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Studies of germanium source material used for the vacuum evaporation of thin germanium films have been carried out by measuring the changes in the electrical properties of sources heated in the temperature range from 1100° to 1600°C. Using standard evaporation techniques and standard boat materials, the source germanium converts strongly to p-type, regardless of initial conductivity or type, and the properties of the resulting films are insensitive to the properties of the source. In a study of the causes of this source conversion, a number of experiments were performed which involved simple evaporation and combined zone-refining and evaporation processes in quartz and graphite boats in vacuum and helium ambients. The results indicate that the prevention of source conversion in vacuum may be attained by utilization of the zone-refining process in graphite, *in situ*, prior to treatment of the germanium as an evaporant. In addition, the results found using this technique confirm the hypothesis of Allen, Buck, and Law [*J. Appl. Phys.* 31:979 (1960)] on the effect of Ge contamination by boron in borosilicate glass vacuum systems.

INTRODUCTION

The evaluation of the electrical characteristics of vacuum-evaporated germanium films has been carried out by a number of investigators (1-7); there is general agreement that the resultant films are always p-type. One of these investigators has reported using both p- and n-type source material. However, no further details on the properties of the source material were given.

In addition to investigations of the film properties (7), we have also been concerned at this laboratory with the source material and changes in its properties when heated in vacuum to evaporation temperatures. In every instance where standard evaporation techniques were employed in the evaporation of germanium source material from n-intrinsic to n-degenerate, the source material was converted to p-type. In addition, the germanium films deposited from these sources were always p-type.

The initial part of this paper describes typical film properties and source properties obtained by using various source containers under about the same conditions of evaporation. The remainder of the paper is concerned with a determination of the causes of conversion of bulk germanium to p-type, when heated to temperatures in the evaporation range and with the prescription of a method to control source purity under such conditions.

NRL Problem R08-35; Project RR 008-03-46-5658. This is a final report on one phase of the problem; work on other phases continues. NOTE: M.D. Montgomery is now at the Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico.

EXPERIMENTAL PROCEDURES

To obviate the presence of copper and copper-like fast diffusers, all germanium samples were initially processed according to the method of Logan (8). Quartz components were etched in CP-8 solution, rinsed with deionized water, and torch fired to 1200°C. All metal parts were similarly etched and air dried. In all cases, the chemically cleaned components were handled only by Whatman No. 40 filter paper.

The vacuum systems consisted of a CVC vacuum evaporator and 5, 10, and 75 liter/sec Vac-Ion systems. Allen, Buck, and Law (9) have hypothesized that boron may be transferred from borosilicate glass during the initial pump-down of glass vacuum systems. In view of the transfer mechanism proposed by them, we attempted at the outset to preclude this by a utilization of the following loading techniques when using Vac-Ion pumps. The heat-treatment, evaporation experiments were always carried out in quartz tubes with a quartz-to-pyrex grade placed remote from any section to be heated during the annealing or pumpdown. The system was flushed with doubly trapped argon, and the quartz tube was heated to approximately 1200°C before sample loading. The insertion of the sample was carried out with the tube still warm and the gas flush on. After torch sealing the openings, the systems were pumped down to the ion pump starting pressure by Vac-Sorb pump. Similar outgassing procedures were used prior to experiments in helium ambient.

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Radio-frequency induction heating was employed in high-vacuum and helium experiments. All graphite crucibles and boats were prefired by rf heating to 1800°C in a helium ambient. In the CVC vacuum system, evaporations were carried out in helical tungsten baskets, in quartz cones indirectly heated by helical tungsten baskets and heat shielded with tantalum cylinders, or by helical Mo filaments cataphoretically coated with Al₂O₃. The latter were prefired in vacuum before loading with germanium.

In the case of *in-situ* zone-refining experiments on the high-vacuum systems, the following procedure was employed. The boats and germanium were loaded as described above. The vacuum system was cyclically baked and torched until a pressure of 10⁻⁸ torr, or better, was attained. Repeated zone-refining passes were carried out with increasing temperature in each successive pass until the pressure during passing was maintained at about 10⁻⁸ torr; the last pass was usually made at about 1400°C. (Total processing usually required between six and twelve passes.) After the last pass, either the pure end or the center section of the boule was reheated as an evaporation source, that is, heated to temperatures between 1150° and 1400°C but never as high as the temperature utilized in the final pass during zone-refining.

In general, the contamination and conversion effects were evaluated by measurements made with a standard four-point-probe system (10). A control sample was intermittently used to check the consistency of this system. When samples were not regular in shape, preliminary measurements were made by adjusting the probe points to the sample contour. Subsequently the samples were mechanically ground and then etched. Four-point probe measurements were made both after grinding and after etching. In the case of evaporated films, platinum contacts served to make the Hall contacts to the films. All samples, whether films or bulk, were also thermal-probed to test for the sign of the carriers.

PROPERTIES OF Ge FILMS AND SOURCE MATERIAL FOR DIFFERENT CONTAINERS

It was observed in this investigation that under normal evaporation conditions the intrinsic source material always converted strongly to p-type. It

was also determined that similar changes occur over a wide range of doping of the source material. The quantitative results are given in Table 1. Also, Table 1 shows the properties of films deposited during heat treatment of the source.* The data show that regardless of the initial character of the source material, from n-intrinsic to n-degenerate, the resultant films are all p-type, and all source material converted to p-type with concentrations ranging from 1×10^{15} to $3 \times 10^{16}/\text{cm}^3$. The use of tungsten evaporators results in an impurity concentration of about $10^{16}/\text{cm}^3$, approximately an order of magnitude higher than the $10^{15}/\text{cm}^3$ concentration found with the indirectly heated quartz cones (compare runs B and C with runs H, D, F, and G). Evaporations from Al₂O₃ baskets have also been performed under conditions similar to those described above. These evaporations have also resulted in source conversion with ultimate concentrations approaching $10^{17}/\text{cm}^3$, exceeding those observed for the tungsten evaporators. Other heating systems such as electron guns and carbon boats have also been employed, all yielding similar conversion effects.

SIMULTANEOUS CONTAMINATION AND CONVERSION EFFECTS WITH QUARTZ AND GRAPHITE CONTAINERS IN VACUUM AND HELIUM AMBIENTS

The results of the previous section show that the magnitude of source conversion in the CVC system was smallest when quartz boats were employed and that the n-type impurity was lost by evaporation from the host at the evaporation temperatures. Since it was possible that in the absence of continual contamination from the quartz, the p-type impurities may be also lost by vacuum evaporation and yield a highly pure source, an investigation of source conversion as a function of temperature was carried out in the evaporation range from 1100° to 1600°C in a simple quartz cone evaporator.

The quartz cone evaporator was calibrated in terms of temperature versus current using a Pt 10% Rh thermocouple. Samples were heated

*These evaporations were performed in the CVC evaporator onto quartz substrates heated to about 300°C. No attempts were made to restrict small variations in temperature or to hold the film thickness constant since previous work (7) has shown that no change in conductivity type can be expected with wide variations in those parameters.

TABLE I
Properties of Evaporated Ge Films With a Measurement of Source Properties Before and After Evaporation

Run	Source Properties Prior to Evaporation		Source Properties After Evaporation		Evaporation Procedures*		Film Properties						
	ρ (ohm-cm)	Type	Conc. (cm^{-3})	ρ (ohm-cm)	Type	Conc. (cm^{-3})	Boat†	Evap Time (Min)	μ_{h} cm^2 V-Sec	Conc. (cm^{-3})	ρ (ohm-cm)	Type	Thickness (Angstroms)
A	58	(n)	2.8×10^{13}	1.20	p	2.8×10^{15}	2	110	35.0	5.0×10^{18}	0.035	p	3000
B	0.10	(n,As)	1.6×10^{16}	0.11	p	3.1×10^{16}	1	14	16.0	3.1×10^{18}	0.13	p	4500
C	0.10	(n,As)	1.6×10^{16}	0.20	p	1.7×10^{16}	1	19	21.0	2.9×10^{18}	0.099	p	9000
D	0.10	(n,As)	1.6×10^{16}	1.00	p	3.4×10^{15}	2	56	3.0	7.6×10^{18}	0.27	p	2400
E	0.0089	(n,Sb)	1.8×10^{17}	0.12	p	2.8×10^{16}	2	60	41.0	1.5×10^{19}	0.01	p	10500
F	0.00004	(n,As)	4.0×10^{19}	3.22	p	1.1×10^{15}	2	70	8.5	4.2×10^{18}	0.18	p	6000
G	58	(n)	2.8×10^{13}	2.00	p	1.7×10^{15}	2	50	2.6	8.4×10^{18}	0.29	p	1500

*Source to receiver distance: 3 in.

†1-Tungsten helix; 2-quartz cone, tungsten helix, tantalum heat shield.

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for 10 minutes at between 1100° and 1600°C; the results are shown by the solid circles in Fig. 1. Again, the conversion to p-type occurred for all samples and, for the same heating times, the final impurity concentration was found to have an exponential dependence on reciprocal temperature. The exponential nature of the data in Fig. 1 suggests a net contamination process from the quartz. To determine whether ambient was a major effect in the conversion data of Fig. 1, the same type of experiment was carried out in helium, and again in a Vac-Ion system at 10^{-8} torr. The measurements on the helium (crossed circle) and high-vacuum (open circle) samples are shown in Fig. 1 and are in agreement with the values obtained from samples processed on the oil-pumped CVC system at 10^{-5} torr. The comparison of these results shows that in the quartz system, ambient does not play a major role in conversion. To confirm the hypothesis that the contamination was originating mainly in the quartz boats, *in-situ* zone-refining experiments

were also performed in both high vacuum and in helium. In this case the procedure was to zone-refine a number of times and then to reheat the pure end of the boule at an evaporation source. In all cases the overall resistivity of the boule was lowered, in addition to the normal segregation of impurities at the impure end of the boule. However, in all cases the reheated pure end of the boule also exhibited very low resistivity values, which indicated simultaneous contamination and conversion effects as a result of the heat treatment used as an evaporation source.

Although the above experiments clearly point to impurity contamination from the quartz itself as the principal cause of conversion, the results did not allow assignment of the separate roles in the conversion process of impurities caused by the reduction of oxides normally present in quartz, by a vacancy quenching mechanism, and by boron transfer. Experiments on the high-temperature heating of germanium in high-purity graphite in both high-vacuum and

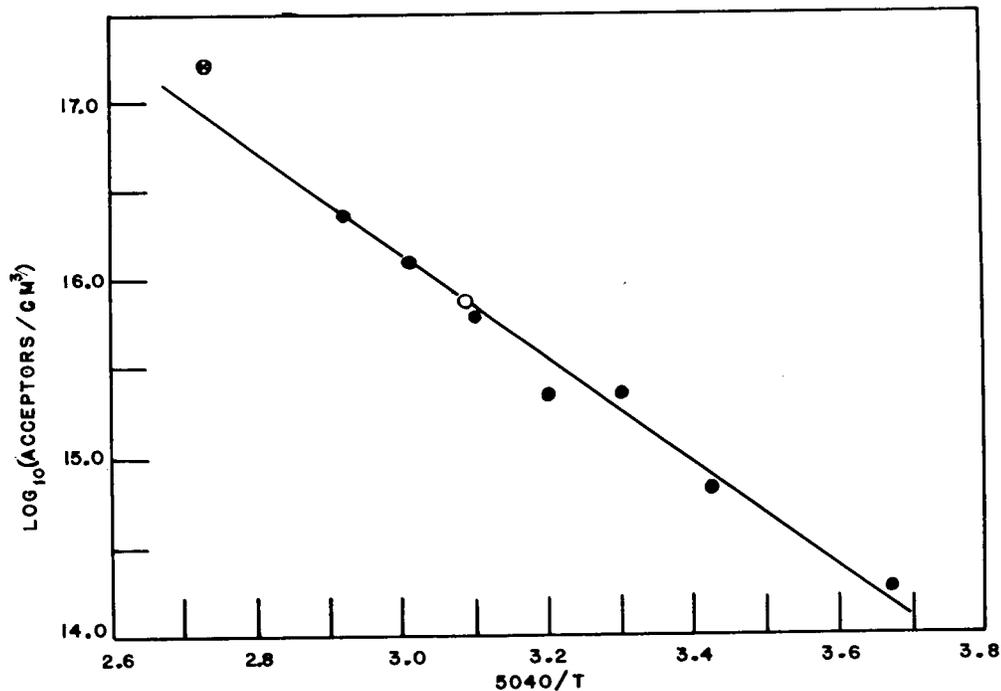


Fig. 1 - Conversion effects of germanium, in quartz cone evaporators, represented by a plot of the logarithm of acceptor concentration vs the reciprocal of absolute temperature. The acceptor concentration was determined by four-point probe measurements on different samples heated for 10 min at temperatures between 1100 and 1600°C. The open circle was determined from a high-vacuum sample, and the crossed circle from a sample heated in helium.

helium ambients resolved this difficulty. That is, when germanium was heated at temperatures as high as 1600°C in a helium ambient, only minor changes in resistivity occurred; typical data are given in the first two rows of Table 2. This result rules out vacancy quenching as a causative factor in the high-temperature conversion process. Also, since no borosilicate glass was involved in the heating system, no boron transfer occurred. However, since similar experiments on germanium in quartz crucibles, heated in helium in the same temperature range, showed strong contamination-conversion effects (indicated in Fig. 1), it is concluded that the predominant cause of conversion in quartz boats is impurity contamination from the boat itself.

It was clear from the vacuum heating of germanium to evaporation temperatures that high source purity could not be obtained with the use of quartz boats. On the other hand, heating in graphite in helium resulted in essentially no conversion effects or resistivity degradation; thus graphite was employed for further vacuum heating experiments. However, consideration of graphite as a container for high-vacuum use presents at the outset two important difficulties: (a) the outgassing of the boat during processing (11) will contaminate the boule,* and (b) the hot graphite in contact with a quartz tube may reduce the oxide impurities normally present in quartz (12) and also contaminate the boule. Since fusion analysis of germanium (13, 14) has shown the presence in germanium of large quantities of the gases most actively gettered by carbon, while other reports show that these gases are normally

electrically inactive in germanium (15), the first difficulty, above, is reduced merely to the problem of handling the outgassing with sufficiently fast pumps. With regard to the second difficulty, the crucibles were suspended off the quartz envelope by quartz pins set in the crucibles in positions remote from the boule; in this manner the reduction of oxides in the quartz envelope would be minimal.

In all cases of high-temperature heating of germanium in graphite, in both high and low vacuum, the germanium was converted and underwent resistivity degradation (typical data are given in the bottom four rows of Table 2). In view of the fact that the earlier experiments had ruled out both vacancy quenching and impurity contamination with high-purity graphite, a boron transfer during pumpdown was clearly indicated. As a test of this postulate, *in-situ* zone-refining of germanium in graphite was carried out in high vacuum. The presence of boron could easily be detected since it has a segregation coefficient of ~ 17 and would thus be transferred to the pure end of the boule. For this purpose a 21-cm long charge of 30 ohm-cm germanium was zone-refined in a high-purity graphite boat on the 75 liter/sec Vac-Ion system, six passes being made; in this case the center section of the boule was reheated as an evaporation source. Figure 2 shows a resistivity profile

*It is to be emphasized that the temperatures normally involved in the evaporation process are 1150°C or greater, and that while high-resistivity germanium is readily obtained by zone-refining at just above the melting point, the same is not customarily true when refining in the temperature range used for the evaporation process.

TABLE 2
Ge Heating in Spectroscopic Graphite Crucibles

Av. Initial Resistivity (Ohm-Cm)	Ambient	Temperature (°C)	Heating Time (Min)	Av. Final Resistivity (Ohm-Cm)
35	He	1360	10	17.0
35	He	1600	10	12.8
35	10 ⁻⁵ torr (CVC)	1300	10	2.0
35	10 ⁻⁵ torr (CVC)	1275	10	2.2
58	10 ⁻⁷ torr (Vac-Ion)	1200	5	5.0
58	10 ⁻⁷ torr (Vac-Ion)	1200	10	2.4

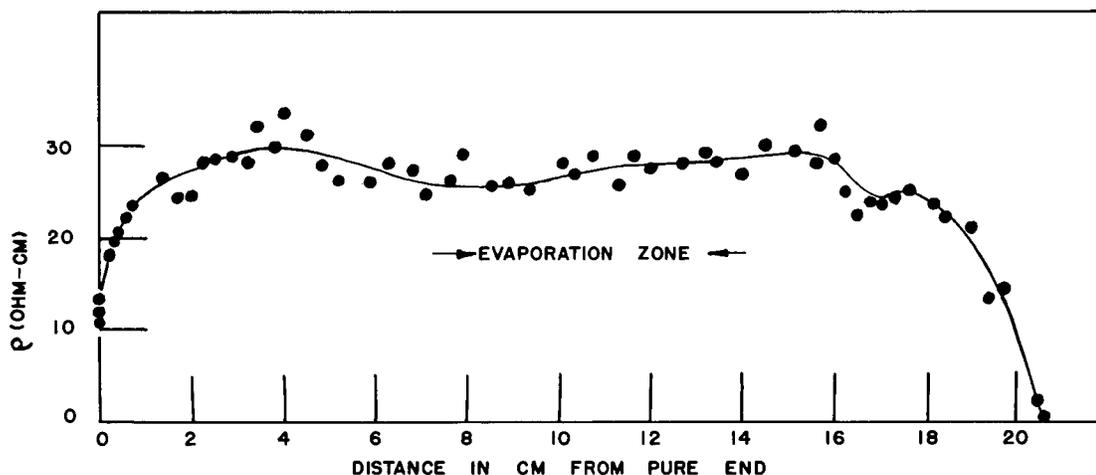


Fig. 2 - Resistivity profile in a germanium boule after zone-refining in a graphite boat in vacuum and then reheating the center section as an evaporation source. The zoning was from left to right. The decrease in resistivity at the pure end indicates the presence of boron.

measured along the germanium-graphite interface of this boule after removal from the vacuum system. The resistivity of this particular boule prior to loading was 30 ohm-cm and the average resistivity in Fig. 2 is still about 30 ohm-cm over the center section. This fact, plus the profile at the impure end, indicates that some contamination had occurred during handling and possibly also from the boat and tube walls. The decrease in resistivity at the "pure" end to ~ 13 ohm-cm shows that boron is present and, in view of the experiments in helium, that it was transferred during the evacuation. The important feature is that the average resistivity of 30 ohm-cm would have been maintained over this whole zone during evaporation. Thus, by this zone-refining and reheating process in graphite, a highly pure evaporation germanium source may be obtained even if there is the possibility of boron transfer and contamination during initial vacuum processing.

CONCLUSIONS

The compilation in Table 3 of the conversion effects in germanium source material heated to temperatures in the evaporation range leads to the following conclusions:

1. The use of standard boat materials, such as tungsten, tantalum, aluminum oxide, and quartz, and standard vacuum processing techniques

always leads to the conversion of germanium source material (ranging from n-intrinsic to n-degenerate) to p-type; the conversion is principally due to contamination from the source container, and its magnitude depends on the particular boat, temperature, and heating time.

2. Even with detailed precautions boron is transferred during pumpdown of borosilicate glass systems and causes conversion effects in germanium; the presence of boron has been detected by zone-refining germanium in boron-free graphite in vacuum. This result confirms the hypothesis of Allen, Buck, and Law (9) on the mechanism of transfer.

3. The technique of zone-refining in graphite, *in-situ*, is shown to remove not only normal processing impurities but also boron; it precludes the necessity of working with pure quartz systems and provides a high-purity, well-controlled source.

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TABLE 3
Summary of Contamination-Conversion Effects in Germanium at High Temperatures

Ambient	Container	Evaporation Technique	Temperature (°C)	Degree of Contamination Conversion*
Vacuum (10 ⁻⁵ -10 ⁻⁸ torr)	W, Ta, and Al ₂ O ₃ crucibles	Straight heating	1150-1600	Strong, increases with temperature
Vacuum (10 ⁻⁵ -10 ⁻⁸ torr)	SiO ₂ crucible	Straight heating	1100-1600	Strong, increases with temperature
Helium	SiO ₂ crucible	Straight heating	1100-1600	Strong, increases with temperature
Helium	SiO ₂ boat	Zone-refine, evaporate, rf heating	1200	Weak-Strong, recontaminates in evap. zone
Vacuum (10 ⁻⁸ torr)	SiO ₂ boat	Zone-refine, evaporate, rf heating	1150-1300	Weak-Strong, recontaminates in evap. zone
Vacuum (10 ⁻⁵ -10 ⁻⁸ torr)	Graphite crucible	Straight heating	1200-1300	Moderate
Helium	Graphite crucible	Straight heating	1200-1600	Very Weak
Vacuum (10 ⁻⁷ torr)	Graphite boat	Zone-refine, evaporate, rf heating	1200	None, i.e., no recontamination in evap. zone

*Strong 0.1 - 0.001 ohm-cm
Moderate 1.0 - 0.1 ohm-cm
Weak 10 - 0.1 ohm-cm
Very Weak 20 - 10 ohm-cm.
None 50 - 20 ohm-cm.

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