

UNCLASSIFIED

NRL Report 6159

# Source Contamination Effects on The Epitaxy of Ge Films on Ge

J. E. DAVEY

*Solid State Electronics Branch  
Electronics Division*

September 28, 1964



**U.S. NAVAL RESEARCH LABORATORY**  
Washington, D.C.

## CONTENTS

Abstract	ii
Problem Status	ii
Authorization	ii
INTRODUCTION	1
EXPERIMENTAL PROCEDURES	1
RESULTS	2
Evaporation From a Tungsten Helix	2
Evaporation From Resistively-Heated, Spectroscopic-Grade Graphite	2
Evaporation From Quartz	6
Evaporation From Carbon in Quartz in Tungsten	7
Evaporation From Al <sub>2</sub> O <sub>3</sub> Cataphoretically Coated on Mo Helices	8
Evaporation From Al <sub>2</sub> O <sub>3</sub> Crucibles Indirectly Heated	10
Evaporation From RF-Heated Spectroscopic Graphite Crucibles	11
SUMMARY AND DISCUSSION	11
ACKNOWLEDGMENT	13
REFERENCES	14

---

## ABSTRACT

The effect of source contamination on the structure of Ge films deposited simultaneously onto single-crystal Ge substrates and amorphous quartz Hall substrates has been investigated. Deposition from the refractory metals, from quartz crucibles, and from extensively outgassed and vacuum-loaded graphite crucibles produce single-crystal films when deposited at a substrate temperature of 350°C; the electrical properties of the films deposited simultaneously onto the Hall substrates are typical of Ge films with good structural properties. Deposition from unoutgassed graphite crucibles (either resistive or radiative heating) and Al<sub>2</sub>O<sub>3</sub> in either crucible or cataphoretic form, produce films ranging from amorphous to polycrystalline when deposited on single-crystal Ge at 350°C. Evaporations from these latter materials will produce single-crystal films on Ge single crystals only for extensive vacuum outgassing and vacuum loading of the Ge charge and for substrate temperatures in excess of 500°C.

## PROBLEM STATUS

The work described in this report is a part of a more comprehensive and continuing project. This is a final report on this phase of the project.

## AUTHORIZATION

NRL Problem R08-44  
Project RR 008-03-46-5673

Manuscript submitted August 4, 1964.

## SOURCE CONTAMINATION EFFECTS ON THE EPITAXY OF Ge FILMS ON Ge

### INTRODUCTION

In studies of the structural properties of amorphous, polycrystalline, and single-crystal Ge films, there has been no general agreement as to: (a) the temperature at which germanium forms polycrystalline (textured) layers under hot deposition on neutral substrates (1-5), and (b) the temperature at which germanium forms single-crystal layers (epitaxial layers) upon single-crystal substrates (6-14). From the lack of agreement, it is patent that many parameters must be taken into account if a meaningful description of these changes is to be made. Some of these parameters are: (a) accurate substrate temperature measurement and control, (b) surface and bulk properties of the substrate, (c) condensation rate, (d) source temperature, (e) impurities from the ambient, and (f) source contamination.

In previously reported work at this laboratory (5), we have found film properties to be strongly dependent upon substrate temperature, however, we have, in the present work, also found marked changes in film properties with different boat materials. In particular, while carbon (15) and refractory oxides (15,16) are in common usage as boat material for vacuum evaporation, it will be shown here that unless rigorous outgassing procedures are employed, the use of those materials may result in Ge film structure ranging from amorphous to films of poor crystallinity on either neutral or single-crystal substrates. This result is interpreted as one major reason for lack of agreement on the conditions for the amorphous-to-crystalline transformation in hot-deposition on neutral substrates and also a major reason for the reported differences in the minimum epitaxial temperature on single-crystal substrates.

### EXPERIMENTAL PROCEDURES

To facilitate quantitative as well as qualitative comparison of the properties of films deposited from different sources, the following technique was employed: (a) in all evaporations two substrates were evaporated onto simultaneously. One was polished quartz containing a predeposited Cr film in a five-probe Hall configuration and the other a 58-ohm-cm polished and etched Ge single crystal (approximately (111) oriented). (b) A close-wound cylindrical oven was used to heat the substrates; this type of oven has good temperature uniformity and has been previously described (10). (c) All source material was 58-ohm-cm germanium. (d) The source-to-receiver distance was always approximately 8 cm. (e) The condensation rate was within a range reported to not be causally (11,17) related to changes in structural properties of Ge films. (f) The evaporation onto the single crystal was arranged physically on the substrate holder so that one half of it was not exposed to the vapor beam. The unexposed portion of the substrate served as a control to ensure that changes had not occurred at the substrate surface which would preclude crystallization in the films or confuse interpretation of structure. (g) After each evaporation the films were examined by reflection-electron diffraction, by x-ray diffraction, by Hall measurement, by four-probe measurements, and by thermal-probe measurement.

Initially, the effects of different boat materials were observed by depositing under the conditions outlined and at a substrate temperature of  $350 \pm 10^\circ\text{C}$ . This temperature was chosen to detect structural changes for the following reason: Weinreich et al. (8), Via and Thun (9), and Pundsack (13) indicate that epitaxy in Ge films will not occur below about

500°C. On the other hand, Davey (10) and Catlin et al. (14) report that epitaxy occurs at temperatures just above 300°C. Thus the observation temperature, in this work, of 350°C is well below the minimum temperature of 500°C and yet enough above 300°C to obviate any possible temperature differences in the earlier work.

For boats for which epitaxy did not occur at 350°C, the evaporations were repeated at 500°C. Individual boat processing will be described below.

## RESULTS

### Evaporation From a Tungsten Helix

In general, the tungsten boats were cleaned by electrolytic etching prior to loading. The structural properties and electrical properties of the films were found to be independent of vacuum outgassing of the tungsten boats prior to loading with the Ge charge if the etching technique was employed. (This is also true for molybdenum as well as tantalum.) Shown in Fig. 1(a) is the diffraction pattern from the "control" half of the single-crystal substrate. The control pattern shows well defined spots and kikuchi lines and an absence of rings; this pattern is typical of a single crystal with a high degree of perfection and demonstrates that no deleterious effects occurred during the evaporation of the germanium. Figure 1(b) is the diffraction pattern from the epitaxied film; this pattern does not exhibit any rings characteristic of polycrystallinity in the surface. The pattern is typical of a good single-crystal film. However, there are extra spots in the pattern; these extra reflections have been previously reported and are interpreted as due to twins (18,19). Figure 1(c) is the diffraction pattern from the film deposited on the quartz Hall substrate and is a mixed [110] and [100] texture; this has also been previously reported (5) for this temperature range. X-ray data obtained from the film on the Hall substrate are shown in Fig. 1(d); these data are also characteristic of a [110] texture with a half width indicative of reasonable particle size in the film (cf Ref. 5). The electrical measurements on this film are given in Table 1. The Hall mobility and carrier concentration values are also typical of previously reported measurements for evaporations from tungsten boats at this substrate temperature (20). These data obtained from films evaporated from tungsten (it is emphasized that other refractory metals such as tantalum or molybdenum yield similar results) will serve as a reference or standard of comparison in relation to the evaporations from other boats to be described below, and will be referred to as W1.

### Evaporation From Resistively-Heated, Spectroscopic-Grade Graphite

Since the history of commercial graphite boats is, in general, not available, we constructed our own in order to minimize contamination effects. The boats were hollowed out from 1/4-in.-diam carbon rods and were simply clamped between large-cross-section Cu rods and resistively heated to the evaporation temperature. Figures 2(a), (b), and (c) show, respectively, the reflection-electron diffraction pattern from the control, the epitaxied film,\* and the film deposited on the Hall substrate; this evaporation is called C1.

While the control, Fig. 2(a) shows an excellent quality surface, Fig. 2(b) shows that the epitaxied film is essentially polycrystalline in view of the strong rings exhibited in the electron diffraction pattern. The diffraction pattern from the Hall substrate indicates a weak [110] texture. The x-ray data shown in Fig. 2(d) confirm the weak [110] texture,

\*The film deposited on the single-crystal substrate will be referred to as the "epitaxied film" for convenience. The structure may range from amorphous to single crystal; the latter is customarily referred to as an epitaxied film.

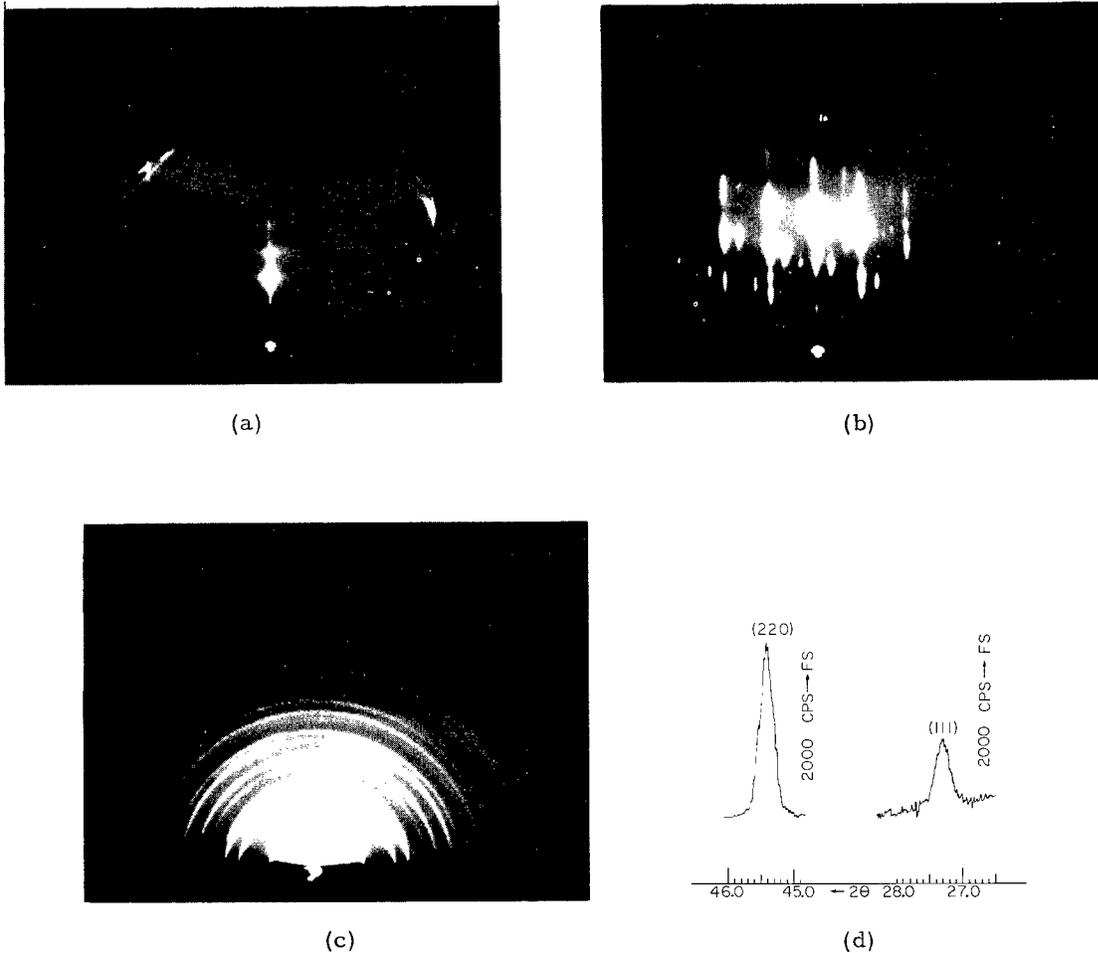
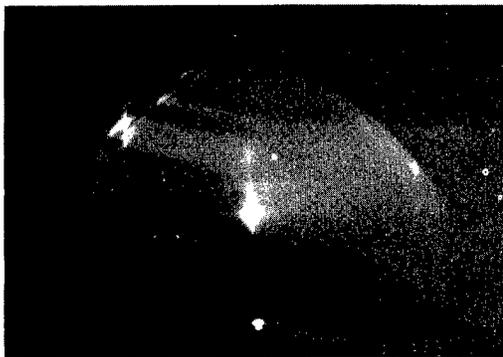


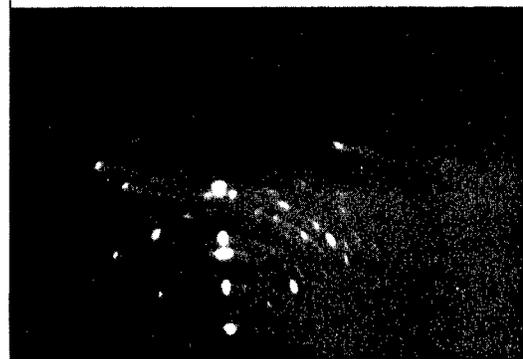
Fig. 1 - Diffraction patterns from Ge films evaporated from a tungsten boat, simultaneously, onto a single-crystal Ge substrate (half of it masked) and a quartz substrate, both held at a temperature of  $350^\circ\text{C}$ . (a) The reflection-electron diffraction (hereafter RED) pattern from the control half (the masked portion) of the single-crystal substrate. (b) The (RED) pattern from the epitaxied Ge film on the single-crystal substrate. (c) The (RED) pattern from the Ge film deposited on the quartz substrate with the Hall configuration. (d) The x-ray diffraction scan of the Ge film on the quartz substrate. X-ray scanning was at  $0.2^\circ/\text{min}$  with  $0.3\text{ MR} - \text{MR} - 0.2^\circ$  slits; all x-ray data were taken under these conditions.

Table 1  
Comparison of X-Ray Data and Electrical Measurements on Films Deposited from Different Boat  
Materials for Different Substrate Temperatures and for Different Outgassing Procedures

Run No.	Substr. Temp (°C)	X-Ray Data For 3° MR - MR - 0.2° Slits						Electrical		Measurements	
		(111) Reflection			(220) Reflection			p Carrier Conc. (cm <sup>-3</sup> )	(cm <sup>2</sup> /V-sec)	(ohm-cm)	four-probe
		Counts Range	Line Intensity (arbit. units)	Half Width (2 units)	Counts Range	Line Intensity (arbit. units)	Half Width (2 units)				
W1	350	2 · 10 <sup>3</sup>	3.32	0.28	2 · 10 <sup>3</sup>	11.40	0.26	1.2 · 10 <sup>18</sup>	500	0.01	0.16
C1	350	5 · 10 <sup>2</sup>	2.05	0.50	5 · 10 <sup>2</sup>	2.30	0.40	-	-	-	5.7
C2	500	5 · 10 <sup>2</sup>	3.30	0.33	5 · 10 <sup>2</sup>	1.90	0.33	6 · 10 <sup>17</sup>	260	0.04	0.7
Q1	350	1 · 10 <sup>3</sup>	3.80	0.30	1 · 10 <sup>3</sup>	4.60	0.34	4.4 · 10 <sup>18</sup>	156	0.009	0.16
CQ1	350	5 · 10 <sup>2</sup>	1.00	0.80	5 · 10 <sup>2</sup>	-	-	-	-	-	29.0
CQ2	500	5 · 10 <sup>2</sup>	3.45	0.50	5 · 10 <sup>2</sup>	1.12	0.60	4 · 10 <sup>17</sup>	800	0.02	0.29
AL1	500	5 · 10 <sup>2</sup>	3.10	0.60	5 · 10 <sup>2</sup>	3.32	0.60	-	-	-	28.0
AL2	350	5 · 10 <sup>2</sup>	1.70	0.70	5 · 10 <sup>2</sup>	1.10	0.80	1.2 · 10 <sup>18</sup>	34	0.16	2.8
C3	350	5 · 10 <sup>2</sup>	2.50	0.50	1 · 10 <sup>3</sup>	7.68	0.29	2.2 · 10 <sup>18</sup>	470	0.006	0.10



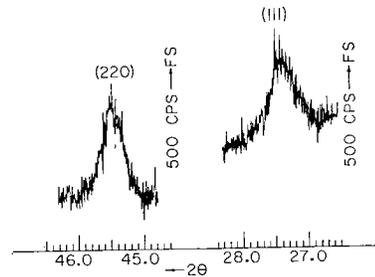
(a)



(b)



(c)



(d)

Fig. 2 - Diffraction patterns from Ge films deposited from a resistively heated spectroscopic grade graphite boat onto a Ge single-crystal substrate and a quartz substrate, both held at 350°C. The sequence of (a), (b), and (d) is the same as in Fig. 1; this sequence will be the same in Figs. 1-9.

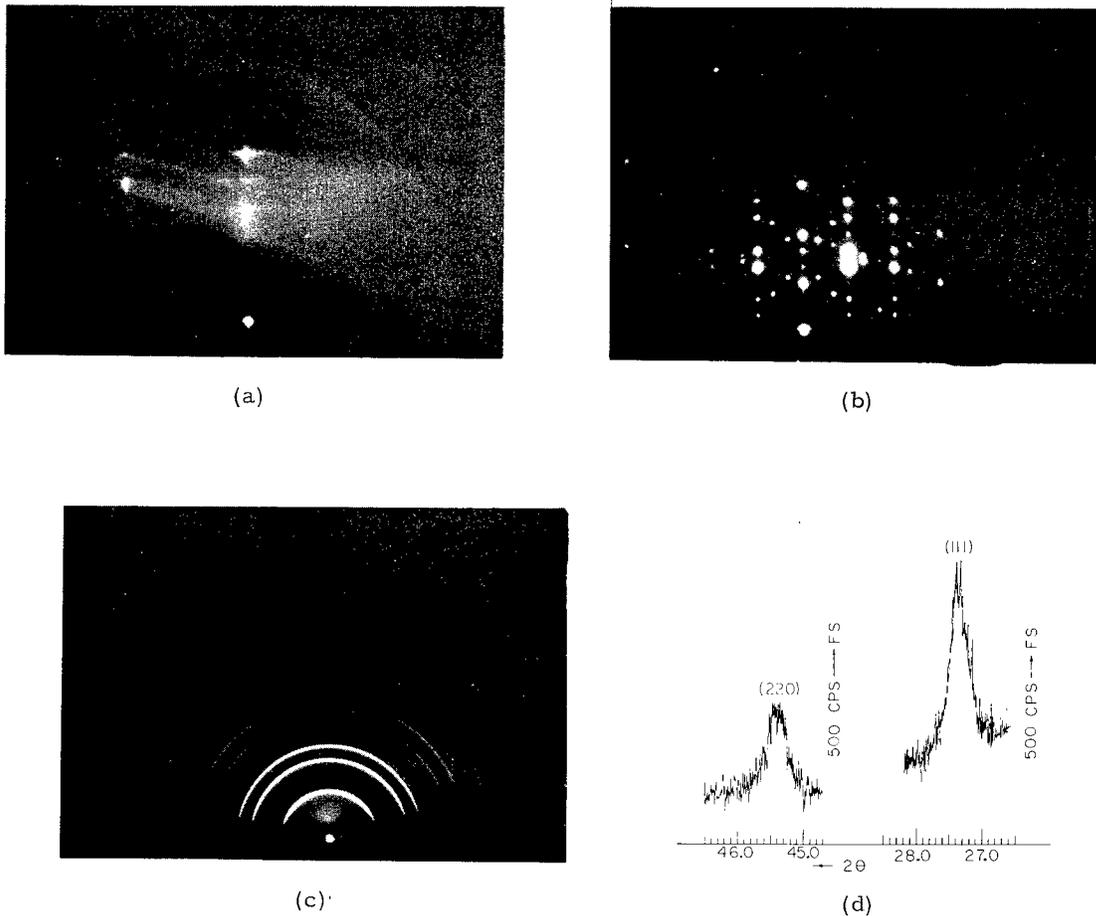


Fig. 3 - Diffraction patterns from Ge films evaporated from a resistively heated spectroscopic grade boat but with the substrates held at 500°C

but a comparison of the quantitative data with that from W1 in Table 1 shows the (220) reflection to be about 1/5 as intense as that from W1 and the half widths of both the (111) and (220) reflections to be nearly twice as wide as for W1; the latter indicates a significant decrease in particle size in C1 and hence a significant decrease in mobility. (It is clear that if the x-ray data show very broad and weak reflections, it can be expected that the mobility will be very low, if at all measurable.) While Hall measurements were carried out for all films, the signal-to-noise ratio in the data from film C1 rendered interpretation impossible. However, an estimate of resistivity from four-probe measurements is given in Table 1; the value of 5.7 ohm-cm is not typical of Ge films deposited at 350°C and indicates very low mobility.

Using the same type of resistively-heated graphite boat but carrying out the deposition at a substrate temperature of 500°C yields the data shown in Fig. 3; this deposition is called C2. While the control (Fig. 3(a)) shows the substrate to have retained a high quality surface during the deposition, the epitaxied film (Fig. 3(b)) shows weak rings characteristic of polycrystallinity in the surface. Certainly the structure of the film in C2 is improved over that obtained with deposition at 350°C, however, Fig. 3(b) shows that even at a substrate temperature of 500°C the structure of films evaporated from resistively-heated graphite boats is not as good as those evaporated from tungsten for a substrate temperature of 350°C. The x-ray data in Table 1 and Fig. 3(d) confirm this as can be

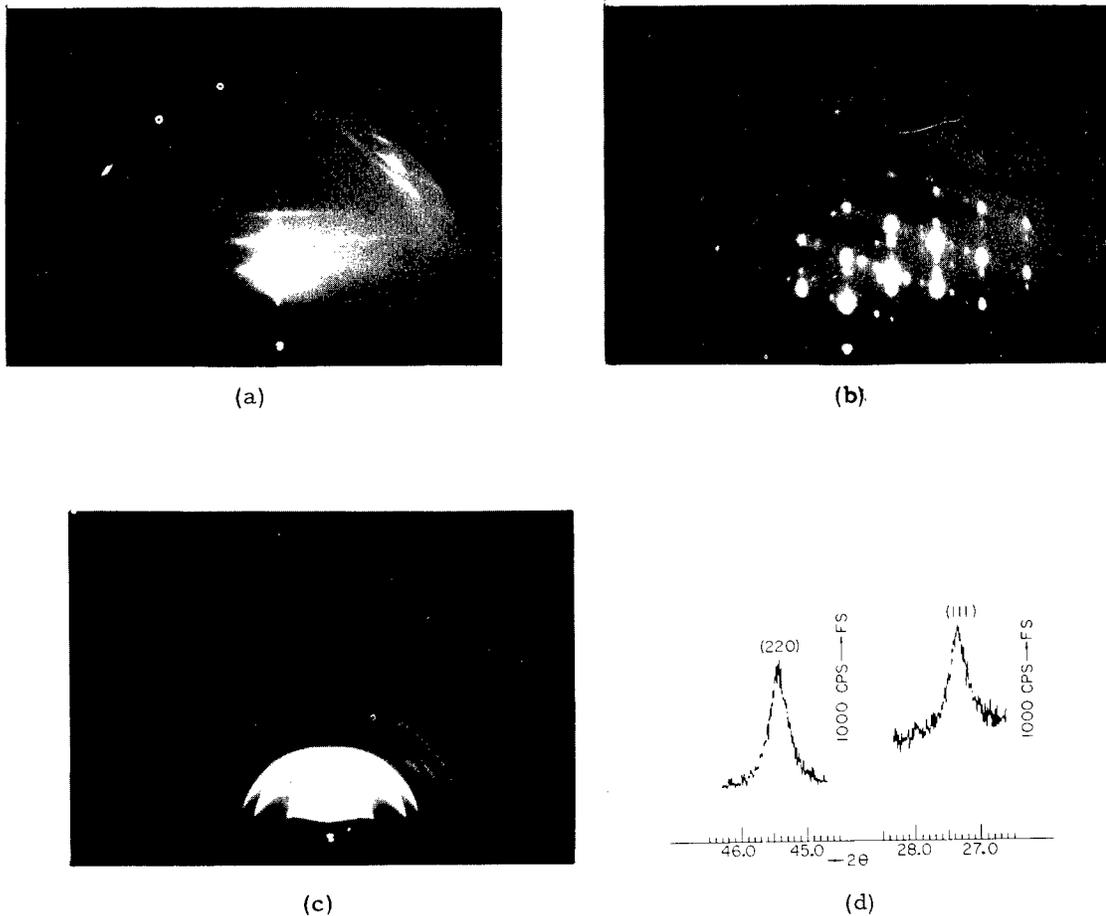


Fig. 4 - Diffraction patterns from Ge films evaporated from indirectly heated quartz cones; substrates were held at 350°C

seen by comparing both the line intensities and the half-width data. That is, even though C2 was carried out at 500°C the half widths of the (111) and (220) for C2 are still broader than those for W1 and point to a lower mobility. The latter is confirmed by the Hall measurements shown in Table 1.

#### Evaporation From Quartz

Cones of quartz were made to dimensions such that an intimate fit in commercial tungsten helices was attained. Figure 4 shows the data obtained from films evaporated from quartz onto substrates held at 350°C. As usual, the control shows excellent structure (Fig. 4(a)). (Since the structure of the controls was not observed to change in any of the depositions, no further reference will be made to them. However, for the sake of comparison, the electron diffraction patterns of the individual controls are shown in all figures.) The epitaxial film shows a twinned pattern (Fig. 4(b)) but no rings and thus no polycrystallinity in the surface. The Bragg lines are well developed and have half widths approaching those of W1 as indicated in Fig. 4(d) and Table 1; this evaporation from quartz is referred to as Q1. The Hall data for Q1 is also given in Table 1 and is similar to that of W1. In an earlier work it was shown that quartz containers can appreciably contaminate the Ge source material (21). The fact that the structure and electrical properties of

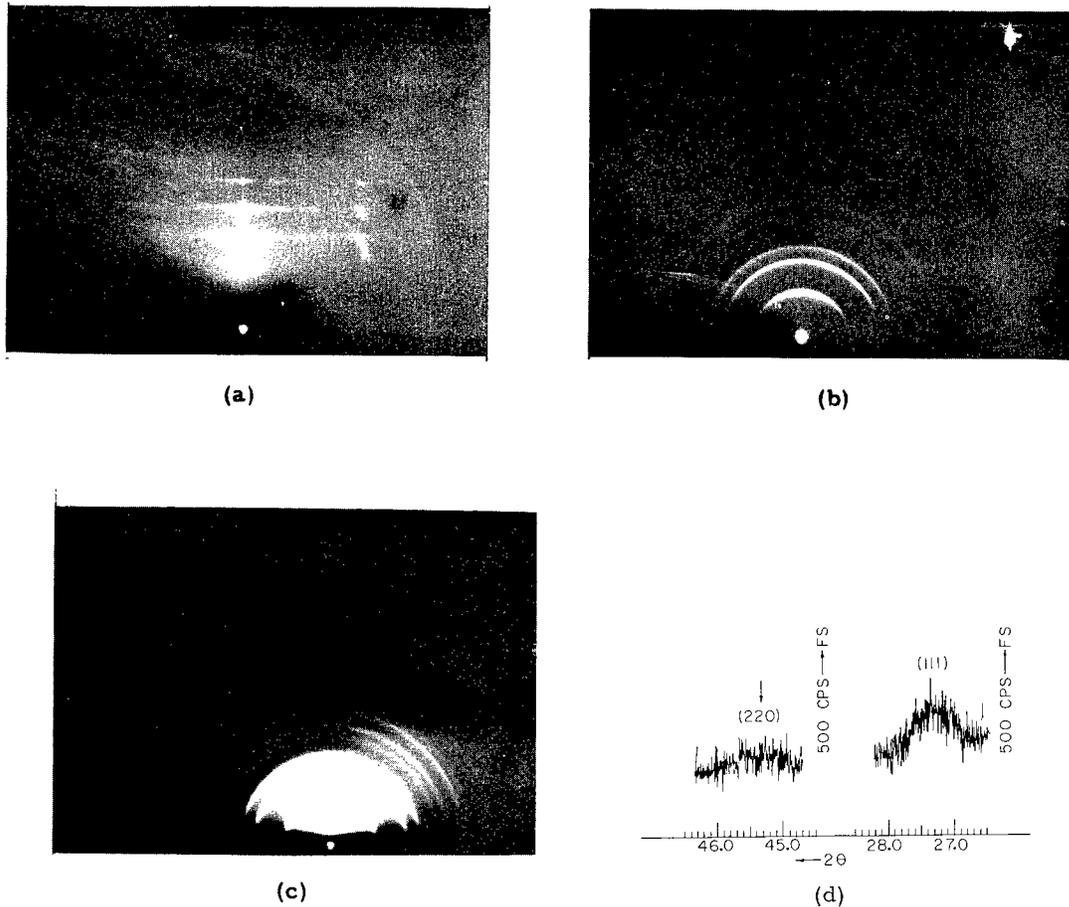


Fig. 5 - Diffraction patterns from Ge film evaporated from the carbon in quartz in tungsten system; the substrates were held at 350°C

the films do not differ appreciably from those evaporated from tungsten seems to indicate that the impurities introduced by the quartz into the melt have no gross effects on film properties.

#### Evaporation From Carbon in Quartz in Tungsten

Using the "Quartz cone" geometry, carbon cones with a small recess (approximately 3/16 in. diam by 1/8 in. deep) were made to fit in the quartz cones which in turn fit in the customary tungsten helix. While it is not clear that this system will produce any different result from that obtained with the resistively-heated graphite, the experiments to be described with this system were carried out for the sake of completeness, since others have reported studying epitaxy in Ge films with similar systems. The results of an evaporation from this system (called CQ1) at a substrate temperature of 350°C are shown in Fig. 5. The electron diffraction pattern of the epitaxied film is shown in Fig. 5(b), and contains rings only. This pattern is characteristic of a polycrystalline deposit and demonstrates that epitaxy from this system will not occur at 350°C substrate temperature. Figure 5(c) shows the deposition on the Hall substrate to be powder in form and not to exhibit any degree of texturing; the breadth of the rings indicates small particle size. The x-ray data in Fig. 5(d) show only a very weak and broad (111) reflection; the sample

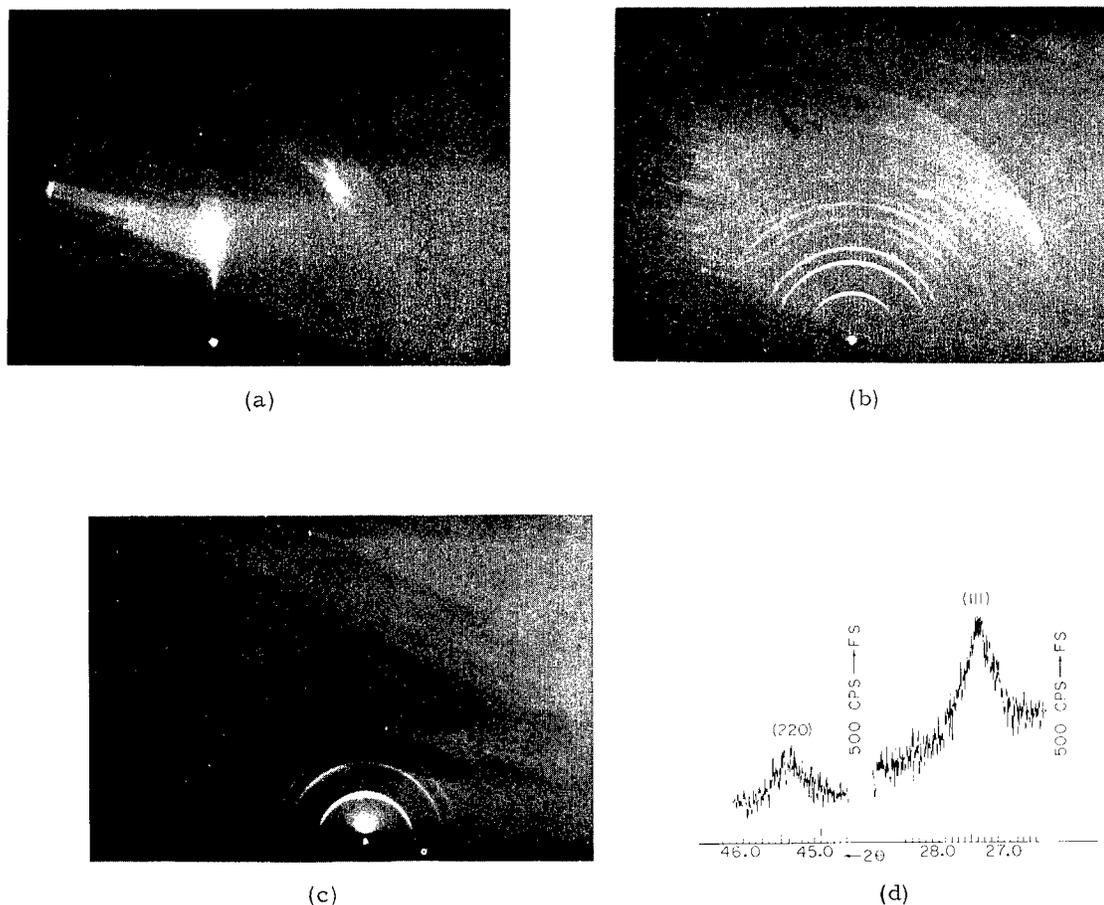


Fig. 6 - Diffraction patterns from Ge films evaporated from the carbon in quartz in tungsten system; the substrates were held at 510°C

is close to being amorphous. No meaningful Hall data could be obtained on this film. Four-probe measurements are, however, shown in Table 1. The high resistivity value confirms the x-ray data and indicates an abnormally low mobility.

The carbon in quartz in tungsten system was also employed for evaporation at a substrate temperature of 510°C. The results of this evaporation, called CQ2, are shown in Fig. 6. Figure 6(b) is the electron diffraction pattern of the epitaxied film and shows the film to be polycrystalline in character. This evaporation system has failed to produce a good single-crystal film even at substrate temperatures in excess of 500°C. Fig. 6(c) shows the diffraction pattern from the film on the Hall substrate and exhibits a [111] texture. The x-ray data on this film confirm the [111] texture as can be seen in Fig. 6(d); the diffraction profiles are still fairly broad, indicating small particle size. The signal-to-noise ratio in the Hall measurements was not good but approximate values are shown in Table 1; the four-probe measurements are also given. The measured Hall mobility is somewhat high in view of the quality of the x-ray data and should be treated with caution.

#### Evaporation From $\text{Al}_2\text{O}_3$ Cataphoretically Coated on Mo Helices

$\text{Al}_2\text{O}_3$  cataphoretically coated on filaments is in common usage as an efficient evaporation configuration and ostensibly should produce little contamination at low-filament

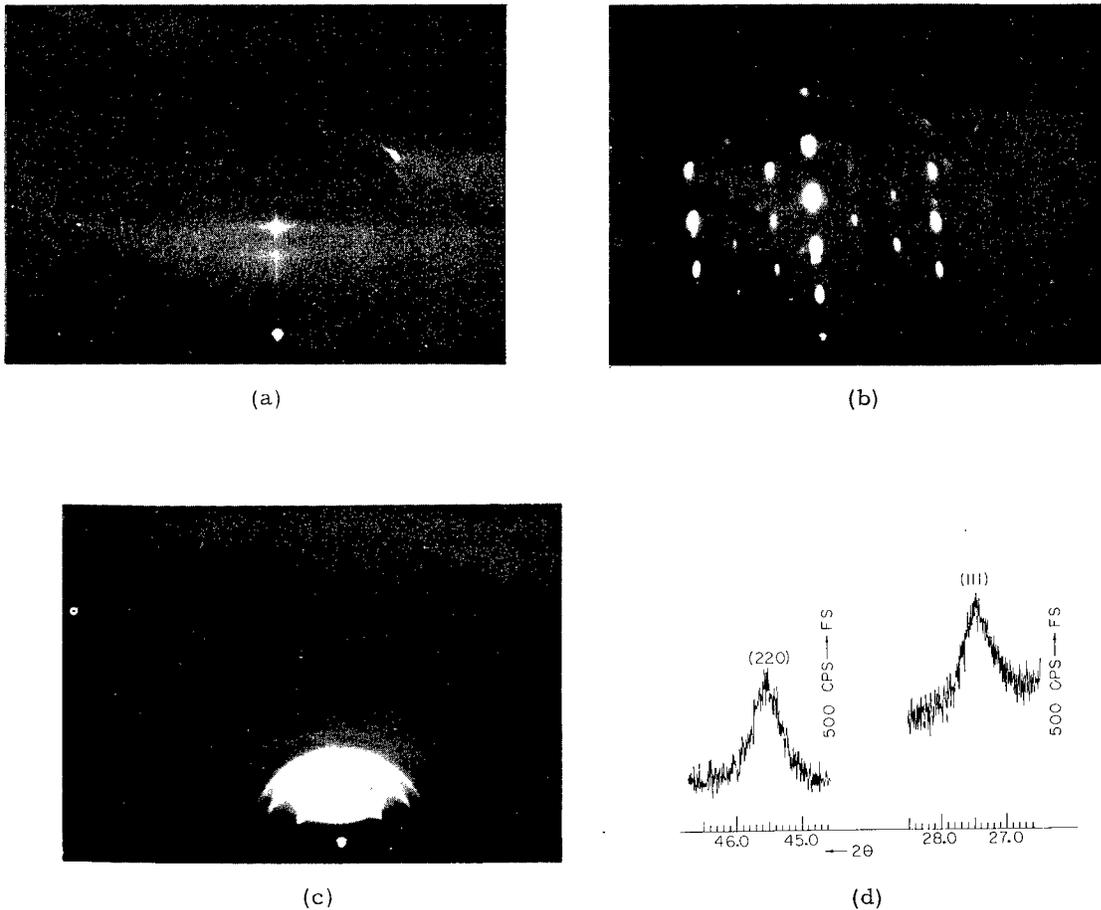


Fig. 7 - Diffraction patterns from Ge films evaporated from a boat of  $\text{Al}_2\text{O}_3$  cataphoretically coated on a Mo helix. The boat was vacuum outgassed and loaded with the Ge charge in the vacuum system. The substrates were held at  $500^\circ\text{C}$ .

temperatures (16). Using this system (without vacuum outgassing the basket), and depositing at a substrate temperature of  $350^\circ\text{C}$  produced films whose resistance (for 6000-Å thickness) exceeded  $10^8$  ohms. Examination by reflection-electron diffraction showed both the film on the single-crystal substrate and the film on the Hall substrate to be amorphous. X-ray scanning of the Hall sample (the same slit systems were used throughout all the measurements) showed no reflections and confirmed the amorphous character of the films.

Since it was clear that contamination products from the boat were inhibiting crystallization at the substrate surfaces, the evaporation from this type of boat was repeated but by first extensively outgassing the boat in vacuum (at about  $1350^\circ\text{C}$ ) and then loading the boat with the Ge charge without opening the vacuum system. Evaporation, after such outgassing, onto substrates held at  $350^\circ\text{C}$ , still produced films of very high resistance ( $\geq 10^7$  ohms for thicknesses of about 6000 Å), which were amorphous as measured by both electron and x-ray diffraction.

Repeating this evaporation procedure at a substrate temperature of  $500^\circ\text{C}$  resulted in about an order of magnitude reduction in resistance and the appearance of the electron diffraction patterns shown in Fig. 7; the data are referred to as AL1. The diffraction

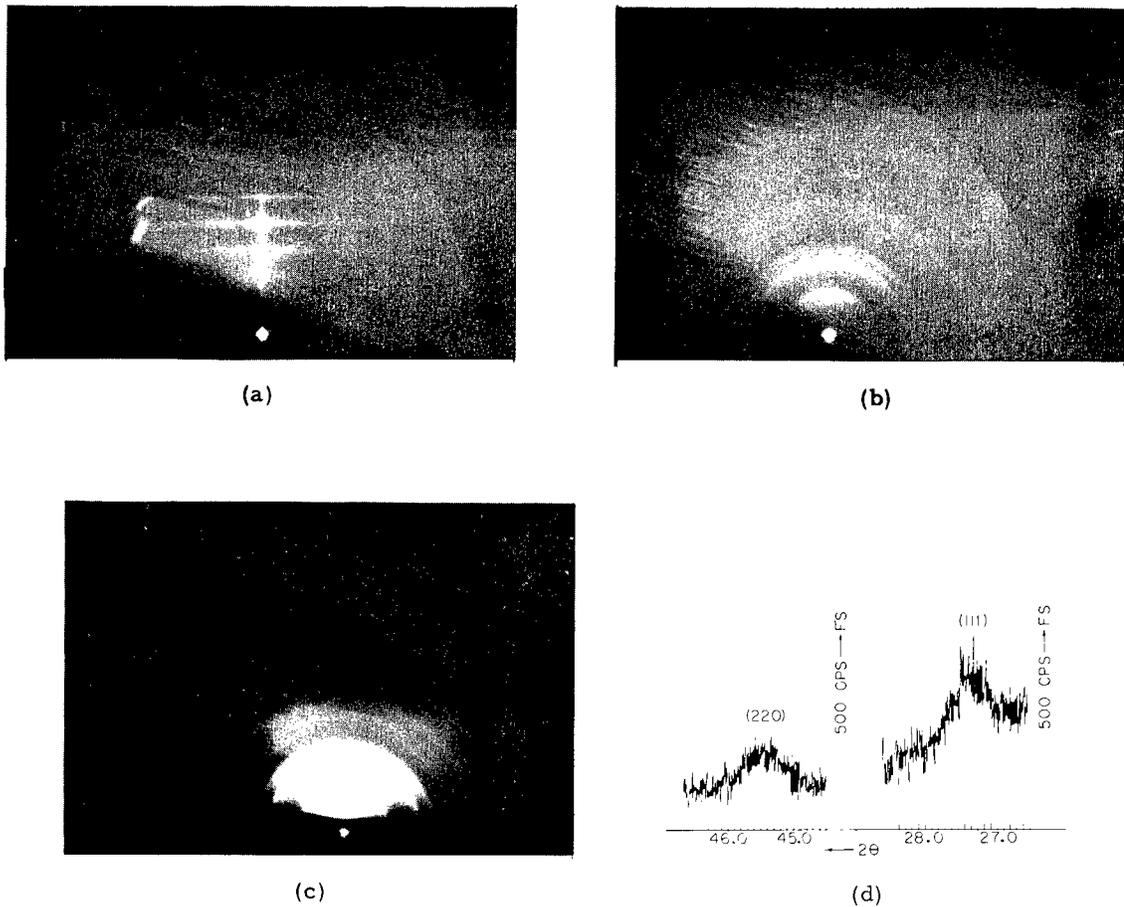


Fig. 8 - Diffraction patterns from Ge films evaporated from an  $\text{Al}_2\text{O}_3$  crucible which was indirectly heated and was vacuum outgassed and vacuum loaded with the Ge charge. The substrate temperature was  $340^\circ\text{C}$ .

pattern of Fig. 7(b) shows a fairly well-developed single-crystal film. The diffraction pattern from the film on the Hall substrate is powder in character; the x-ray data in Fig. 7(d) show a weak [110] with broad diffraction profiles. Even though Fig. 7(b) indicates fair crystallinity, meaningful Hall measurements could not be made on this film. The value obtained from four-probe measurements is indicative of the poor mobility which may be inferred from the diffraction profiles.

#### Evaporation From $\text{Al}_2\text{O}_3$ Crucibles Indirectly Heated

In these evaporations the boats were high-purity  $\text{Al}_2\text{O}_3$  crucibles which were suspended in tungsten helices and heated by radiation from the tungsten helix. The system was heat shielded with a Ta cylinder containing an orifice through which the germanium was evaporated. The first evaporation from this system was carried out at a substrate temperature of  $350^\circ\text{C}$  with no vacuum outgassing of the boat prior to loading. The 5400-Å film deposited had a resistance in excess of  $10^8$  ohms and was amorphous by both electron and x-ray diffraction measurements.

The same type system was again employed for evaporation but after extensive outgassing of the crucible and with vacuum loading of the Ge charge. The results of a deposition from the outgassed system are shown in Fig. 8 and in Table 1; this deposition is referred to as

AL2 and was carried out at a substrate temperature of 340°C. Fig. 8(b) shows that the polycrystalline deposit with small particle size has been formed on the single-crystal substrate and that even the extensive outgassing and vacuum-loading procedures were not sufficient to allow an epitaxy to take place. The electron diffraction pattern from the film on the Hall substrate exhibits no texture and also indicates small particle size; these observations are confirmed by the x-ray data shown in Fig. 8(d).

#### Evaporation From RF-Heated Spectroscopic Graphite Crucibles

The results of 3B and D, above, indicate that outgassing effects occurring during the evaporation may be severe enough to inhibit crystallization at the substrate surface if graphite is used as the boat material. However, it has been shown in an earlier work (21) that source contamination effects with graphite containers may be minimal if proper outgassing procedures are employed. Thus, the following procedures were employed in the evaporation. The crucible was held in a quartz tube graded to a Pyrex tube which in turn was coupled through a port in an adapter flange to a CVC vacuum evaporator. The crucible was 2 in. long and was cut from a 1-in.-diam spectroscopic purity graphite rod. A 1/4 in. diam by 1/4 in. deep recess was put in one end to hold the Ge charge and 1/16-in.-diam quartz pins were imbedded in the sides and bottom of the crucible to prevent it from touching and becoming contaminated by the quartz tube walls during the outgassing and evaporation. The Ge charge to be evaporated was held on the back of the shutter and could be dropped into the crucible, via a quartz funnel, when the shutter was opened. After pumping to about  $10^{-5}$  torr, the rf source was coupled (from outside the quartz container) to the graphite crucible and the latter was outgassed several times at temperatures between 1400 and 1500°C for periods up to 10 min. After the crucible cooled, the shutter was opened and the Ge charge dropped into the crucible (this was carried out under vacuum). The shutter was reinserted, the rf applied, the Ge charge melted, the shutter reopened, and the evaporation carried out at a substrate temperature of 350°C.

Figure 9 and Table 1 show the results of this evaporation, which is referred to as C3. The diffraction pattern of the epitaxied film in Fig. 9(b) shows no rings characteristic of polycrystallinity and is of the same character as Fig. 1(b). That is, the diffraction pattern is typical of a single crystal. The pattern also shows, however, the extra reflections typical of twinning also observed in Fig. 1(b). The diffraction pattern from the film on the Hall substrate, shown in Fig. 9(c), shows a good [110] texture with some incipient [100]. The x-ray diffraction profiles shown in Fig. 9(d) are nearly as intense as those of W1, and are in agreement with the electron diffraction measurements; the texture is [110]. The half width of the (220) reflection (cf Table 1) is about the same as that observed in W1 and indicates fair particle size. The electrical measurements are given in Table 1 and are also in good agreement with the data obtained from W1.

#### SUMMARY AND DISCUSSION

In general, it is assumed that the source container (boat) plays a little role in the determination of the electrical or structural properties of thin metal or semiconducting films. However, in the case of refractory metal boats, Heavens (22) has clearly demonstrated that the source material can be transferred to the substrate. Similarly, since carbon is an excellent getter (23), it can be expected that, unless prior outgassing techniques are employed, the gettered gases will be outgassed in the vapor beam during evaporation and will be transferred to the substrate; this is probably true, to some extent, of all porous boat materials. In the case of  $Al_2O_3$  on molybdenum, in cataphoretic form, there is the additional problem of the reduction of the oxide if high temperatures are used to heat the boat. In view of these possibilities, the properties of Ge films have been investigated under similar conditions of evaporation but from a variety of boat materials; the principal results as applied to the epitaxied films are summarized in Table 2 in

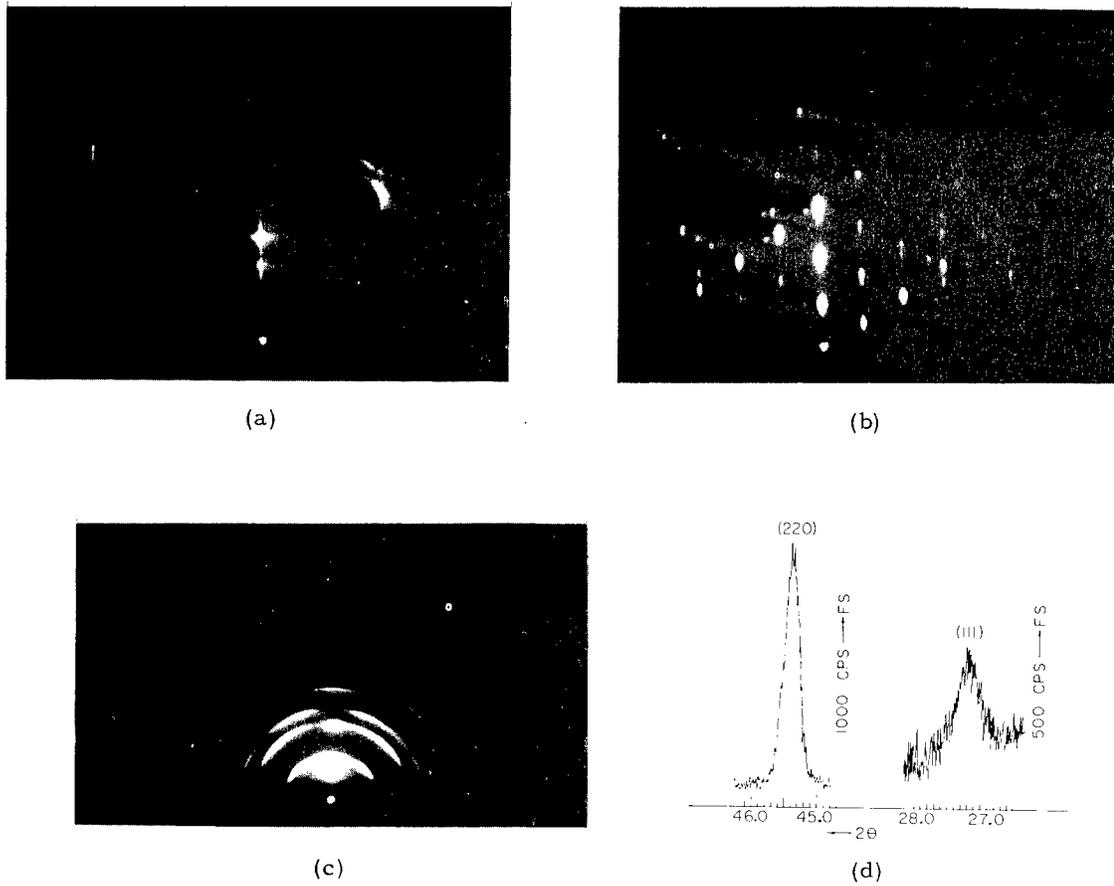


Fig. 9 - Diffraction patterns from Ge films evaporated from an rf heated spectroscopic grade graphite crucible. The crucible was vacuum outgassed (rf) and loaded in vacuum with the Ge charge. The substrates were held at 350°C.

Table 2  
Qualitative Comparison, by Electron Diffraction, of the Structure of Epitaxied Ge Film  
for Different Boat Materials and for Different Outgassing Procedures

Boat Material	External Loading of Charge	Vacuum Outgassed	Vacuum Loading of Charge	Structure Observed by Electron Diffraction of Ge Films Deposited on Single-Crystal Ge	
				Substrate Temperature = 350°C	Substrate Temperature = 500°C
W, Ta, Mo	X			single crystal, no rings	
W, Ta, Mo		X	X	single crystal, no rings	
Quartz Cone in W Helix	X			single crystal, no rings	
Graphite Resistive Heating	X			polycrystalline	borderline polycrystalline to single crystal (weak rings)
Graphite In Quartz in W	X			polycrystalline	polycrystalline
Al <sub>2</sub> O <sub>3</sub> on Mo	X			amorphous	
Al <sub>2</sub> O <sub>3</sub> on Mo		X	X	amorphous	
Al <sub>2</sub> O <sub>3</sub> on Mo		X	X		single crystal, no rings
Al <sub>2</sub> O <sub>3</sub> crucible	X			amorphous	
Al <sub>2</sub> O <sub>3</sub> crucible		X	X		single crystal, no rings
Graphite Crucible RF Heated		X	X	single crystal, no rings	

qualitative form. It can be observed that Ge evaporated from either the refractory metals or from quartz crucibles will form single-crystal films on Ge single crystals at substrate temperatures of 350°C. In the case of graphite, whether resistively heated or indirectly heated, without vacuum outgassing and loading, the Ge films deposited on Ge single crystals at 350°C are polycrystalline. With the use of rf heating, vacuum outgassing, and vacuum loading, evaporation of Ge from graphite crucibles produces single-crystal films at a substrate temperature of 350°C.

In the case of Al<sub>2</sub>O<sub>3</sub>, whether cataphoretically coated or in crucible form, the Ge films deposited at 350°C (from either outgassed or unoutgassed boats) are amorphous in character. However, if the boats are extensively outgassed and the deposition carried out at 500°C, or better, the Ge films are single crystal.

Ge films deposited at 500°C from unoutgassed resistively heated graphite were in general polycrystalline, although in some cases the rings in the diffraction patterns were very weak and it may be assumed that single-crystal films would be formed with further increase in temperature, above 500°C.

These results demonstrate that Ge films can be vacuum deposited in single-crystal form, on single-crystal substrates held at temperatures of 350°C, providing the source container itself does not contribute desorbed gases to the vapor beam. On the other hand, it may be concluded that unoutgassed boats must be used with extreme caution if meaningful interpretations of "epitaxy temperature" and the amorphous-to-crystalline change are to be made from data obtained with such boats. It seems clear from these results that this phenomena is one major cause for the discrepancies in the "epitaxy temperature" found in the literature.

#### ACKNOWLEDGMENT

The author wishes to express his gratitude to Howard L. Grant for carrying out all of the evaporations described in this work.

## REFERENCES

1. Glocker, R., and Hendus, H., Z. Elektrochem 48:327 (1942)
2. Richter, H., and Fürst, O., Z. Naturforsch 6A:38 (1951)
3. Richter, H., and Schneider, R., Z. angew. Phys. 11:277 (1959)
4. Fischer, E.W., and Richter, H., Ann. Physik 16:13 (1955)
5. Davey, J.E., J. Appl. Phys. 32:877 (1961)
6. Semiletov, S.A., Kristallografiya 1:542 (1956)
7. Kurov, G.A., Semiletov, S.A., and Pinsker, Z.G., Kristallografiya 2:59 (1957)
8. Weinreich, O., Dermit, G., and Tufts, C., J. Appl. Phys. 32:1170 (1961)
9. Via, G.G., and Thun, R.E., 8th National Vacuum Symposium, Oct. 1961
10. Davey, J.E., J. Appl. Phys. 33:1015 (1962)
11. Sloope, B.W., and Tiller, C.O., J. Appl. Phys. 33:3458 (1962)
12. Schalla, R.L., Thaller, L.H., and Potter, A.E., Jr., J. Appl. Phys. 33:2554 (1962)
13. Pundsack, A.L., J. Appl. Phys. 34:2306 (1963)
14. Catlin, A., Bellemore, A.J., Jr., and Humphris, R.R., J. Appl. Phys. 35:251 (1964)
15. Holland, L., "Vacuum Deposition of Thin Films," New York:John Wiley and Sons, 1956
16. Johnson, P.D., J. Amer. Ceram. Soc. 33:168 (1950)
17. Terry, L.E., and Williams, J.D., Spring Meeting, Electrochem. Soc., Toronto, May 1964
18. Georges, Blet, Compt. Rend. 255 (No. 5):972 (1962)
19. Pashley, D.W., Phil. Mag. 4:316 (1959)
20. Davey, J.E., Tiernan, R.J., Pankey, T., and Montgomery, M.D., Solid-State Electronics 6:205 (1963)
21. Davey, J.E., and Montgomery, M.D., Trans. of the American Vacuum Society 9th, 444(1963)
22. Heavens, O.S., Phys. Soc. Lond. Proc. 65B:788 (1952)
23. Dushman, S. (Lafferty, J.M., ed.) Scientific Foundations of Vacuum Technique, 2nd ed., New York:John Wiley and Sons, Chap. 7 (1962)

DOCUMENT CONTROL DATA - R&D		
<i>(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)</i>		
1. ORIGINATING ACTIVITY <i>(Corporate author)</i> U.S. Naval Research Laboratory Washington, D.C. - 20390		2a. REPORT SECURITY CLASSIFICATION <b>UNCLASSIFIED</b>
		2b. GROUP -
3. REPORT TITLE  Source Contamination Effects on the Epitaxy of Ge Films on Ge		
4. DESCRIPTIVE NOTES <i>(Type of report and inclusive dates)</i> Final Report on one phase of the problem.		
5. AUTHOR(S) <i>(Last name, first name, initial)</i>  Davey, John E.		
6. REPORT DATE September 28, 1964	7a. TOTAL NO. OF PAGES 18	7b. NO. OF REFS 23 refs.
8a. CONTRACT OR GRANT NO. NRL Problem 52R08-44	9a. ORIGINATOR'S REPORT NUMBER(S)  NRL Report 6159	
b. PROJECT NO. RR 008-03-46-5673	9b. OTHER REPORT NO(S) <i>(Any other numbers that may be assigned this report)</i>	
c.		
d.		
10. AVAILABILITY/LIMITATION NOTICES  Unlimited availability - OTS-\$.50 per copy		
11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY	
13. ABSTRACT  The effect of source contamination on the structure of Ge films deposited simultaneously onto single-crystal Ge substrates and amorphous quartz Hall substrates has been investigated. Deposition from the refractory metals, from quartz crucibles, and from extensively outgassed and vacuum-loaded graphite crucibles produce single-crystal films when deposited at a substrate temperature of 350°C; the electrical properties of the films deposited simultaneously onto the Hall substrates are typical of Ge films with good structural properties. Deposition from unoutgassed graphite crucibles (either resistive or radiative heating) and Al <sub>2</sub> O <sub>3</sub> in either crucible or cataphoretic form, produce films ranging from amorphous to polycrystalline when deposited on single-crystal Ge at 350°C. Evaporations from these latter materials will produce single-crystal films on Ge single crystals only for extensive vacuum outgassing and vacuum loading of the Ge charge and for substrate temperatures in excess of 500°C.		

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Crystallographic structure of films as determined by electron diffraction and by x-ray diffraction Epitaxy of germanium films Textured germanium films Electrical Properties of germanium films Influence thereon of gassy and ultrapure boat materials						

INSTRUCTIONS

1. **ORIGINATING ACTIVITY:** Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization (*corporate author*) issuing the report.
- 2a. **REPORT SECURITY CLASSIFICATION:** Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.
- 2b. **GROUP:** Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.
3. **REPORT TITLE:** Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.
4. **DESCRIPTIVE NOTES:** If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.
5. **AUTHOR(S):** Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.
6. **REPORT DATE:** Enter the date of the report as day, month, year; or month, year. If more than one date appears on the report, use date of publication.
- 7a. **TOTAL NUMBER OF PAGES:** The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.
- 7b. **NUMBER OF REFERENCES:** Enter the total number of references cited in the report.
- 8a. **CONTRACT OR GRANT NUMBER:** If appropriate, enter the applicable number of the contract or grant under which the report was written.
- 8b, 8c, & 8d. **PROJECT NUMBER:** Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.
- 9a. **ORIGINATOR'S REPORT NUMBER(S):** Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.
- 9b. **OTHER REPORT NUMBER(S):** If the report has been assigned any other report numbers (*either by the originator or by the sponsor*), also enter this number(s).
10. **AVAILABILITY/LIMITATION NOTICES:** Enter any limitations on further dissemination of the report, other than those

imposed by security classification, using standard statements such as:

- (1) "Qualified requesters may obtain copies of this report from DDC."
- (2) "Foreign announcement and dissemination of this report by DDC is not authorized."
- (3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through \_\_\_\_\_."
- (4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through \_\_\_\_\_."
- (5) "All distribution of this report is controlled. Qualified DDC users shall request through \_\_\_\_\_."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. **SUPPLEMENTARY NOTES:** Use for additional explanatory notes.
12. **SPONSORING MILITARY ACTIVITY:** Enter the name of the departmental project office or laboratory sponsoring (*paying for*) the research and development. Include address.
13. **ABSTRACT:** Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.  
 It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as (TS), (S), (C), or (U).  
 There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.
14. **KEY WORDS:** Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, roles, and weights is optional.