current, argon pressure and cathode-anode spacing in the case of sputtering and in the case of evaporation, source temperature, source-substrate distance, and residual

gas pressure) are used. For each set, deposition is carried out as a function of substrate temperature. The various sputtering and evaporation parameters used as well as the corresponding substrate temperature range are summarized in Table I for each particular film-substrate system. In the case of sputtering, purified argon was used as the working gas and the cathode-anode spacing was kept at 5.7 cm in all experiments.

TABLE I

FORMATION CONDITIONS USED FOR VARIOUS SETS OF FILMS *
ON VARIOUS SUBSTRATES

SET NO.	SUBSTRATE	DEPOSITION TEMPERATURE	TEMPERATURE INTERVALS	SPUTTERING PARAMETERS
1	DISLOCATION FREE Ge [111]	280-500	50	3000V, 30MA, 60μ ARGON
		265-455	50	3000V, 20MA, 45μ ARGON
		320-370	20	3000V, 10MA, 35μ ARGON
		335		3000V, 4MA, 22μ ARGON
		235-300	10	3000V, 3.5MA, 19μ ARGON
		235-300	5	3000V, 3.0MA, 17μ ARGON
		190-280	10	3000V, 2.4MA, 16μ ARGON
2	DISLOCATION FREE Ge [100]	280-500	50	3000V, 30MA, 60μ ARGON
		320-370	20	3000V, 10MA, 35μ ARGON
		335		3000V, 4MA, 22μ ARGON
3	NON-DISLOCATION FREE Ge [111]	280-420	50	3000V, 30MA, 60μ ARGON
		265-420	50	3000V, 20MA, 45μ ARGON
4	CaF_2 [111] SINGLE CRYSTAL	340-455	40	3000V, 30MA, 60μ ARGON
		295-475	40	3000V, 20MA, 45μ ARGON
		295-415	15	3000V, 10MA, 35μ ARGON
		300-380	20	3000V, 6MA, 28μ ARGON
5	MICA	280-500	50	3000V, 30MA, 60μ ARGON
6	Si [111] SINGLE CRYSTAL	400-465	20	3000V, 20MA, 45μ ARGON
		350-500	50	3000V, 10MA, 35μ ARGON
		375-465	50	3000V, 6MA, 28μ ARGON
7	QUARTZ	340-500	50	3000V, 30MA, 60μ ARGON
		400-465	20	3000V, 20MA, 45μ ARGON
		350-500	50	3000V, 10MA, 35μ ARGON
		345-465	50	3000V, 6MA, 18μ ARGON
8	CERAMIC	320-370	20	3000V, 10MA, 35μ ARGON

*SET NO.'S 1-10 Ge FILMS
11, 12 GOLD FILMS
13 SILVER FILMS

TABLE I (CONT)

FORMATION CONDITIONS USED FOR VARIOUS SETS OF FILMS ON VARIOUS SUBSTRATES

SET NO.	SUBSTRATE	DEPOSITION TEMP (°C)	TEMP INTERVALS (°C)	EVAPORATION PARAMETERS
9	DISLOCATION FREE Ge [111]	480-200	30	*RGP $\sim 2 \times 10^{-7}$ TORR **S-S DISTANCE - 8" POWER TO ELECTRON GUN: 2.5KV, 400 ma
		355-300	50-5	RGP $\sim 1 \times 10^{-7}$ TORR S-S DISTANCE - 8" POWER TO ELECTRON GUN: 2.5KV, 350 ma
		500-400	50	RGP $\sim 10^{-6}$ TORR S-S DISTANCE - 8" POWER TO ELECTRON GUN: 3 KV, 400 ma
10	GLASS	515-385	50	RGP $\sim 3 \times 10^{-6}$ TORR S-S DISTANCE - 8" DEPOSITION RATE ~ 1000-7290 A°/HR
11	GOLD ON NaCl [200]	400-200	50	RGP $\sim 10^{-7}$ TORR S-S DISTANCE - 10" DEPOSITION RATE ~ 150A°/MIN
		400-250	50	RGP $\sim 10^{-4}-5 \times 10^{-8}$ TORR S-S DISTANCE - 10" DEPOSITION RATE ~ 150A°/MIN
12	GOLD ON GLASS	400-200	50	RGP $\sim 10^{-7}$ TORR S-S DISTANCE - 10" DEPOSITION RATE ~ 150A°/MIN
		350	–	RGP $\sim 10^{-4} - 10^{-7}$ TORR S-S DISTANCE - 10" DEPOSITION RATE ~ 150A°/MIN
13	Ag ON NaCl [100]	300-100	50	RGP $\sim 10^{-7}$ TORR S-S DISTANCE - 10" DEPOSITION RATE ~ 200A°/MIN

*RGP - RESIDUAL GAS PRESSURE
**S-S - SOURCE-SUBSTRATE

B. FILM ANALYSIS

1. Structural Analysis and Geometrical Analysis

Structural characterization of the film is made using electron reflection diffraction. Each film is observed over the entire surface to determine any differences in lattice orientation from one film region to another. The film orientation is compared directly with the lattice orientation of the substrate. Only those films are classified as single crystals for which diffraction patterns indicate single crystal structure and for which, in addition, the orientation remains identical over the entire surface of the film. Electron microscopy of surface replicas and optical microscopy are being used to investigate surface structures. Film thickness is measured using a Tolansky type interferometer. Sample dimensions, when necessary (for electrical measurements) are determined using a Gaertner Optical Comparator.

2. Electrical and Related Measurements - Equipment and Procedures

The electrical and electronic parameters of interest are carrier concentration, mobility, and type, resistivity and magneto-resistive effects, both at room temperature and as a function of temperature. Measurements with thin films of gold evaporated on various insulating substrates and with germanium sputtered and evaporated on germanium and other conducting and insulating substrates have been in progress.

Films are produced in a configuration which allows the performance of as many of the desired measurements as possible. The configuration chosen is one based on work done at the Bell Telephone Laboratories. Two

mil stainless steel masks were fabricated to allow deposition of films in this configuration. Sputtering dictates the use of masks of materials with low sputtering rates, such as tantalum. At present films are sputtered in a rectangular configuration and tabs are painted on to produce essentially the same configuration as shown in Figure 5.

After the samples are removed from the vacuum systems, lead wires are indium soldered on or thermal compression bonded to the paint using a Kulicke and Soffa Model 410 Thermal Compression Bonder and one mil annealed gold wire. Perhaps the best system, and one we hope to initiate upon completion of our multiple mask, multiple source device, is to evaporate low resistance leads on a film in a second evaporation immediately following the initial deposition. The films would then be immediately ready for measurement and the chances of contamination or physical damage minimized.

The sample is then mounted on a phenolic board which fits into a specially designed holder mounted on the framework of our Varian Four Inch Electromagnet System. This holder aligns the sample in the desired plane. All measurements needed to determine electrical parameters can be made with the sample in one position.

For the determination of the Hall mobility and the carrier type, four inch untapered pole caps and a working field between two and ten kilogauss have been used. Based on the manufacturer's (Varian Associates) calibration with a one inch operating gap the field is uniform to within 1% over a one inch radius which is several times the size of our largest samples. To keep leakage flux to a minimum a special shield of Conetic alloy has been designed and fabricated.

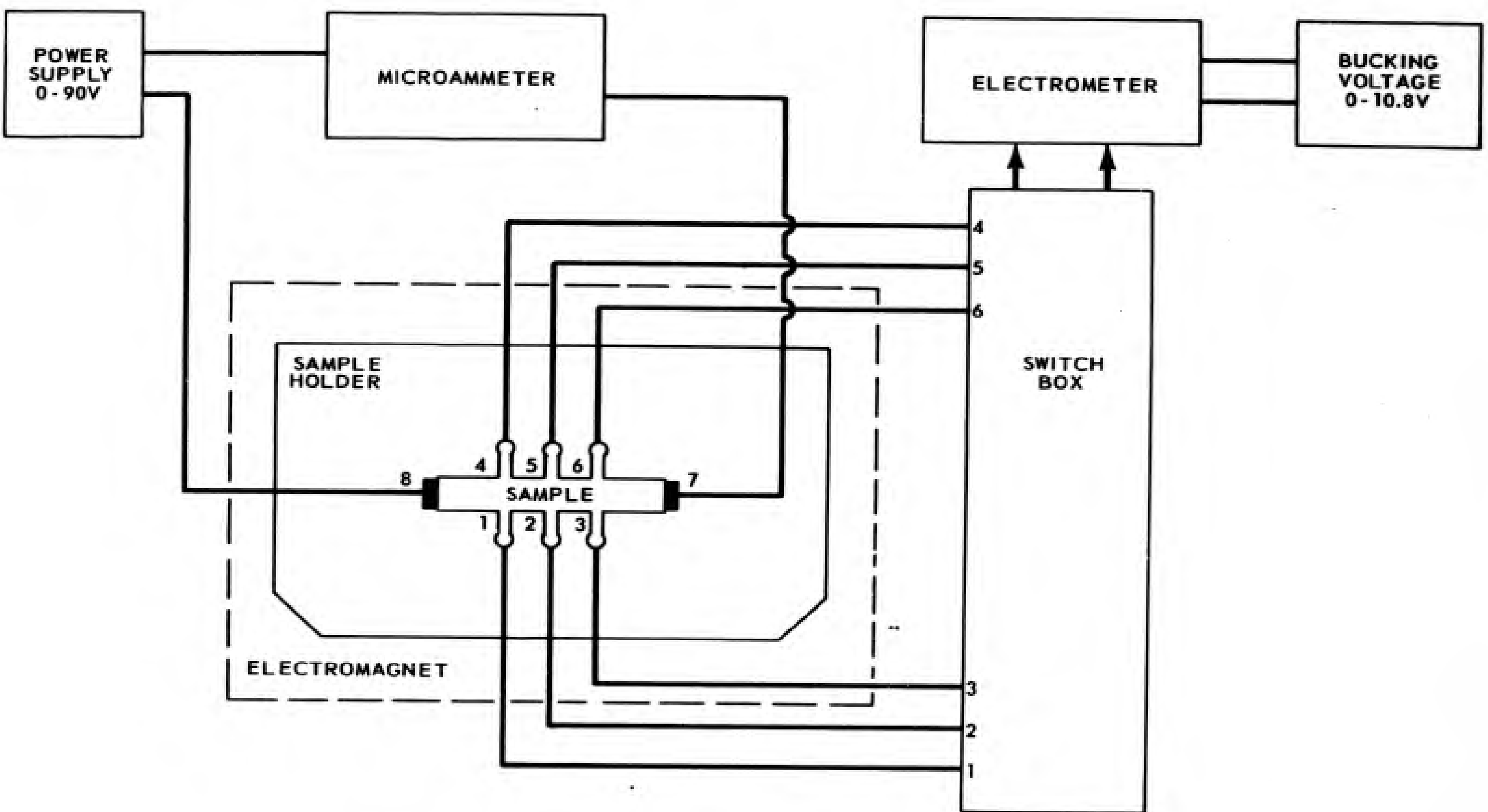


Figure 5. Block Diagram of Hall Effect Apparatus.

Magnetic field strength is measured using a Dyna-Empire Inc. D-79 Gaussmeter, which measures between ten gauss and 30 kilogauss to within 2.5%.

The current through the sample is measured using a Leeds and Northrup type 9836A Stabilized DC Microampere Amplifier. Using a self contained meter, this is a 1% instrument. The current is controlled by a battery potentiometer system which allows a wider latitude and sensitivity than is available from commercial power supplies. Currents through the films are kept as low as possible to avoid heating effects. When more current is required than the Leeds and Northrup device can handle (over 1 μa), 1% D'Arsonval type meters, of suitable range, are employed.

The various voltages developed across the sample are measured with a Cary 31CV Electrometer. This device has an input impedance of 10^{16} ohms and is a .25% instrument with a sensitivity of 10 μa. It may also be used as a highly sensitive ammeter to measure currents in the 10^{-17} ampere range. A bucking voltage has been inserted in the feedback circuit of the electometer in order to compensate for any linear misalignment in the tabs on the samples. The entire circuit is diagrammed in Figure 5.

The desired readings consist of voltage and current values with and without the presence of the magnetic field. Longitudinal readings give resistivity and magnetoresistance effect while transverse readings give the Hall coefficient. The carrier type is determined from the sign of the Hall voltage relative to the direction of the field and the current flow. Before the Hall apparatus was completed, an Electro Impulse Model Te-1 Thermoelectric Probe was used to determine carrier type on the basis of

the sign of the thermoelectric voltage generated in the sample by a hot probe. The homogeneity of the film is determined from a comparison of the readings taken at the various possible positions. It is also possible to cancel the effect of most extraneous magnetic and thermodynamic effects by taking readings of the four possible combinations of current and magnetic field direction and averaging the results.

Minority carrier lifetime measurements have been initiated using an Electro Impulse Semiconductor Lifetime Apparatus. When coupled with a Tektronix Type 555 Dual Beam Oscilliscope and Type D plug-in unit it is possible to measure lifetimes down to one microsecond.

At present a dewar with a quartz window is being fabricated which will make it possible to carry out all of the measurements described above as a function of temperature in the range between 77 K and 600 K. This information will be used to determine impurity activation levels in our semiconductor films.

A great many of the films we encountered have been prepared on substrates of identical material or in some other sort of conducting substrate. If the films are 2.5 micron thick or thicker they may be measured using a four point probe such as our Chaffin Laboratories Model 500. Films several hundred microns thick or thicker have been measured after lapping off the substrate. No adequate method exists, however, for films having a thickness of 1000 Å or less. Methods for such measurement are being devised. No clear cut results have been obtained as yet.

III. RESULTS AND DISCUSSION
A. SPUTTERING

1. Effect of Sputtering Parameters - - Ge-Ge and Ge-CaF_2 Systems

It has been possible to determine rather well-defined epitaxial temperatures (minimum temperature for the formation of single crystal films) and equally well defined amorphous-crystalline transition temperatures as a function of sputtering parameters for the two film-substrate systems of Ge on Ge [111] and Ge on CaF_2 [111] . This is illustrated in Figure 6 which shows examples of the reflection electron diffraction patterns of the films obtained for Ge on Ge [111] at temperatures ranging from 280°C to 500°C for one particular set of sputtering parameters (3000V, 30 m.a., 60μ argon) and in Figure 7 which shows a similar set for Ge on CaF_2 [111] at temperatures ranging from 295°C to 475°C for a second set of sputtering parameters (3000V, 20 m.a., 45 μ argon). For each set of materials identical sputtering parameters are used at all substrate temperatures. In practice, the transition points were definable within ±10°C intervals. On inspecting the diffraction patterns for the Ge-Ge [111] set of Figure 6 it can be observed that at 280°C, the film obtained is amorphous, while at 340°C and above the films obtained are crystalline. As the substrate temperature is raised above the amorphous-crystalline transition point the degree of orientation increases. At 340° the film is polycrystalline, at 380°C and above the film shows increasingly preferred orientation, and finally, at 500°C single crystal of [111] orientation are formed, indicating complete epitaxial growth. It is obvious that similar observations can be made for the Ge-CaF_2 [111] set in Figure 7. The structural

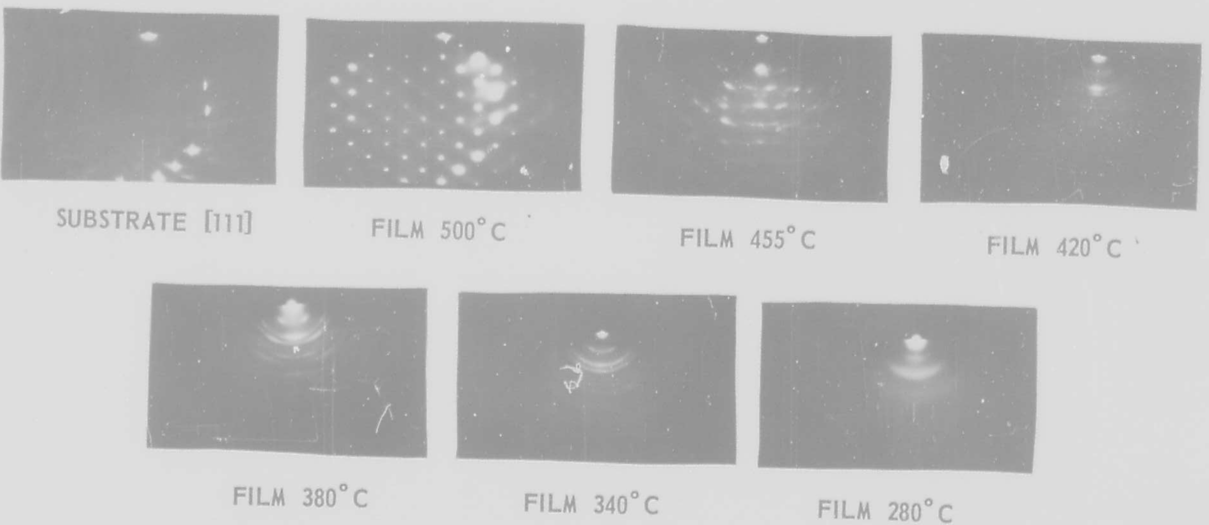


Figure 6. Reflection Electron Diffraction Patterns of Ge Films on [111] Ge Substrates at Various Substrate Temperatures: Sputtering Parameters (3000 V, 30 m.a.).

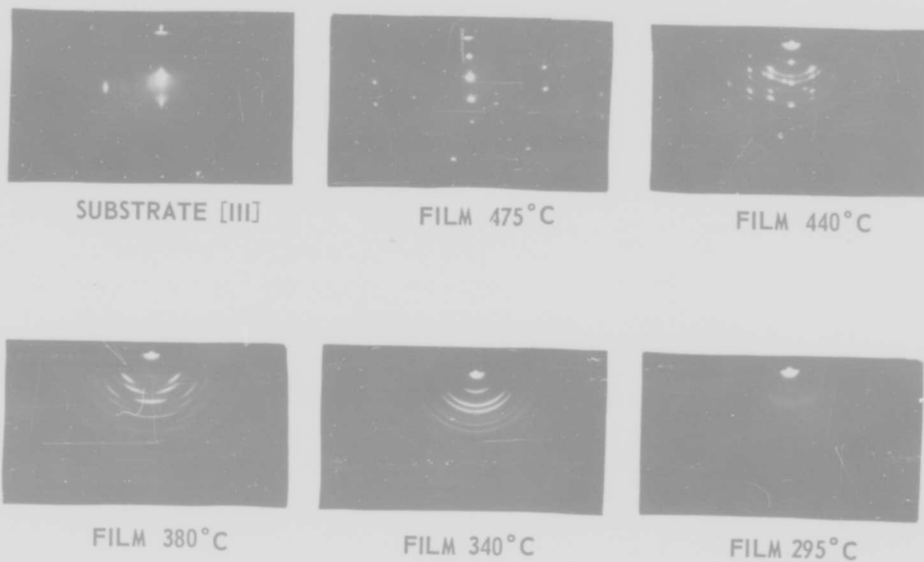
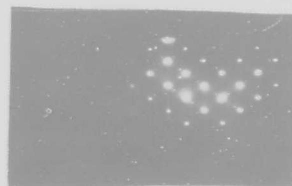


Figure 7. Reflection Electron Diffration
Patterns of Ge Films on [111] CaF_2 Substrates at
Various Substrate Temperatures: Sputtering Parameters (3000 V, 20 m.a.).

quality again increases with substrate temperature. The epitaxial temperature lies between 440°C and 475°C for this case (sputtering parameters: 3000 V, 20 m.a.) and the amorphous-crystalline transition temperature between 300°C and 340°C. It is also interesting to note that using the same series of substrate temperatures and identical sputtering parameters with Ge [100] substrates as with Ge [111] substrates of Figure 6, identical results were obtained. That is to say, the epitaxial temperature limit lies between 455°-500°C and the amorphous-crystalline transition temperature between 300-340°C for both [111] and [100] dislocation free germanium for the same set of sputtering parameters (3000 V, 30 m.a.). As an additional example, in Figure 8, a [100] single crystal film formed on the [100] single crystal substrate at 500°C is shown. Here again, complete epitaxial growth is apparent.

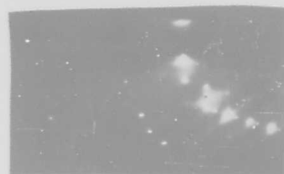
A similar comparison of substrate temperature and film structure is shown in Figure 9 for films formed at a second set of sputtering parameters for Ge on Ge [111] . In this case the sputtering parameters were 3000V, 10 m.a., and 35 μ argon pressure, resulting in a lower sputtering rate than the rate corresponding to the previous set. The electron diffraction patterns indicate that at substrate temperatures of 320 and 330°C the films are amorphous. However, a sharp transition to oriented polycrystal is observed in the films formed at 350°C. Finally at 370°C completely oriented single crystals are obtained. Again, as in the previous case, the films show [111] orientation on the [111] substrates and [100] orientation on the [100] substrate. These results show that for this sputtering rate, or this set of sputtering parameters, the epitaxial temperature lies between 350-370°C.

SUBSTRATE [100]



FILM [100]

SUBSTRATE [111]



FILM [111]

Figure 8. Reflection Electron Diffraction Patterns of Ge Single Crystal Films on [100] and [111] Ge Substrates at 500°C: Sputtering Parameters (3000 V, 30 m.a.).

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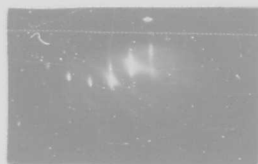
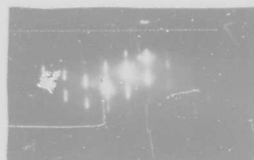
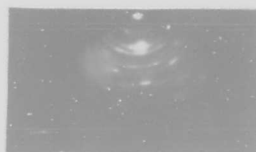


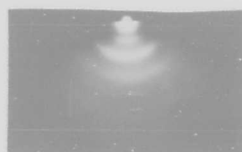
SUBSTRATE [111]



FILM [111] ; 370°C



FILM; 350°C



FILM; 330°C

FILM 320°C

SUBSTRATE [100]

FILM [100] ; 370°C

Figure 9. Reflection Electron Diffraction Patterns of Ge Films on Ge Substrates at Various Substrate Temperatures: Sputtering Parameters (3000 V, 10 m.a.).

When the results for the various sputtering parameters which are listed in Table II for both Ge-Ge [111] and Ge-CaF_2 [111] systems, are graphically summarized, i.e., sputtering rates, or in this case sputtering currents, are plotted versus substrate temperatures - diagrams, analogous to metallurgical phase diagrams, result defining regions yielding exclusively either single crystal, polycrystalline, or amorphous structures. These diagrams are shown in Figure 10. A consistent dependence of both the epitaxial temperature and the amorphous-crystalline transition temperature on the sputtering parameters is observed. It can be seen that the epitaxial temperature in both cases proves to be a very strong function of the sputtering current while the amorphous-crystalline transition temperature is relatively insensitive to this parameter.

In the case of Ge on Ge [111], for which a more complete set of data has been obtained and therefore deserves a somewhat more detailed description, it can be seen that three unique transition regions are observed. At low sputtering rates direct transitions occur from amorphous to single crystal films as the substrate temperature is raised. At higher sputtering rates (relative to the experimental range) two distinct transitions occur as the substrate temperature is raised, one from amorphous to polycrystalline and one from polycrystalline to single crystal. Between the two transition points, the degree of orientation increases with increasing temperature. It should be noted that the experimental conditions corresponding to any transition "point" led invariably to uncontrollable film structures, i.e. either type of structure would be obtained if films were deposited simultaneously on

TABLE II

EFFECT OF SUBSTRATE TEMPERATURE ON STRUCTURE FOR Ge ON [111] Ge AND Ge ON [111] CaF_2

SUBSTRATE MATERIAL	SUBSTRATE TEMP, °C	SPUTTERING PARAMETERS	FILM STRUCTURE
[111] DISLOCATION-FREE - GERMANIUM	280	3000V, 30MA, 60 ARGON	AMORPHOUS
" "	340	"	POLYCRYSTALLINE
" "	380	"	POLYCRYSTALLINE WITH PREFERRED ORIENTATION
" "	420	"	POLYCRYSTALLINE WITH BETTER THAN PREFERRED ORIENTATION
" "	455	"	POLYCRYSTALLINE WITH HIGH ORIENTATION
" "	500	"	SINGLE CRYSTAL
[111] DISLOCATION-FREE - GERMANIUM	115	3000V, 20MA, 45 ARGON	AMORPHOUS
" "	265	"	AMORPHOUS
" "	300	"	PRACTICALLY AMORPHOUS
" "	340	"	POLYCRYSTALLINE WITH PREFERRED ORIENTATION
" "	340	"	POLYCRYSTALLINE WITH PREFERRED ORIENTATION
" "	380	"	POLYCRYSTALLINE WITH HIGH ORIENTATION
" "	420	"	SINGLE CRYSTAL
" "	455	"	SINGLE CRYSTAL
[111] DISLOCATION-FREE - GERMANIUM	320	3000V, 10MA, 35 ARGON	AMORPHOUS
" "	330	"	AMORPHOUS
" "	350	"	POLYCRYSTALLINE WITH VERY HIGH ORIENTATION
" "	370	"	SINGLE CRYSTAL
[111] DISLOCATION-FREE - GERMANIUM	335	3000V, 4MA, 22 μ ARGON	SINGLE CRYSTAL, POLYCRYSTAL, AMORPHOUS
[111] DISLOCATION-FREE - GERMANIUM	300	3000V, 3.5MA, 19 μ ARGON	SINGLE CRYSTAL
" "	290	"	SINGLE CRYSTAL
" "	280	"	SINGLE CRYSTAL. POLYCRYSTAL, AMORPHOUS
" "	270	"	AMORPHOUS
" "	235	"	AMORPHOUS
[111] DISLOCATION-FREE - GERMANIUM	300	3000V, 3MA, 17 μ ARGON	SINGLE CRYSTAL
" "	280	"	SINGLE CRYSTAL
" "	275	"	SINGLE CRYSTAL
" "	270	"	SINGLE CRYSTAL
" "	265	"	SINGLE CRYSTAL, POLYCRYSTAL, AMORPHOUS
" "	255	"	AMORPHOUS
" "	235	"	AMORPHOUS
[111] DISLOCATION-FREE - GERMANIUM	280	3000V, 2.4MA, 16 μ ARGON	SINGLE CRYSTAL
" "	255	"	SINGLE CRYSTAL
" "	235	"	SINGLE CRYSTAL
" "	220	"	SINGLE CRYSTAL AMORPHOUS
" "	205	"	AMORPHOUS
" "	190	"	AMORPHOUS
[111] CaF_2	475	3000V, 20MA 45 μ ARGON	SINGLE CRYSTAL
"	435	"	POLYCRYSTAL WITH HIGH ORIENTATION
"	380	"	POLYCRYSTALLINE, SLIGHTLY PREFERRED
"	340	"	POLYCRYSTALLINE
"	295	"	AMORPHOUS
[111] CaF_2	415	3000V, 10MA, 35 μ ARGON	SINGLE CRYSTAL
"	395	"	POLYCRYSTAL (CLOSE TO SINGLE CRYSTAL)
"	380	"	POLYCRYSTALLINE, PREFERRED ORIENTATION
"	340	"	POLYCRYSTALLINE
"	295	"	AMORPHOUS
[111] CaF_2	380	3000V, 6MA, 28 μ ARGON	SINGLE CRYSTAL
"	360	"	POLYCRYSTALLINE, PREFERRED ORIENTATION
"	340	"	POLYCRYSTALLINE
"	300	"	AMORPHOUS

TEMPERATURE (DEGREES CENTIGRADE)

SINGLE CRYSTAL

POLYCRYSTALLINE

AMORPHOUS

○ SINGLE CRYSTAL
▲ POLYCRYSTALLINE
● AMORPHOUS

0 8 16 24 32
CURRENT
Ge ON [111] Ge
a.

SINGLE CRYSTAL

POLYCRYSTALLINE

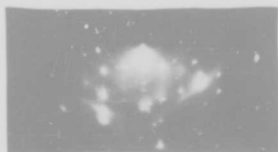
AMORPHOUS

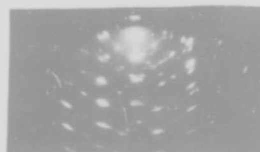
0 8 16 24 32
CURRENT
Ge ON [111] CaF_2
b.

Figure 10. Effect of Sputtering Current and Substrate Temperature on Film Structure.

several substrates. This instability was most pronounced at a specific, intermediate sputtering rate, at which all three transition regions merge in a triple point. At this point all three types of structure can be obtained with the sputtering conditions defining this point. For example, during an experiment six identical substrates were simultaneously exposed to the triple point sputtering conditions (335°C, 4 m.a., 3000V). Figure 11 shows three out of six films formed. Of the six films formed, two were amorphous, one polycrystalline, two highly oriented polycrystalline, and one single crystalline in structure. For the range in which data are available, the Ge - CaF_2 [111] systems behave in the same manner, except that the epitaxial temperatures are higher. The trend of the data indicates that a triple point condition will probably also exist for the Ge - CaF_2 [111] system.

It can be seen in Figure 10a for Ge on Ge [111] that the slope of the epitaxial temperature limit sharply decreases at the triple point. The cause for this can be implied from the fact that the sputtering current is not directly indicative of the film growth rate but only of the flux density of atoms impinging on the substrate. In fact the growth rate at any particular current setting is a very sensitive function of the substrate temperature. Figure 12 demonstrates this effect for the Ge - Ge [111] system. As the substrate temperature increases the growth rate decreases and the higher the temperature the greater the decrease. Furthermore, this dependence of growth rate on substrate temperature becomes more pronounced as the sputtering current (or incidence rate) increases. This observation leads


335° C


335° C

335° C

Figure 11. Reflection Electron Diffraction Patterns of Ge Films on [111] Ge Substrates at "Triple Point": Sputtering Parameters (335°C, 3000 V, 4 m.a.).

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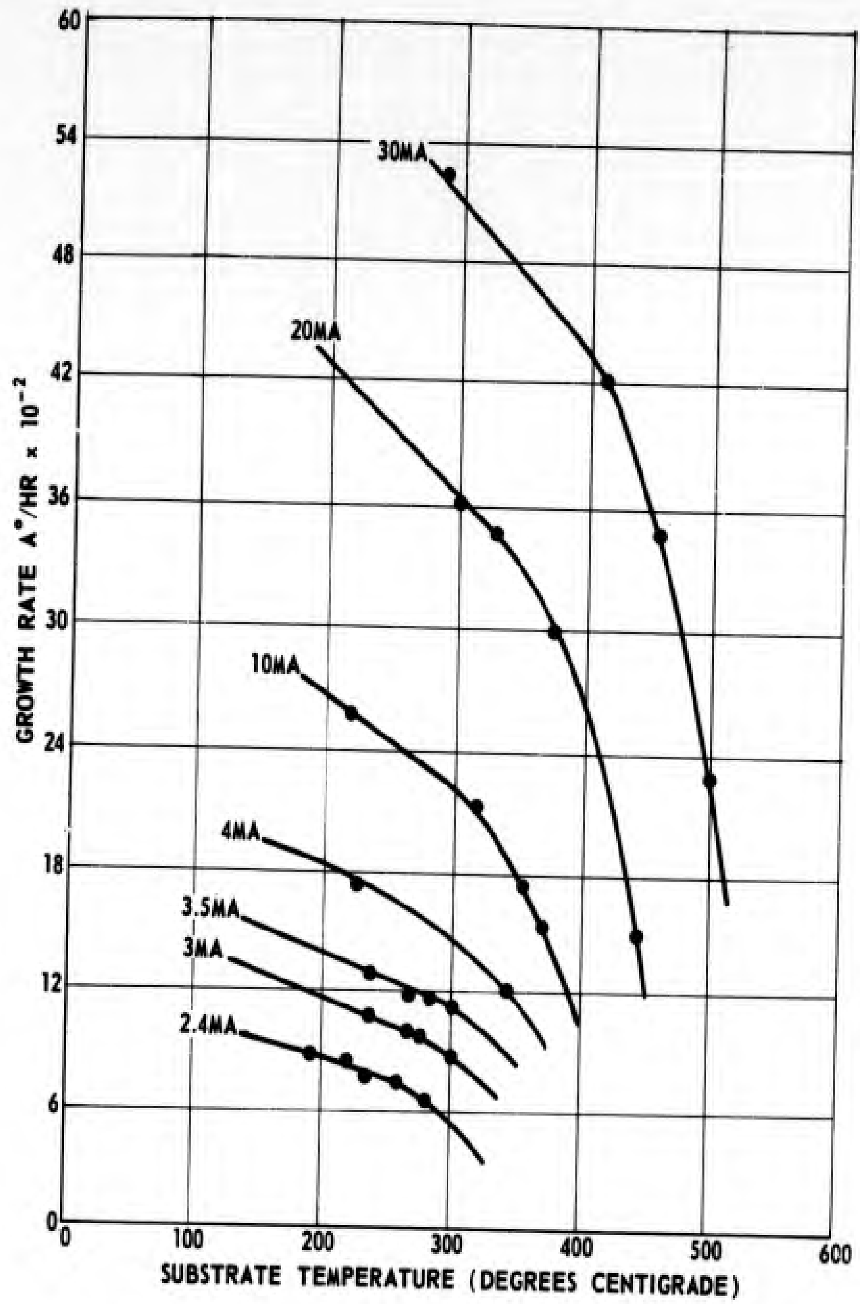

Figure 12. Growth Rate vs Substrate Temperature at Various Sputtering Currents for Ge on [111] Ge.

to the implication that the theory of supersaturated vapors is applicable to describing, in part, the epitaxial growth process.

This theory predicts that the rate of condensation is a very sensitive function of the temperature because the degree of supersaturation, and, in turn, the number of stable nuclei in a vapor decreases rapidly with increasing temperature. It is not difficult to see that during the formation of films the growth rate is equivalent to the rate of condensation in the supersaturation model. The corresponding mathematical relations should therefore be applicable to either case.

Similar observations were made by Walton, Rhodin, and Rollins[6] in their study of nucleation of silver on rock salt. Their study was concerned with the nucleation rate as a function of incidence rate and substrate temperature. The same general trends were observed, i.e. the rate of nucleation decreases with increasing substrate temperature for the same incidence rate. Increasing the incidence rate produces a more pronounced dependence of nucleation rate on substrate temperature.

While the vapor model should serve to predict growth rate it must be considerably modified to predict the degree of structural quality obtained during the growth process. The probability for arriving atoms to enter into an epitaxial arrangement will by necessity depend on the surface mobility of these atoms, their meantime of stay, the surface energy distribution of the substrate lattice, the degree of energy exchange with the surface phonons, and the surface condition or topography.

Figure 13 seems to be quite revealing in this respect. Here the same data as shown in Figure 10 are replotted in terms of actual growth rate and substrate temperatures. Only the data points near the transition limits

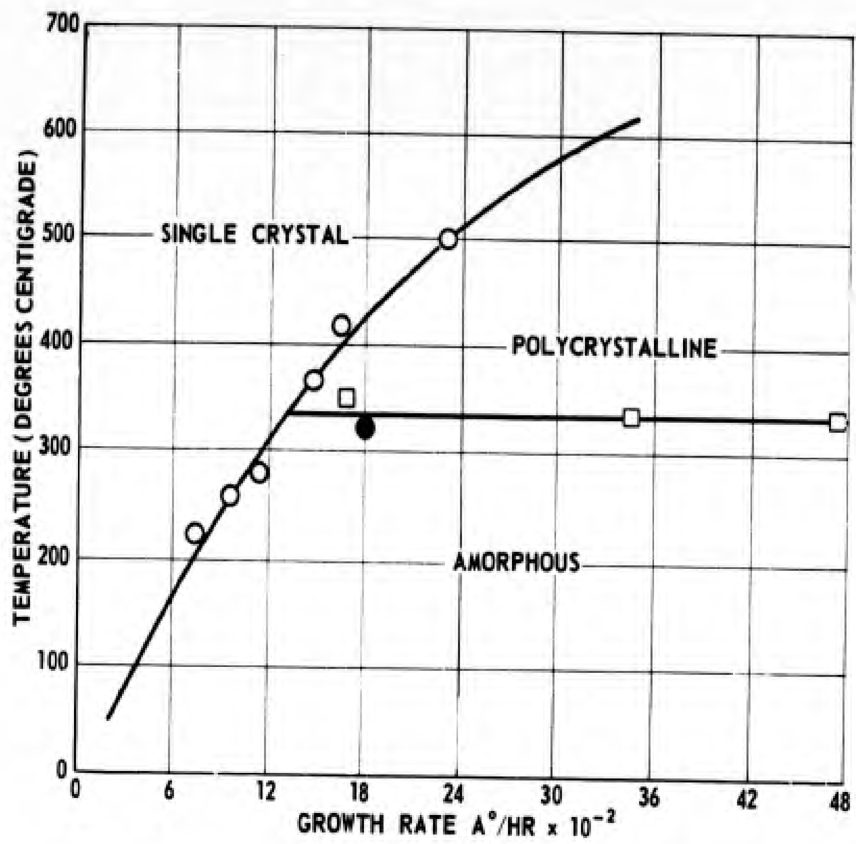

Figure 13. Effect of Growth Rate and Substrate Temperature on Film Structure for Ge on [111] Ge.

are indicated. It can easily be seen that in these coordinates the epitaxial temperature limit is now a relatively continuous function of the growth rate, even near the triple point. This may imply that, over the temperature range of observation, the surface mobility of adsorbed atoms or growth nuclei has the controlling influence on the epitaxial temperature.

In support of the findings to date we are considering the following theoretical approach:

Epitaxial film formation is treated in terms of two mechanisms:

1. Condensation of impinging atoms
2. Ordering of condensed atoms or nuclei

The condensation process, in our approach, terminates when the atoms are physically adsorbed.

In order to obtain epitaxi the physically adsorpted atom must be capable of diffusing into nearest neighbor positions of the host lattice. Such diffusion will only take place if two conditions hold: 1) the nearest neighbor positions must represent a preferred position, i.e., lower energy position than the site of physical adsorption, which is certainly the case if the host lattice consists of atoms identical to the impinging atoms (Ge on Ge); and 2) the time it takes for the adsorpted atom to diffuse into the preferred, epitaxial position must be shorter than the time for condensation of one atomic layer, since otherwise the diffusion process cannot be completed due to the barrier formed by the newly absorbed atoms in the diffusion path (leading to amorphous films).

Condition 2 may be expressed in terms of the time constants τ_D and τ_C, where

τ_D = the average time required for diffusion into preferred, epitaxial positions, and

τ_c = the average time required for the condensation of one atomic layer.

According to this model, epitaxi is only feasible if

$$\tau_D < \tau_c$$

and can be represented by the following two expressions:

$$\tau_D = A\left(d_0^2/\nu\right)\exp.\left(Q_D/kT_s\right) \qquad (1)$$

$$\tau_c = a_0/R_g \qquad (2)$$

where d_0 = distance for single diffusion jump

Q_D = activation energy for surface diffusion

T_s = substrate temperature

R_g = measured growth rate

a_0 = thickness of a monolayer

A = temperature insensitive function determined by the entropy and lattice structure of the substrate

A lower limit on the epitaxial temperature can be obtained from these expressions in the following way - using the condition for epitaxy ,

we get

$$A\left(d_0^2/\nu\right)\exp\left(Q_D/T_{epit.}\right) < a_0/R_g$$

Rearranging results in the following expression

$$T_{epit.} > Q_D/k\left[C - \ln R_g\right]^{-1} \qquad (3)$$

where $C = \ln \frac{a_0\nu}{A d_0^2}$

The relation given in (3) may be used to determine epitaxial temperature if Q_D is known, or may be used to determine Q_D since epitaxial temperature and corresponding growth rate can be experimentally determined (Figure 13). The value of Q_D can then be compared with values determined by other methods. Expression (3) therefore, provides a working relation to check the theoretical model against the experimental findings.

From the data shown in Figure 12, it can be seen that the growth rate is a non-linear function of the incidence rate (current) and substrate temperature i.e., $R_g = F(R_i, T_s)$. As already discussed the observed dependence of growth rate on substrate temperature and incidence rate indicates that the condensation process of the epitaxial growth process can be described, in part, by the theory of supersaturated vapors. This is further indicated by the work of Rhodin and Walton already mentioned.

Rhodin, et al., derive the following expressions for the nucleation rate in terms of incidence rate and substrate temperature:

$$I_1 = 4R^2/\nu \, N_0 \exp.\left[(2Q_{ad} - Q_D)/kT\right] \quad (4)$$

single atom clusters

$$I_3 = 4R\left(R/\nu N_0\right)^3 \left[\exp\left(4Q_{ad} + E_3 - Q_D\right)/kT\right] \quad (5)$$

for clusters consisting of three atoms

Since our observed growth rates showed a similar dependence on substrate temperature and incidence rate, we conclude that growth rate is proportional to the nucleation rate and can be represented by expressions

similar to Equation (4). The expression must be modified since in Rhodin's work the film and substrate materials are different, whereas, our work is, at present, concerned with identical film substrate combination. This work is now in progress.

2. <u>Effect of Sputtering Parameters - Other Systems</u>

As indicated in the introduction, work has also been done with germanium sputtered onto other substrates (single crystal mica, single crystal silicon [100] , and amorphous quartz). The results for these cases are as yet incomplete; however, trends similar to those reported in the previous section have been observed.

As yet, no epitaxial temperature have been determined for the sputtered films listed. However both amorphous and polycrystalline films were produced in all systems. Interestingly enough, in all cases where the amorphous-crystalline transition temperature was defined, this temperature occured between 300°C and 340°C. This, as may be recalled, is the identical range where this transition point was found for the Ge-Ge and Ge-CaF_2 systems. The other trend that prevailed in all cases was, that the degree of orientation of the polycrystalline films formed above the transition temperature increased with increasing temperature. Conversely, the degree of orientation at a given temperature decreased with increasing sputtering currents. The results of these experiments are summarized in Table III. Examples of reflection electron-diffraction patterns of germanium films on various substrates as a function of substrate temperature, are shown in Figure 14.

TABLE III

DATA ON OTHER SUBSTRATES

SUBSTRATE	SUBSTRATE TEMPERATURES AND SPUTTERING PARAMETERS	FILM STRUCTURE
MICA	3000V, 30MA	
	280	AMORPHOUS
	380	POLYCRYSTALLINE
	420	POLYCRYSTALLINE
	455	POLYCRYSTALLINE
	500	POLYCRYSTALLINE WITH PREFERRED ORIENTATION
	3000V, 10MA	
	320	AMORPHOUS
	370	POLYCRYSTALLINE
Si SINGLE [111] ORIENTATION	3000V, 20MA	
	465	POLYCRYSTALLINE WITH PREFERRED ORIENTATION
	445	POLYCRYSTALLINE WITH PREFERRED ORIENTATION
	415	POLYCRYSTALLINE
	400	POLYCRYSTALLINE
	3000V, 10MA	
	500	POLYCRYSTALLINE WITH PREFERRED ORIENTATION
	425	POLYCRYSTALLINE WITH PREFERRED ORIENTATION
	350	POLYCRYSTALLINE
	3000V, 6MA	
	465	POLYCRYSTALLINE WITH BETTER THAN PREFERRED ORIENTATION
	400	POLYCRYSTALLINE WITH PREFERRED ORIENTATION
	375	POLYCRYSTALLINE WITH PREFERRED ORIENTATION
QUARTZ	3000V, 30MA	
	500	POLYCRYSTALLINE WITH PREFERRED ORIENTATION
	420	POLYCRYSTALLINE WITH PREFERRED ORIENTATION
	340	AMORPHOUS
	3000V, 20MA	
	465	POLYCRYSTALLINE WITH PREFERRED ORIENTATION
	445	POLYCRYSTALLINE WITH PREFERRED ORIENTATION
	415	POLYCRYSTALLINE WITH SLIGHTLY PREFERRED ORIENTATION
	400	POLYCRYSTALLINE
	3000V, 10MA	
	500	POLYCRYSTALLINE WITH PREFERRED ORIENTATION
	425	POLYCRYSTALLINE WITH PREFERRED ORIENTATION
	350	AMORPHOUS
	3000V, 6MA	
	465	POLYCRYSTALLINE WITH PREFERRED ORIENTATION
	400	POLYCRYSTALLINE WITH PREFERRED ORIENTATION
	375	POLYCRYSTALLINE WITH PREFERRED ORIENTATION
	345	AMORPHOUS
CERAMIC	3000V, 10MA	
	320	AMORPHOUS
	330	AMORPHOUS
	350	POLYCRYSTALLINE
	370	POLYCRYSTALLINE WITH PREFERRED ORIENTATION

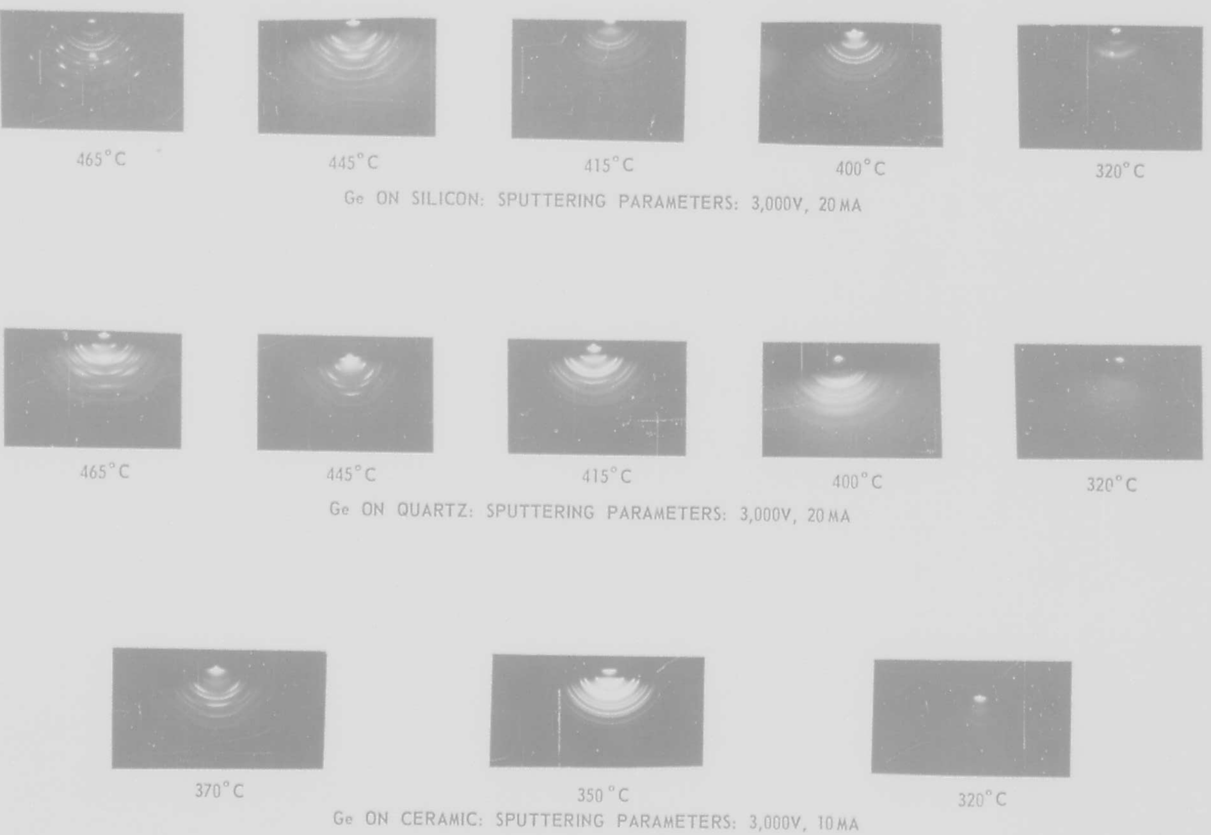

Figure 14. Reflection Electron Diffraction Patterns of Ge Films Sputtered Onto Various Substrates as a Function of Substrate Temperature.

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3. Annealing Treatments

Effects of annealing on the structural characteristics of germanium films on germanium substrates have been observed. In particular, films which gave amorphous and polycrystalline electron diffraction patterns before heat treatment were studied. The amorphous films were heat treated to about 500°C. Observations of the films after heat treatment showed that a structural change from amorphous to polycrystalline, showing some preferred orientation, had taken place. Reflection electron diffraction patterns of the film before and after heat treatment are shown in Figure 15. The exact temperature at which this transition takes place has not yet been determined. Results of heat treatment of germanium films reported by other investigators[7] indicates that the transition temperature is about 370°C.

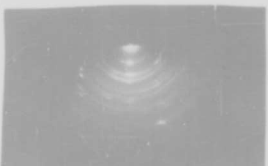
Germanium films, polycrystalline before heat treatment, showed also definite structural changes. For example, a polycrystalline film with some preferred orientation changed to a polycrystalline film with a high degree of orientation when heat treated at 550°C. Reflection electron diffraction patterns for this change are shown in Figure 16.

No transformation to single crystal states were obtained by uniform annealing.

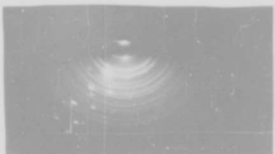
4. Effect of Film Thickness

During the course of this work several interesting and consistent observations were made on the thickness effect. Most films used for the systematic comparison in this paper were in the thickness range of 3000 Å. These include all those listed in Table II. At these thicknesses small

FILM BEFORE
ANNEALING



FILM AFTER ANNEALING
AT 500°C



FILM AFTER ANNEALING
AT 500°C

FIGURE 15. AMORPHOUS TO POLYCRYSTALLINE, SHOWING SOME DEGREE AT ORIENTATION.

FILM BEFORE
ANNEALING

FILM AFTER ANNEALING
AT 550°C

FIGURE 16. POLYCRYSTALLINE, PREFERRED TO POLYCRYSTALLINE
WITH HIGHER DEGREE OF ORIENTATION.

Figures 15 and 16. Reflection Electron Diffraction Patterns of Ge Films on Ge [111]
Substrate Before and After Annealing Treatments.

variations (of the order of hundreds of angstroms) produced no significant effects on the structural characteristics of these films.

However, when films of approximately 100 Å were compared with 3000 Å films formed under the same conditions the degree of structural quality was always considerably greater in the thin films. For example, as shown in Figure 17, sputtered films of Ge on Ge [111] at 455°C showed highly oriented polycrystallinity in the 3000 Å films while the corresponding 100 Å films were single crystal in structure. The sputtering parameters for both types of film were identical (30 m.a., 3000 V, 60 μ Argon).

5. Initial Silicon Experiments

The deposition of silicon is difficult and requires careful experimentation and special equipment. Very high substrate temperatures (over 1000°C) are required for epitaxial growth. Since these high temperatures accelerate oxidation processes, extreme care must be taken to maintain an ultra clean system before and during deposition. The sputtering system is equipped to handle the sputtering of silicon. To date, however, the number of silicon sputterings performed has been very limited due to constant use of the sputtering system for germanium sputtering reported above.

Sputterings of silicon on single crystal silicon substrates, both [111] and [100] orientation have been performed as a function of substrate temperature. The sputtering parameters used were 5000V, 20 m.a., 45 argon, and C-A spacing of 5.7 cm. To date single crystal films of Si have not been epitaxially deposited.

Substrate temperatures up to 750°C have been used. Higher substrate temperatures will be required for epitaxial growth. Such experiments

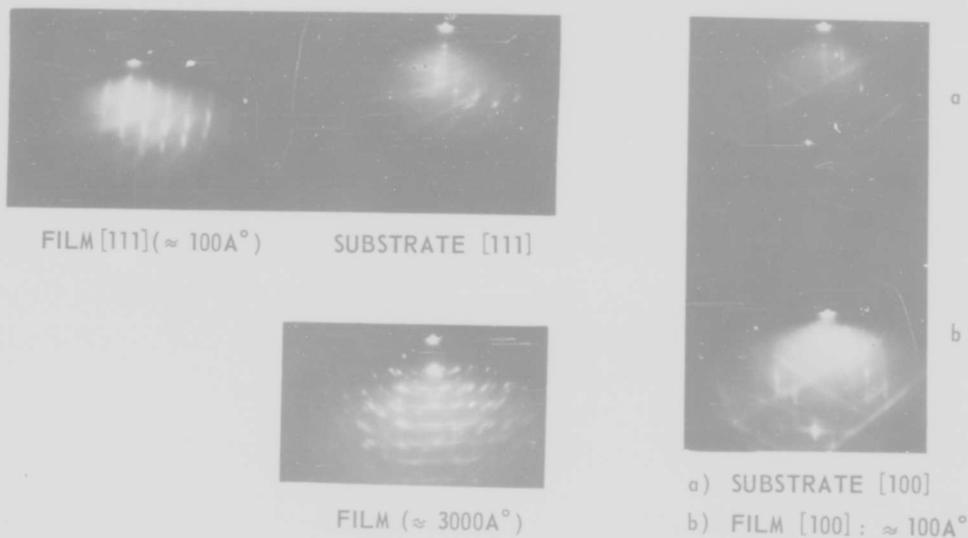


Figure 17. Reflection Electron Diffraction Patterns of Ge Films of Two Thicknesses on Ge Substrate: Sputtering Parameters (3000 V, 30 m.a. 455°C).

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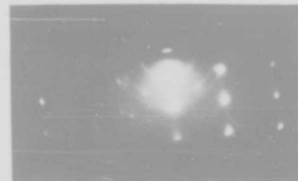
are now in progress. However, the annealing of silicon films sputtered onto silicon substrates has resulted in some interesting observations.

Silicon films which gave amorphous patterns in reflection electron diffraction before heat treatment were annealed in a high vacuum furnace to $\approx$ 1100°C. The electron diffraction patterns after heat treatment revealed a large structural change; very highly oriented films were obtained after heat treatment. Examples of reflection electron diffraction patterns of the films before and after heat treatment are shown in Figure 18. The structure change in the case of silicon appears to be more pronounced than in the case of germanium. The temperature of transition, as in the case of germanium has not yet been determined. Further annealing studies, both with germanium and silicon, are in progress.

Si FILM ON [111] Si BEFORE ANNEALING



Si FILM AFTER ANNEALING AT $\approx 1100^{\circ}$ C

Figure 18. Effect of Annealing on Structure of Silicon Films.

B. EVAPORATION

1. Germanium on Germanium

Germanium films have been deposited by evaporation onto single crystal germanium substrates (both [111] and [100] orientations) and analyzed for their structural quality by electron reflection diffraction. The structural features of the films were then correlated with the deposition conditions as in the case of sputtered films. The deposition parameters considered include substrate temperature, rate of deposition, and residual gas pressure in the vacuum chamber. Due to the nature of the evaporation process, in particular, the three parameters already mentioned are investigated simultaneously and, as a result, a considerable amount of data is needed in order to draw meaningful conclusions. While the series of experiments on the evaporation of germanium is still in progress, the general features of the results have already become quite evident. These will be discussed below.

The experiments on evaporation of germanium include the determination of the epitaxial temperatures and amorphous-crystalline transition temperatures as a function of rate of deposition and residual gas pressure as in the case of sputtering. The rate of deposition is being varied by varying source temperature. As in the case of sputtering, an increase in structural quality of the film with substrate temperature is observed for a particular rate of deposition (source temperature). As an example, Figure 19 shows the reflection electron diffraction patterns of films obtained for Ge on [111] Ge at substrate temperatures ranging from 200°C to 420°C for one

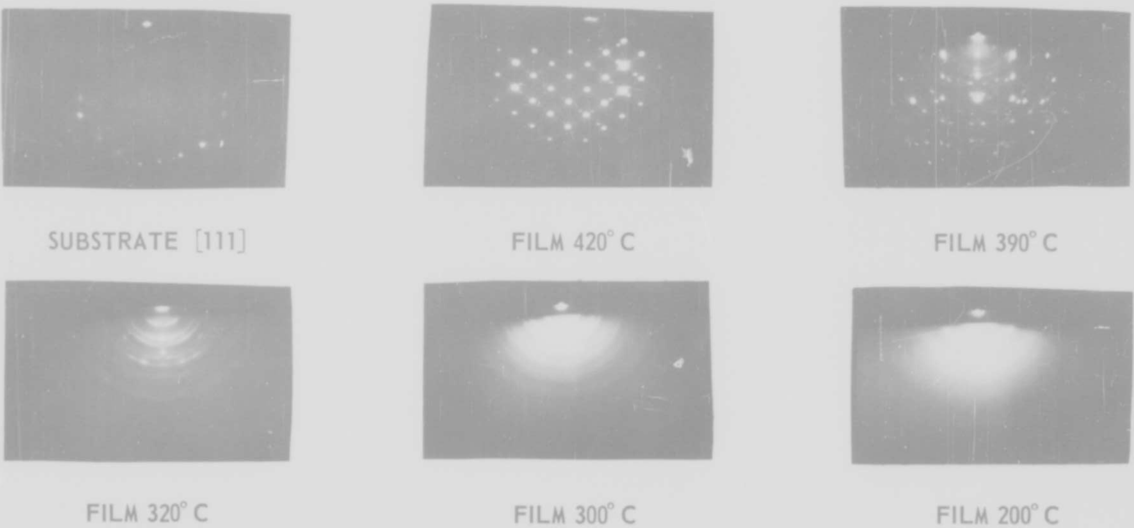


Figure 19. Reflection Electron Diffraction Patterns of Ge Films Evaporated on [111] Ge Substrate at Various Substrate Temperatures for One Deposition Rate.

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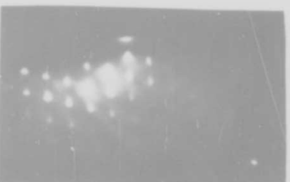
set of evaporation parameters. On inspecting the diffraction patterns, it can be observed that at 200°C the film obtained is amorphous, while at 300°C and above the films obtained are crystalline. As the substrate temperature is raised above the amorphous-crystalline transition point the degree of orientation increases. At 320°C the film is polycrystalline, at 390°C highly oriented polycrystal and, finally, at 420°C single crystal of [111] orientation is formed. The epitaxial temperature limit for this particular rate of deposition lies between 390°C and 420°C. For this particular series, the vacuum in the system was in the 10^{-7} Torr range. Depositions using substrates having [100] orientation resulted in the same transition temperatures as those observed using [111] oriented germanium substrates.

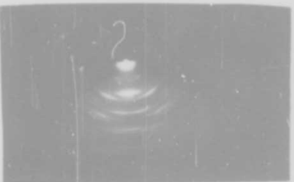
The general features of the results obtained with evaporation, show the same trends as those established for sputtering. High substrate temperature favors the deposition of single crystal film as demonstrated in Figure 19. Low rate of deposition and low residual gas pressure also tend to favor deposition of single crystal films. Figure 20 demonstrates the effect of rate of deposition. Reflection electron diffraction patterns of films deposited at 300°C at 200A°/hr and 600 A°/hr are compared. The film obtained at the lower rate is single crystal while that at the higher rate is polycrystalline with preferred orientation. The same is true for films obtained at 500°C. The film deposited at a growth rate of 1392A°/hr is single crystal while the film deposited at 7290A°/hr is polycrystalline.

Table IV and V lists the results of deposition of Ge on Ge, by evaporation, Although the observations are, as yet, incomplete, the film structure

[111] SUBSTRATE 300° C



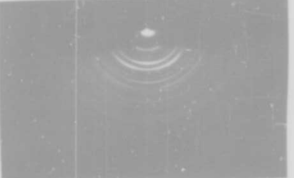
FILM 300° C
GROWTH RATE = 200 A°/HR



FILM 309° C
GROWTH RATE > 600 A°/HR

[111] SUBSTRATE 500° C

FILM 500° C
GROWTH RATE = 1392 A°/HR



FILM 523° C
GROWTH RATE = 7290 A°/HR

Figure 20. Reflection Electron Diffraction Patterns of Ge Films Evaporated on [111] Ge Substrates at Various Growth Rates.

TABLE IV
EFFECT OF SUBSTRATE TEMPERATURE ON STRUCTURE FOR
Ge ON Ge [111]

SUBSTRATE MATERIAL	SUBSTRATE TEMP (°C)	EVAPORATION PARAMETERS	FILM STRUCTURE
DISLOCATION FREE GERMANIUM [111]	480	*RGP ~ 2 x 10^{-7} TORR **S-S DISTANCE ~ 8" ***V, C ~ 2.5KV, 400ma GROWTH RATE ~ 1800A°/HR	SINGLE CRYSTAL
"	450	" "	SINGLE CRYSTAL
"	420	" "	SINGLE CRYSTAL
"	390	" "	POLYCRYSTALLINE WITH HIGH ORIENTATION
"	320	" "	POLYCRYSTALLINE WITH PREFERRED ORIENTATION
"	300	" "	POLYCRYSTALLINE
"	200	" "	AMORPHOUS
DISLOCATION FREE GERMANIUM [111]	355	RGP ~ 10^{-7} TORR S-S = 8" V, C ~ 2.5KV, 350ma	SINGLE CRYSTAL
"	350	" "	POLYCRYSTALLINE WITH HIGH ORIENTATION
"	300	" "	POLYCRYSTALLINE
DISLOCATION FREE GERMANIUM [111]	300	RGP ~ 10^{-7} TORR S-S = 8" V, C = 3KV, 250ma	SINGLE CRYSTAL
DISLOCATION FREE GERMANIUM [111]	300	RGP ~ 6 x 10^{-7} TORR S-S = 8" V, C ~ 3KV, 250ma	SINGLE CRYSTAL
DISLOCATION FREE GERMANIUM [111]	515	RGP ~ 10^{-6} TORR S-S = 8" GROWTH RATE > 6000A°/HR	POLYCRYSTALLINE
"	500	RGP ~ 10^{-6} TORR S-S = 8" V, C ~ 3KV, 400ma GROWTH RATE ~ 1820A°/HR	SINGLE CRYSTAL
"	450	RGP ~ 10^{-6} TORR S-S ~ 8" V, C ~ 3KV, 400ma GROWTH RATE ~ 1020A°/HR	SINGLE CRYSTAL
DISLOCATION FREE GERMANIUM [111]	400	RGP ~ 10^{-6} TORR S-S ~ 8" V, C ~ 3KV, 200ma GROWTH RATE ~ 1020A°/HR	SINGLE CRYSTAL

*RGP = RESIDUAL GAS PRESSURE
**S-S = SOURCE-SUBSTRATE DISTANCE
***V,C = VOLTAGE AND CURRENT OF THE ELECTRON BEAM

TABLE V
EFFECT OF GROWTH RATE ON STRUCTURE FOR
Ge ON Ge [111]

SUBSTRATE MATERIAL	SUBSTRATE TEMP (°C)	GROWTH RATE	FILM STRUCTURE
DISLOCATION FREE GERMANIUM [111]	300	200A°/HR	SINGLE CRYSTAL
"	309	>600A°/HR	POLYCRYSTALLINE WITH PREFERRED ORIENTATION
"	500	1392A°/HR	SINGLE CRYSTAL
"	523	7290A°/HR	POLYCRYSTALLINE

TABLE VI
DATA OF GERMANIUM FILMS DEPOSITED ONTO GLASS SUBSTRATES

GLASS TEMPERATURE (°C)	RESIDUAL GAS PRESSURE	GROWTH RATE	FILM STRUCTURE
385	2.0×10^{-6}	1000A°/HR	POLYCRYSTALLINE WITH INCREASING ORIENTATION ↓
450	3.2×10^{-6}	1392A°/HR	
500	3.8×10^{-6}	1638A°/HR	
515	5.0×10^{-7}	7290A°/HR	

obtained at several growth rates appear to fall into the corresponding structural regions of the growth rate-temperature diagram established for sputtered germanium films. This is demonstrated by means of a few sample data points, in Figure 21. The solid curves in Figure 21 are the curves determined from the sputtered results (same curves shown in Figure 13). The data points correspond to the evaporated results.

2. Germanium on Other Substrates

Germanium has also been deposited by vacuum evaporation onto other substrates including [111] and [100] Si, [111] CaF_2, amorphous quartz and microscope glass slides. These data are still incomplete. However, preliminary data are also consistent with the corresponding data obtained by sputtering. In the case of glass substrates, electron reflection diffraction patterns of these films showed that all films are polycrystalline. However, as in the case of other substrates, the structural quality of the film improved with increasing substrate temperature. In Table VI some of the data of germanium deposited on glass substrates is listed. The corresponding electron reflection diffraction patterns of these films are shown in Figure 22.

3. Evaporation of Gold - General Summary

Four types of experiments were carried out in the vacuum evaporation of gold. First, gold films were deposited onto rock salt substrate at various substrate temperatures. Under the experimental conditions, the minimum substrate temperature for obtaining single crystal gold film on rock salt was found to be in the neighborhood of 250°C. Secondly, gold

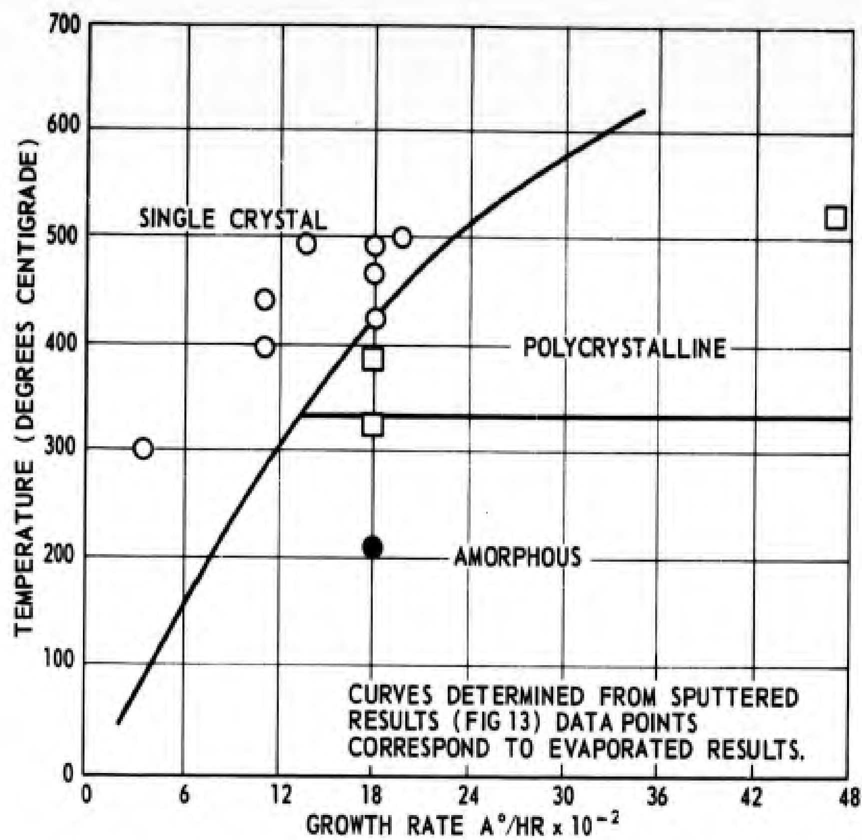
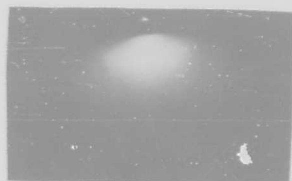
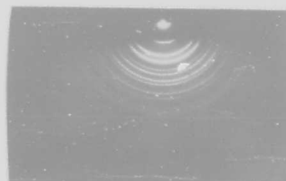


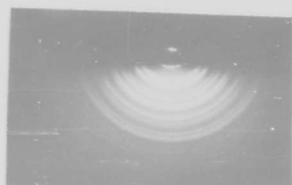
Figure 21. Effect of Growth Rate and Substrate Temperature on Film Structure for Ge on Ge [111].



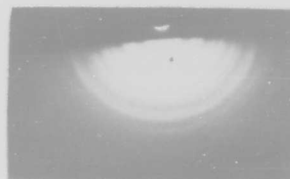
GLASS SUBSTRATE



FILM 500° C



FILM 450° C



FILM 385° C

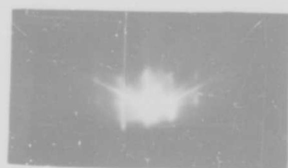
Figure 22. Reflection Electron Diffraction Patterns of Ge Films Evaporated Onto Glass Substrates at Various Substrate Temperatures.

films were deposited onto rock salt substrate at two pressures. It was verified that the pressure of residual gases does affect the structure of the film formed. Thirdly, a number of experiments was carried out on the deposition of gold onto microscope glass slides. Although, no single crystals were formed as yet, as the substrate temperature was increased from 200° to 400°C, the structural quality of the film formed was improved gradually. At 350° and 400°C the films obtained were very highly oriented. Fourth, the experiments on the effect of residual gases were repeated on the deposition of gold onto glass substrate at a constant substrate temperature. With a decrease of the residual gas pressure, an improvement was again observed on the structural quality of the film formed.

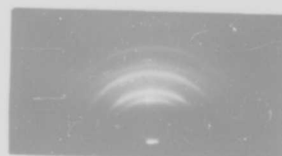
In all the experiments on gold films, molybdenum source boats were used. The evaporation was carried out at a temperature slightly above the melting point of gold. The distance between the source and the substrate was kept at 10 inches for all the experiments. The rate of evaporation at the substrate surface was kept at approximately 150 A°/min. Most of the films fell into the thickness range 500-700A°. Some of them were as thick as 200 A° or as thin as 100-200A°. Unless noted otherwise, the films cited as examples in this report were in the thickness range 500-700A°.

4. Effect of Substrate Temperature - Gold on Rock Salt

For this series of experiments, typical results are tabulated in Table VII. The corresponding plates of electron beam diffraction patterns are shown in Figure 23.



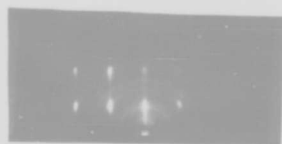
(a) NaCl (200)



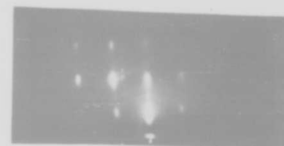
(b) 200°C AND
2.4×10^{-7} TORR

(c) 250°C AND
4.2×10^{-7} TORR

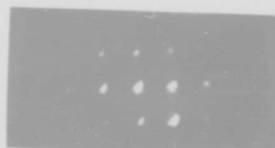
(d) 250°C AND
$.6 \times 10^{-7}$ TORR



(e) 300°C AND
3.0×10^{-7} TORR



(f) 350°C AND
1.0×10^{-7} TORR



(g) 400°C AND
2.0×10^{-7} TORR

Figure 23. Electron Diffraction Patterns of NaCl [200] Substrates and of Gold Films Deposited Onto it at Various NaCl Temperatures.

TABLE VII. EFFECT OF SUBSTRATE TEMPERATURE - GOLD FILMS DEPOSITED UPON ROCK SALT

Figure Number 23	T °C	P (Torr)	Structure of Film	Na Cl Orientation
a	---	---	Substrate	200
b	200	2.4×10^{-7}	Polycrystalline*	200
c	250	4.2×10^{-7}	Polycrystalline with preferred orientation	200
d	250	0.6×10^{-7}	Single Crystal	200
e	300	3.0×10^{-7}	Single Crystal*	200
f	350	1.0×10^{-7}	Single Crystal	200
g	400	2.0×10^{-7}	Single Crystal	200

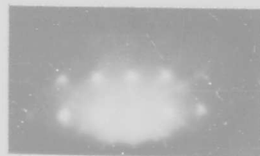
*Film thickness 100-200 A°

Under the specified conditions of evaporation described above, it may be noted that the minimum temperature at which a single crystal film of gold may be obtained by vacuum evaporation is in the neighborhood of 250°C in the 10^{-7} Torr range. All the gold films deposited at 200°C were polycrystalline. All the gold films deposited at 300°C or above were single crystals in the 10^{-7} pressure range. At 250°C, some of the films were polycrystalline with preferred orientation, but most of them were single crystals. The apparent influential parameter was pressure (see below).

5. <u>Effect of Residual Gas Pressure - Gold on Rock Salt</u>

As an initial evaluation of the effect of the residual gases, two pressure ranges, 10^{-4} and 10^{-7} Torr, and two substrate temperatures, 350°C and 400°C, were selected. The results are tabulated in Table VIII. As indicated, at both substrate temperatures, polycrystalline films were obtained at 1×10^{-4} Torr, but single crystal films were obtained at 1 to 2×10^{-7} Torr. Figure 24 represents the corresponding electron diffraction patterns.

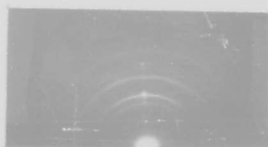
(a) 250°C AND 2×10^{-6} TORR



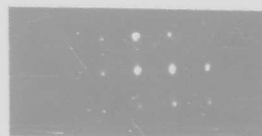
(b) 250°C AND 5×10^{-8} TORR

(c) 350°C AND 1×10^{-4} TORR

(d) 350°C AND 1×10^{-7} TORR



(e) 400°C AND 1×10^{-4} TORR



(f) 400°C AND 2×10^{-7} TORR

Figure 24. Electron Diffraction Patterns of Gold Films Deposited Onto NaCl [200] at Various NaCl Temperatures and Pressures of Residual Gases.

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TABLE VIII. EFFECT OF SUBSTRATE TEMPERATURE AND RESIDUAL GAS PRESSURE - GOLD FILMS DEPOSITED UPON ROCK SALT

Figure Number 24	T °C	P (Torr)	Structure of Film
a	250°C	$2x10^{-6}$	Polycrystalline with preferred orientation
b	250°C	$5x10^{-8}$	Single Crystal
c	350°C	$1x10^{-4}$	Polycrystalline
d	350°C	$1x10^{-7}$	Single Crystal
e	400°C	$1x10^{-4}$	Polycrystalline
f	400°C	$2x10^{-7}$	Single Crystal*

*Film thickness 100-200 A°

6. <u>Effect of Substrate Temperature - Gold on Glass</u>

When gold films were deposited on glass substrates, at various glass temperatures, the pressure of the residual gases was held in the 10^{-7} Torr range. Some of the results are summarized in Table IX and the corresponding electron diffraction patterns are shown in Figure 25.

TABLE IX. EFFECT OF SUBSTRATE TEMPERATURE - GOLD FILMS DEPOSITED UPON GLASS

Figure Number 25	T °C	P (Torr)	Structure of Film
a	200°C	$2.4x10^{-7}$	All films are poly-
b	250°C	$4.2x10^{-7}$	crystalline with
c	300°C	$1.2x10^{-7}$	preferred orientation.
d	350°C	$1x10^{-7}$	The degree of orientation
e	400°C	$1x10^{-7}$	increases with the increase
			of the glass temperature.

As the glass temperature was increased, the structural quality of the film formed was significantly improved though no single crystal films were obtained, even at 400°C. These results, coupled with those discussed before, clearly demonstrate the interdependence of the substrate structure and the film structure.

7. Effect of the Residual Gas Pressure - Gold on Glass

Only one glass temperature, 350°C, was used. As in the case of the rock salt substrate, the structural quality of the film was found to improve significantly with the decrease of the pressure of the residual gases. Two of the results are shown in Table X and the electron diffraction patterns are shown in Figure 26.

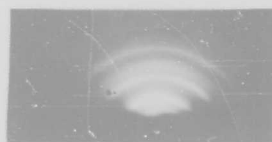
TABLE X. EFFECT OF RESIDUAL GAS PRESSURE - GOLD FILMS DEPOSITED UPON GLASS

Figure Number 26	T °C	P (Torr)	Structure of Film
a	350	$1x10^{-4}$	Polycrystalline
b	350	$1x10^{-7}$	Polycrystalline with preferred orientation

8. Evaporation of Silver

Crystalline films of silver have been deposited by vacuum evaporation on single crystal NaCl which had been freshly cleaved, along the [100] plane just prior to installation into the vacuum system. The substrates were pre-annealed at 300°C for a period of approximately one hour. The silver was evaporated from a tantalum boat heated to 1110°C. Evaporation was performed at several substrate temperatures ranging from 300°C to room temperature. The depositions were made in a vacuum maintained at about 10^{-7} mm Hg during the evaporation. The silver films were observed with transmission electron diffraction and x-ray diffraction. Diffraction patterns were observed over many areas of the specimen. The results of representative experiments are listed in Table XI.

(a) 200°C AND
2.4×10^{-7} TORR



(b) 250°C AND
4.2×10^{-7} TORR

(c) 300°C AND
1.2×10^{-7} TORR

(d) 350°C AND
1×10^{-7} TORR

(e) 400°C AND
1×10^{-7} TORR

Figure 25. Electron Diffraction Patterns of Gold Films Deposited onto Glass Substrate at Various Glass Temperatures

(a) 1×10^{-4} TORR

(b) 1×10^{-7} TORR

Figure 26. Electron Diffraction Patterns of Gold Films Deposited Onto Glass Substrate at 350°C and Two Different Pressures

Figures 25 and 26. Electron Diffraction Patterns of Gold Films Deposited Onto Glass Substrates.

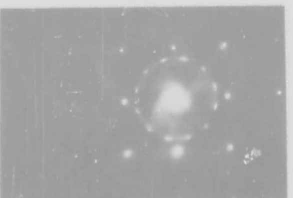
TABLE XI. EFFECT OF SUBSTRATE TEMPERATURE - SILVER FILMS DEPOSITED UPON ROCK SALT

Substrate Temperature	Film Thickness	Rate of Dep.	Pressure	Film Structure
100°C	3000A°	200A°/min.	10^{-7}	Polycrystalline
150	3000A°	"	"	Polycrystalline with High Orientation
300°C	3000A°	"	"	Single Crystal

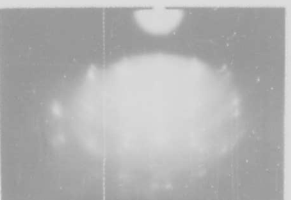
Electron diffraction patterns, shown in Figure 27, of the single crystal films showed the typical uniform square array of spots indicative of single crystal cubic structure. When examined by x-ray diffraction very sharp peaks were noted at the d-spacings corresponding to the [100] planes of both NaCl and Ag with no peaks occurring at any of the other spacings corresponding to other planes of Ag. This also indicates that single crystal Ag films were deposited. The d-spacings found were identical within the resolution limit to bulk material. Ag films prepared at lower temperatures were observed to be polycrystalline with varying degrees of orientation. Figure 27 shows the reflection electron diffraction pattern of a silver film deposited on [100] NaCl at a substrate temperature of 150°C. The film shows a high degree of orientation although it is not single crystal. The epitaxial temperatures for deposition of Ag on [100] NaCl at 10^{-7} Torr and a rate of 200 A°/min will, therefore, be found between 150°C and 300°C, probably closer to 150°C.

These results, although incomplete, do indicate, as in the case of Ge and Au, that for a given deposition rate, an increase of deposition temperature gives improved orientation. This result is in agreement with those reported by Sloope and Tiller[1] on evaporation of silver on NaCl. Complete systematic studies with Au and Ag, as those reported on the sputtering of germanium are in progress in this laboratory.

NaCl SUBSTRATE



FILM 300°C



FILM 150°C

Figure 27. Electron Diffraction Patterns of Silver Films Evaporated Onto Rock Salt at 300°C and 150°C.

C. ELECTRICAL PROPERTIES

1. General Discussion

A great deal of interest has been expressed recently in the electrical properties of thin films of semiconductors. Both experimental and theoretical investigations of these properties have been made. However, because of the complicated nature of semiconductors, progress in the understanding of their electrical properties has been slow.

The experimental measurements of electrical properties of semiconductor film show little agreement from one measurement to the other. This is probably due to the sensitivity of the electrical process to various factors; irregularities in the film, due to substrate surface variations, film continuity, etc., can cause radical deviations in the measurements. Therefore, it is of utmost importance to perform extremely careful, systematic experimental measurements, under conditions as controlled as possible, of the electrical properties of thin film semiconductors. Such experimental evidence is necessary in order to obtain a theoretical description of the electrical process in semiconduction. In this respect, a theory of electrical properties of thin film semiconductors has been developed recently.(8) Certain predictions result from this theory, i.e., mobility and Hall coefficient vary with film thickness, and the conductivity and Hall coefficient are anisotropic with respect to film orientation. These predictions can be experimentally checked with careful, systematic studies.

Preliminary investigations of the electrical properties of the films described in the previous sections have been made. Attempts to correlate

the electrical characteristics of the films with the deposition conditions and film structure are now in progress, and will be a part of the future program.

With the systematic results on structural characteristics of thin films of semiconductors as a function of deposition parameters reported in the preceding sections, a characterization of the electrical properties of semiconducting thin films in the same manner should be a valuable contribution both to basic and applied research efforts.

2. Results

Electrical measurements were made as described in the experimental section and appropriate values calculated from the following relationships:

a) $R_{Hall} = \frac{V_{Hall}\, t}{IB}$ $\mathrm{cm^3/coulomb}$

b) Carrier concentration = $\frac{3\pi}{8e} R_{Hall}$ $\mathrm{hole/cm^3}$

c) Carrier mobility = $\frac{8}{3\pi} \frac{R_{Hall}}{\rho}$ $\mathrm{cm^2/Volt\ sec.}$

where V_{Hall} is the Hall voltage, I is the current in amperes, t the thickness in amperes, B the field strength in gauss, and ρ the resistivity in ohm-cm. The calculated values may be used for purposes of comparison but are not to be considered absolute since the conditions under which the above expressions are derived may not be valid for thin films.[3]

Table XII lists the range of values obtained for Ge vacuum deposition on glass and some values reported in the literature[3] for Ge vacuum evaporated on single crystal CaF_2 under approximately the same conditions.

Table XIII lists the range of values obtained for Ge sputtered on amorphous Quartz and single crystal CaF_2. It should be remembered that these data include the electrical values for films of different thicknesses prepared under various conditions.

Before any correlation between structural and electrical properties can be made, more data must be obtained. This data must include the effect of film thickness and substrate surface conditions. It is interesting to note, however, that all films which were structurally classified as amorphous were of much higher resistivity than the polycrystalline and single crystal films. This result verifies that the structural quality of the film does effect the electrical characteristics. However, no conclusions can be drawn without further experimentation.

3. N-Type Films

In two cases, under different conditions, N type films of Ge on Quartz have been obtained. To the authors knowledge N type films have not been previously obtained. Table XIV lists the pertinent data for one of these samples. This film exhibits a higher Hall coefficient, and higher mobility than any of our other samples. The second film appeared to be discontinuous and, therefore, the measured values unreliable. Additional work is now in progress to pin down the exact conditions for the deposition of N type films.

TABLE XII
RANGE OF VALUES OF ELECTRICAL PROPERTIES FOR VACUUM EVAPORATED Ge

SUBSTRATE	ρ (Ω cm)	R_{HALL} (cm^3/coul)	N (carr/cm^3)	μ (cm^2/Vsec)
GLASS	.264 – 4.08	3.81 – 18.60	$3.98 \times 10^{17} - 2.40 \times 10^{18}$	6.30 – 32.60
CaF_2*	.07 – .1	6 – 12	$6 \times 10^{17} - 1 \times 10^{18}$	50 – 150

*REFERENCE (3)

TABLE XIII
RANGE OF VALUES OF ELECTRICAL PROPERTIES FOR SPUTTERED Ge

SUBSTRATE	ρ (Ω cm)	R_{HALL} (cm^3/coul)	N (carr/cm^3)	μ (cm^2/Vsec)
CaF_2	.06 – 5.38	.20 – 17.81	$4.15 \times 10^{17} - 3.64 \times 10^{19}$	.405 – 41.1
QUARTZ (AMORPHOUS)	.02 – 2.0	.423 – 9.97	$7.37 \times 10^{17} = 1.74 \times 10^{19}$	.546 – 47.1

TABLE XIV
PROPERTIES OF N TYPE FILM

SUBSTRATE	ρ (Ω cm)	R_{HALL} (cm^3/coul)	N (carr/cm^3)	μ (cm^2/Vsec)
QUARTZ	5.36	920	7.99×10^{15}	145.89

IV. CONCLUSIONS AND FUTURE WORK

The systematic dependence of the structural characteristics of sputtered germanium films on their formation conditions has been demonstrated for two systems, Ge on Ge [111] , Ge on CaF_2 [111] . The investigations with evaporated germanium films and with other film-substrate systems, prepared by sputtering and evaporation, indicate that a systematic dependence can probably very generally be expected for all systems.

This study has revealed some interesting phenomena, which may eventually lead to a better understanding of the epitaxial process. Diagrams, analogous to phase diagrams defining regions of sputtering rate and substrate temperature yielding exclusively either single crystal, polycrystalline, or amorphous structures have been established for Ge on Ge [111] and Ge on CaF_2 [111] .

In the case of Ge on Ge [111] , three unique transition regions were observed. At low sputtering rates direct transitions from amorphous to single crystal films occur as the substrate temperature is raised. At high sputtering rates (relative to the experimental range) two distinct transitions occur from amorphous to polycrystalline and from polycrystalline to single crystal film - as the substrate temperature is raised. In the high rate ranges the degree of orientation increased with increasing temperature between the two transition points. Finally, all transition regions merge in a triple point which can be exactly determined experimentally. At this point apparently random results are obtained with respect to film structure. Noteworthy seems to be the relative insensitivity of the amorphous-crystalline transition points to the sputtering parameters and the substrate

materials.

The existence of a very definite relationship between the sputtering current, substrate temperature, and film growth rate can be concluded from the results of the work on Ge-Ge [111] .

Based on the data at hand it is felt that progress on the theoretical description of epitaxi by sputtering, and probably other techniques can be achieved. A qualitative theoretical model is presented. This model couples the theory of supersaturated vapor, which primarily appears to define growth rate as a function of environment, with surface kinetic techniques which, at least in the present experimental ranges, seems to control the film ordering mechanism.

To date, none of the less intensely studied sputtered and evaporated systems have yielded data which are in basic conflict with the results obtained from the principal film-substrate systems studied here. The same holds true for all related data available from other sources, e.g.[1][2][3]. Electrical measurements of the films prepared by sputtering and evaporation have been made. At present, characterization of electrical properties of these films is limited to individual films; further electrical measurements are needed, and planned before the electrical characteristics of the films can be correlated with the structural characteristics.

In two cases, N-type films of Ge on quartz have been obtained. This is the first time, to the authors knowledge, that N-type films of Ge have been prepared. Work is now in progress to determine the exact conditions which result in N-type films and also to compare the electrical properties of these films with those of the p-type films.

The results of the work performed during this research period and reported here, suggest the following immediate future programs. The first task will be the formulation and establishment of a quantitative theory of epitaxial growth based on the qualitative models already presented, applicable to a limited number of material systems. In order to accomplish this task, it is necessary to extend the parametric study, initiated in the previous phases, for the purchase of filling in a number of information gaps.

Referring to the qualitative model discussed earlier, this will include the investigation of the effects of the kinetic energy in the incident beam on the growth rate of the germanium films. The results to date (Figure 12) show the effects of flux density on the growth rate in terms of sputtering current only. A change of current, under these conditions, changes the flux density, mainly in terms of the number of atoms per cc in the sputtering beam. A change in sputtering voltage, on the other hand, would change the flux density in terms of kinetic energy. The investigation to be performed, then, will involve the effect of flux density on the growth rate in terms of sputtering voltage. Such a systematic study of the effects of the kinetic energy of the impinging atoms is essential because: (1) a minimum kinetic energy is required before the vapor atoms can overcome the potential barrier which controls their nearest approach to the substrate atoms and (2) the magnitude of the kinetic energy controls, to some extent, the accommodation of the excess energy which must be transferred during the adsorption process.

The effects of kinetic energy of the impinging atoms will be investigated both by sputtering and vacuum evaporation processes since the

objective, in all cases, is not only the determination of the influence of the formation parameters, but a comparative evaluation of the effects of the deposition techniques, cathode sputtering and UHV evaporation. In this connection as stated earlier, with the present vacuum evaporation unit, it is not possible to work in regions of background pressure lower than the middle 10^{-8} Torr, although its measured ultimate pressure is in the low 10^{-9} torr range. A new UHV system is now being installed which will permit working pressures in the 10^{-9} - 10^{-10} torr region (ultimate pressure 10^{-11} torr range). In addition, a second sputtering system, which can be outgassed to lower pressures than the present unit (10^{-7} torr versus 10^{-6} torr), will be in use. These new units, aside from increasing the possible output of the experimental results, will reduce the effects of residual impurities on the film quality.

In addition to the study of the effect of kinetic energy of the impinging atoms, a more detailed study of the effects of substrate characteristics will be made. Based on the theoretical model, both the lattice geometry and the thermal characteristics of the substrate are important for the condensation and ordering process. Such effects as surface mobility, surface energy distribution, bonding energy, barriers between unlike atoms, all depend on the substrate characteristics. The two substrates studied in detail to date, Ge and CaF_2, cannot separate all these effects: more film-substrate systems must be investigated to formulate a quantitative theory. In this connection the study will be extended to include non-ordered substrates, i.e. quartz, already initiated under the present research period. Such results are significant both from a theoretical and

practical standpoint.

As indicated earlier, further electrical measurements of films prepared by sputtering and evaporation are necessary before characterization of the electrical properties of these films in terms of structural characteristics can be made. Such measurements are planned. Further work on the preparation and characterization of N-type films is also planned. It is hoped that such studies will result in the clarification of the electrical conduction mechanisms of both the p and N-type films.

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