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Epitaxial Vapor Growth of Ge Single Crystals in a Closed-Cycle Process

Abstract: The Ge-I_2 disproportionation reaction in a sealed tube will deposit Ge epitaxially upon Ge seeds at a typical rate of 10μ/hr at a typical temperature of 400°C. Dislocations are of the same kind and approximate concentrations as observed in ordinary melt-grown Ge. Chemical purity is comparable to the best melt-grown Ge. The fraction of donors transferred from the source material to the deposited material is nearly unity over a wide range of concentrations, while the fraction of acceptors transferred is considerably less than unity. However, either *n*-type or *p*-type Ge can be deposited, and by using two sources within the same tube alternating layers can be obtained.

Introduction

Previous work[1-3] has shown that it is possible to use the reversible disproportionation reaction

$$2GeI_2 \rightleftharpoons Ge + GeI_4 \qquad (1)$$

to grow germanium single crystals epitaxially on germanium seed crystals. For a fixed amount of iodine, the equilibrium shifts to the right as the temperature is reduced. It is therefore possible to transport germanium from a high-temperature source region to a deposition region of lower temperature by allowing the reaction products in each temperature region to circulate to the other region in a cyclic manner. The purpose of this paper is to describe the details on such a cyclic process for the deposition of pure germanium and also to indicate how the process can be modified to allow the growing epitaxial deposits* to be doped with suitable impurities.

The rate of transport depends on the two temperatures, the circulation rate and the pressure (total amount of iodine). In typical experiments the operating pressures range from a fraction of an atmosphere to several atmospheres, the lower temperature is ~400°C and the higher one ~550°C. Circulation in the closed system is effected by a combination of gaseous diffusion and convection. The particular embodiment of the process to be discussed is the simplest one— namely, a single closed cylindrical tube containing several temperature regions. Other configurations are also feasible.

Growths of elemental semiconductors (especially silicon) have also been produced by other processes involving halogens (X). Two of the most important such processes presently in commercial use with silicon are:

(a) The Van Arkel reaction[4] (pyrolytic decomposition)

$$SiX_4 \rightleftharpoons Si + 2X_2 \qquad (2)$$

(and also sometimes $2SiHX_3 \rightarrow 2Si + 2HX + 2X_2$);

(b) the displacement or reduction reaction typified by

$$SiX_4 + 2Zn \rightarrow 2ZnX_2 + Si \qquad (3)$$

or

$$SiX_4 + 2H_2 \rightarrow 4HX + Si\,.$$

[See Refs. 5-7.]

Clearly these reactions are chemically entirely different from the disproportionation reaction (1). The first of the above reactions (2) can be made cyclic by recirculating the halogen X_2, but the deposition occurs in the high-temperature zone where the silicon halide (and doping agent halide) decompose on the seed material after having been formed at a lower temperature. Such a reaction thus does not have the important advantage of the disproportionation reaction which allows the deposition to be carried out in the cooler portion of the system.

Finally, epitaxial growths of germanium have been prepared by evaporating the element in a high vacuum on a heated substrate.[8] In order to obtain epitaxy over the whole surface of the growing deposit, the seed must be held at temperatures within 50°C of its melting point.[8,9] Again the important advantage of the disproportionation reaction is lost. In addition the growth rates achievable are very small and the inconvenience of operating in a vacuum is great.

*A deposit is said to be *epitaxial* if its crystalline orientation corresponds to the crystalline orientation of the substrate or seed.

In the Ge-I_2 disproportionation reaction, the deposition process takes place at $\sim 400°C$, a temperature at which diffusion rates for typical impurities are lower than those at the melting point by a factor of about 10^3. The concentration of impurities at the growing surface can in principle be changed in a time which is small compared to the crystal growth rate. Moreover, two or more sources of impurity in addition to the source of pure germanium can be used either singly or simultaneously to supply doping impurities at predetermined rates. Thus, in comparison with other procedures for doping crystals, it is more feasible to obtain *special impurity distributions* within the limits set by solubility. There is some evidence that these limits are broader than those found in melt and diffusion doping.[10]

The closed-cycle process was chosen for this investigation over the open-cycle one previously investigated,[2,3,11,12,13] because it was simpler to control at this stage of development and because the purity of the deposit would depend far less on that of the iodine used and not at all on the purity of the transport gas which is used in the open-cycle process. This experimental arrangement thus afforded a better opportunity to relate the purity and perfection of the deposit to the essentials of the process.

Apparatus and materials

For a typical deposition, a quartz tube about 25 mm outside diameter and closed at one end was loaded with a quartz rack holding several wafers of seed Ge, roughly rectangular in shape and from 1 to 10 sq cm in area; 50 to 100 g of source Ge in one or several pieces; and 5 to 300 mg of I_2. Generally, the source Ge was positioned at one end of the tube and the seed Ge at the other end. The I_2 was positioned near the closed end of the tube and during pumpdown was kept from evaporating away by putting the closed end of the tube in a cold bath. The tube was then pumped to a pressure of 10^{-5} mm or lower and either sealed off or first backfilled with a reduced pressure of H_2 or an inert gas and then sealed off. The length of the tube for this simple arrangement was usually 15 to 25 cm. Undoubtedly, the diameter and general configuration of the tube could be important in special circumstances, but they have not been found to be critical in the experiments reported here.

In order to heat the loaded closed tube, nichrome ribbon was spirally wound directly on the middle portion of a quartz tube with an inside diameter of approximately 28 mm and a length of 60 to 100 cm. Then a larger quartz tube was slid over the winding to reduce heat loss without losing visibility to the furnace chamber. Several windings usually were used to provide the desired temperature profile, but under particular conditions a single long winding was used, with aluminum foil sleeves wrapped around the outer furnace tube in regions where higher temperatures were desired. The temperature was measused by a thermocouple threaded through the length of the furnace tube between the sealed tube and the furnace wall. The thermocouple junction could be positioned by moving the cold ends of the thermocouple. This arrangement eliminated the need for insulating beads and thereby permitted a very low heat capacity of the thermocouple.

The source Ge was not always monocrystalline nor in one piece. The use of several pieces increased the surface area, which in turn increased the reaction rate between GeI_4 vapor and the source Ge. If very small granules were used, however, cleaning and drying became troublesome and the reaction rate was not perceptibly increased. When comparisons were to be made between impurity concentrations in the source and in the deposit, uniformly-doped monocrystals of source Ge in one piece or a few large pieces were preferable.

Seed Ge of various shapes were employed, and the depositing Ge oriented itself epitaxially at rates depending upon orientation, temperature and pressure. For polycrystalline seeds, the deposit was found to be correspondingly polycrystalline. The effect that dislocation density might have on the deposited Ge was studied separately,[14] but the deposits were still monocrystalline even when the seeds had dislocation densities of $\sim 10^5/cm^2$. The possibility was considered that elastic or plastic deformation of thin substrate wafers could occur, but such effects were not important in the normal deposition runs reported here. Generally, the seed wafers were etched in dilute white etch (ten parts HNO_3, one part HF, and six parts H_2O) until nearly mirror-smooth. However, fracture surfaces and even lapped surfaces were also used. The positioning of the seeds in the tube was determined to some extent by the course of convection currents.

Because GaAs has a lattice constant equivalent to that of Ge and an electronic structure which is similar, it was used successfully as seeds. The deposited Ge was completely epitaxial. Semiconductor junctions (heterojunctions) were formed between the Ge and GaAs and were made the subject of further studies which are still in progress.[15,16]

The iodine was specially purified by two sublimations beyond ACS specifications. Arc-spectrographic analyses of the iodine have shown that impurities were present in the approximate range of 0.0001% to 0.001%. However, the concentrations would vary from one batch of iodine to another without making any perceptible difference in the purity of the deposited Ge. The impurities generally found in the iodine were Mg, Ca, Cd, Mn, Ni, Fe, and Si. None of these impurities, however, was ever detected in the deposited Ge. Cu was sometimes present in the iodine, but never detected for certain in the deposit. The arc-spectrographic analyses did not, of course, reveal whether the impurities were free or combined. Very likely, they were combined with iodine, and thereby kept out of the deposit to a considerable extent. Of interest was the fact that no special precautions had to be taken to avoid contamination by Cu, the notoriously bad recombination center in Ge.

Procedure

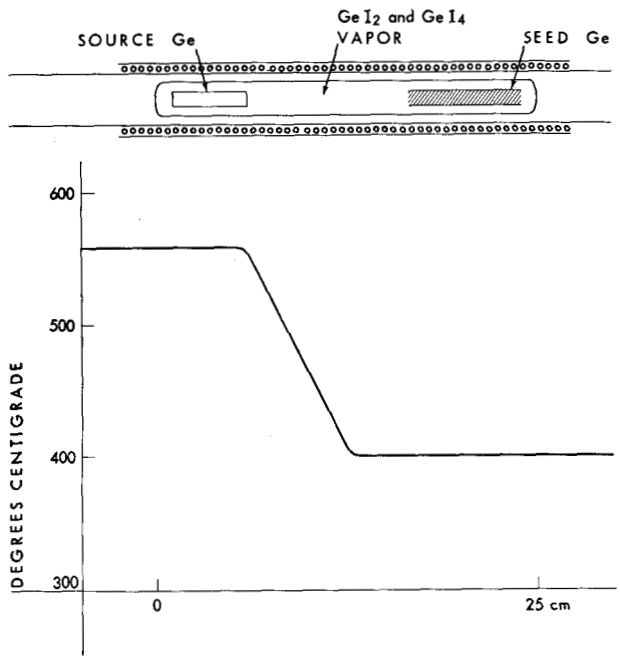
As discussed earlier, it is believed that the deposition occurs according to the disproportionation reaction

$2GeI_2 \rightleftharpoons GeI_4 + Ge$. As the temperature increases, the reaction proceeds towards the left; and towards the right as the temperature decreases. Therefore, the source Ge zone is held at a higher temperature than is the seed Ge zone. The motion of the gas occurs by diffusion and convection.

The sealed tube is positioned in the furnace as shown in Fig. 1. As the tube is heated, the color of the gas in the tube is violet at first, which is the characteristic color of I_2, and then it becomes yellowish-green, indicating that reaction with the Ge has occurred. The temperature profile indicated in Fig. 1 is typical of a usual run. Normally, the lower temperature region (the seed region) is kept as cool as possible without permitting GeI_2 to condense; when low I_2 concentrations are used, the temperature of the substrate region can be kept lower than that shown.[17] The temperature of the source region was found to be not very critical. Depositions were usually carried out with source temperatures ranging from 480° to 700°C.

What happens during the initial stage of the reaction is not yet fully understood.[14,18] The oxide film which is certain to be present on both the source and seed Ge is wholly or partially removed, either by direct chemical reaction with the I_2 or mechanically as a result of the penetration of I_2 through cracks in the oxide. The seed Ge can be given more extensive vapor etching when desired by raising the seed zone temperature higher than the temperature in the other regions during the initial part of a deposition run. For applications in which the early deposited portion is critical, the Ge which has been etched away ought not be allowed to deposit on the seeds. Therefore it is then advantageous to allow this Ge to deposit somewhere in the tube not occupied by the source or seed Ge. A "dump zone" for this purpose is described in a modified closed-tube configuration in a Letter to the Editor in this issue.[16]

Figure 1 **Diagram of "closed-tube" method of vapor growth.**



Under the conditions described in Fig. 1, the deposition rate is 75 to 200μ/day; the duration of the run is determined by the thickness desired. For many cases, a thickness of 500 to 700μ was sufficient for measurements, and the run duration was 7 to 10 days. Convection currents in the vapor decidedly affect the uniformity of the thickness of the deposit. Tilting the tube and furnace affords some degree of control of the convection currents. Positioning the tube and furnace vertically with the seed region above the source region has yielded still better uniformity of thickness but increased the difficulty of maintaining sharp temperature gradients. The near-horizontal position has been generally preferred in the experiments as being more convenient.

After the run is completed, specimens for electrical measurements are prepared by lapping away all of the seed Ge and then cutting the deposited Ge into regular measurement samples of the order of one sq cm in area and about 500μ in thickness.

Results

Growth rates depended considerably upon I_2 concentration over the wide range of concentrations tried. Using the typical conditions shown in Fig. 1, roughly approximate deposition rates are shown in Table 1. There are several reasons why the data in Table 1 were only approximate. First, convection currents affect the deposition rate, and much of the data were taken before any attempts were made to control the convection currents. Second, since the deposits (especially the thicker deposits) were not of uniform thickness, the average thickness had to be estimated. (This nonuniformity itself was due largely to convection currents.) Third, in runs of longer duration, the polycrystalline extraneous deposit which often occurs on the tube walls received progressively more of the depositing Ge at the expense of the Ge growing on the substrates. For the typical temperature profile shown in Fig. 1, an I_2 density of 4.5 mg/cm^3 was a maximum, because with higher I_2 densities a liquid phase (GeI_2) begins to form in the seed region throughout the run.

Table 1 **Deposition rates.**

I_2 density in mg/cm^3	*Ge deposition rate in μ/day*
0.03	5 - 10
0.3	25 - 50
2.0	75 - 200
4.5	200
30*	24 000

*This run was made by G. A. Silvey, Miss P. J. McDade and H. S. Ingham using a special furnace with a temperature of 600°C in the seed region and ~850°C in the source region.

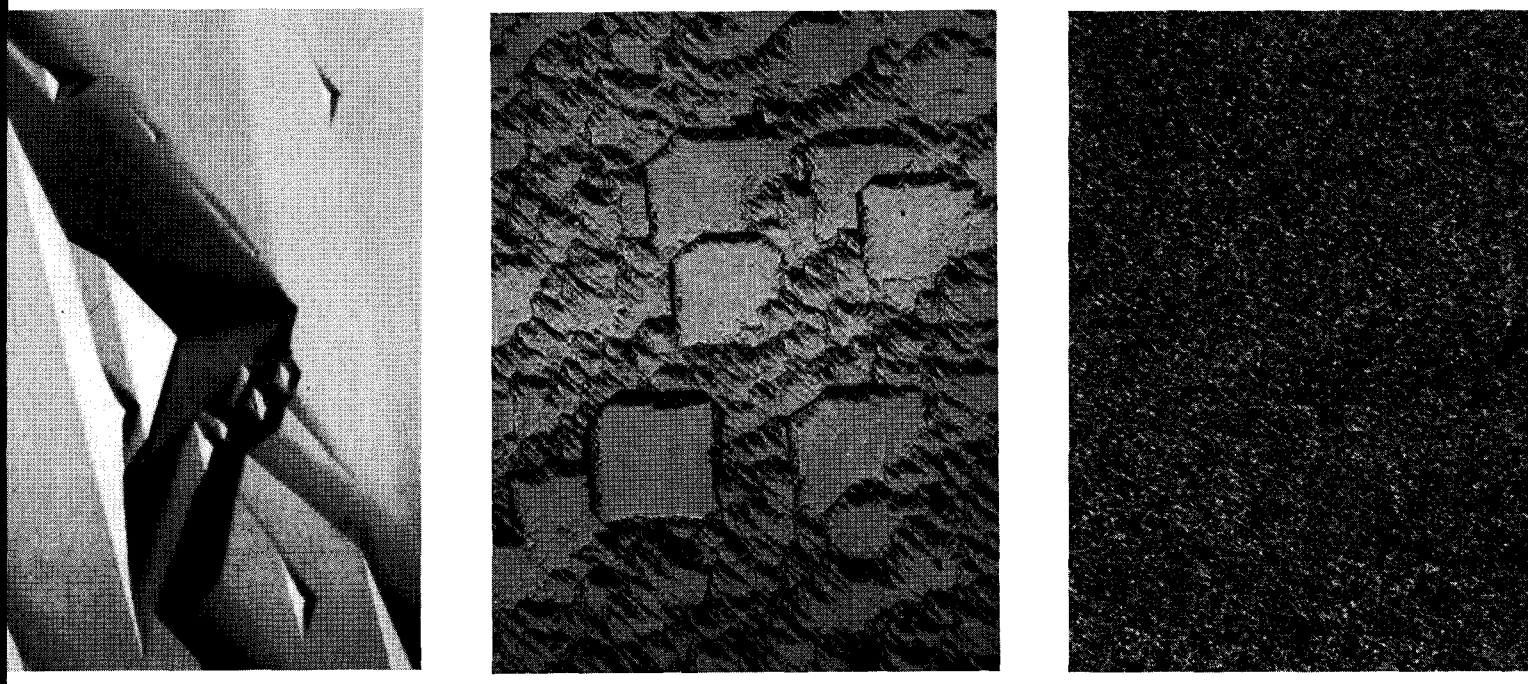


Figure 2 **Deposited Ge surfaces. (50×)**
Left to right: a) on a (111) plane; b) on a (100) plane; c) on a (110) plane.

As one would expect, the growth rate depended markedly upon crystal orientation. The ⟨100⟩ directions grew the most slowly of the several orientations measured. Also, while non-epitaxial growth was rare, it was more prone to occur on {100} planes than on any other, when rapid deposition occurred. The next slowest growth rate was in the ⟨111⟩ directions. However, unlike the rectangular pyramids sometimes seen on {100} surfaces, growth on {111} planes was almost invariably accompanied by triangular pyramids which accelerated the growth all over the seed face and not only in the immediate vicinity of the pyramids. Figure 2 shows surfaces of typical deposits on {111}, {100}, and {110} planes. The most rapid of the three principal crystallographic directions was the ⟨110⟩ directions. Also, growth in {110} planes was free of pyramids, and tended to be more uniform in thickness. Growth in the ⟨211⟩ directions was tried also, and in appearance as well as uniformity, the {211} planes were equivalent or slightly superior to the {110} planes.

In Fig. 2 the appearances are typical, but, of course, wide variations are possible. For example, the sizes and spatial distribution of pyramids in the {111} surfaces (Fig. 2a) vary widely; often the pyramids are accompanied by small pits and well-defined growth steps. On {100} surfaces, rectangular pyramids sometimes are evident in places where the rectangular figures are present in Fig. 2b. Textures on {110} surfaces are sometimes coarser and sometimes finer than that shown in Fig. 2c; if the orientation is slightly off the {110} planes, the coarser texture resembles shingles.

Figure 3a is a 7× photomicrograph of the deposit on the top and edge of a disk-shaped seed, the axis of which is in a ⟨110⟩ direction. Figure 3b is a 7× photomicrograph of the bottom of the disk after lapping and etching the bottom in white etch while the top and edge were masked. The circular trench marks the interface between seed and deposit. Because the disk was not rotated during the deposition process, there is more growth on one side than the other; however, it can be seen that growth is most rapid in the ⟨110⟩ directions and slowest in the ⟨100⟩ directions. The outgrowths on the {100} faces are quadrilateral pyramids and non-epitaxial growth. The well-defined etch line between the seed and deposit will be discussed at some length further on in this paper and in an accompanying note in this issue.[14]

Besides the different growth rates on the different crystalline orientations, there are other kinds of thickness nonuniformity:

(1) Deposited surfaces have random ripples in the contour of the surface with periodicities of approximately a micron or less. Some surfaces have a matte or satiny appearance, and are characteristic of deposits on {110} or {211} planes. Other surfaces, notably the {111} and to a lesser extent the {100}, are glossy; if these surfaces have ripples, the peaks are probably closer together than visible-light wavelengths.

(2) The larger-scale aperiodic ripples in the contour of deposited surfaces are due, it is believed, to crystalline defects. An example of this kind of nonuniformity is the pyramid formation observed on {111} and {100} surfaces. The {110} and {211} surfaces are practically free of this kind of nonuniformity.

(3) Deposits on faces of any crystalline orientation show a large-scale deviation from a perfect plane of the order of tens or hundreds of microns extending laterally over an entire seed, which is usually of the order of centimeters in length and width. This type of deviation might be likened to a snowdrift in appearance. It is due to variations in the rate at which GeI_2 molecules impinge upon different regions of the seed surfaces which, in turn, depends upon convection currents and the gaseous diffusion characteristics of the system. Generally speaking, deposition is heavier in regions nearest the source Ge, and along the upper edge when seed slabs are vertical or nearly so.

It is believed that it would be nearly impossible to eliminate the first kind of nonuniformity on {110} or {211} surfaces. Eliminating the second kind, which occur mainly in {111} and {100} surfaces, would be difficult but certainly not hopeless, and could be circumvented by using {110} surfaces. Eliminating the third kind is a matter of designing a tube which equalizes the convection currents striking the seeds.

Epitaxiality was determined approximately by etching the edge of a fairly thick seed plus deposit with a preferential etch such as 2:1:1 H_2O:HF:H_2O_2. Generally similar appearance and similar specular reflection from both the substrate and the deposit is a fairly reliable indication that the deposit is epitaxial to within a few degrees. In addition, the same kinds of X-ray diffraction measurements as have been made on other vapor-grown Ge[2,11,19] indicate that the deposit is epitaxial.

Even though the deposits were epitaxial, a sharp boundary line at the interface between the deposit and substrate almost invariably was delineated by lapping and etching an edge of the specimen. Fig. 3b shows a typical interface boundary which occurred whether or not the deposit and substrate were of the same conductivity type. Simple *in situ* vapor etching (during the initial part of the deposition run) by inverting the normal temperature profile in Fig. 1 does not eliminate the boundary. Various mechanisms for this phenomenon have been hypothesized and are being investigated.[14,18] It would seem that if a *p-n* junction coincided with such a disturbed plane, the electrical properties of the junction would be quite inferior to those of a comparable alloy or diffused junction; this is often the case.[16,20] A study of the interface etch line in Fig. 3b does not indicate that the inter-

Figure 3a

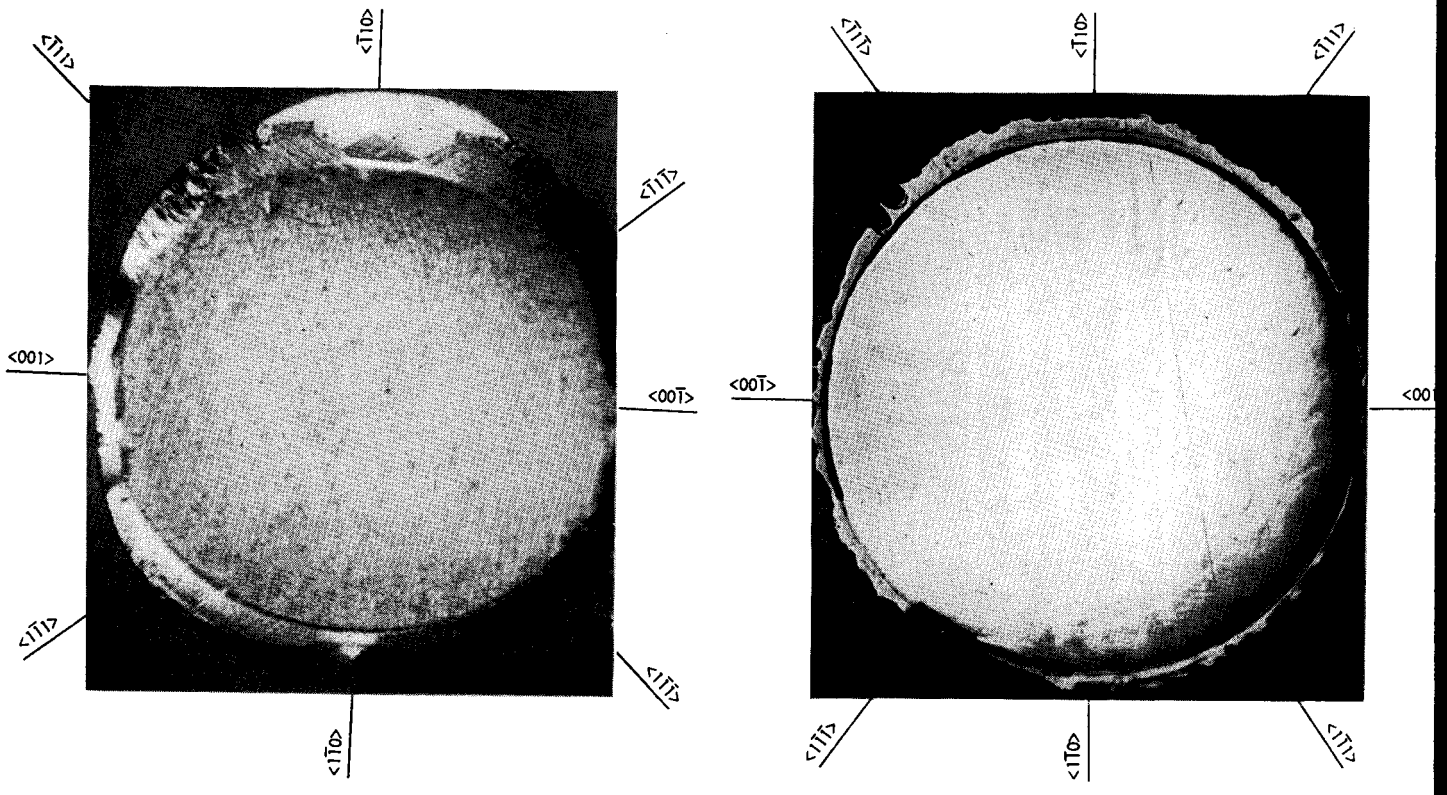
Heavy deposit on the top and edge of a Ge disk-shaped seed with a ⟨110⟩ axis. (7×)

This is the unetched obverse side of the disk shown in Fig. 3b. The central portion represents the growth in the (110) plane, while the peripheral region is the growth in various other planes. The indicated crystallographic directions are only approximate.

Figure 3b

Photomicrograph of bottom of deposited disk shown in Fig. 3a after lapping and etching bottom while top and edge were masked. (7×)

The circular trench marks the interface between the seed (central region) and the deposit (peripheral region). The indicated crystallographic directions are only approximate. Rotated 180° about the $[\bar{1}10]$–$[1\bar{1}0]$ axis from its position in Fig. 3a.



face boundary depends upon crystalline orientation; the slight variation in the highlights are probably due to the etching behavior of the white etch.

Back-reflection X-ray Laue patterns of vapor-grown Ge are equivalent to those of good melt-grown crystals. Also, carrier mobilities in vapor-grown Ge are as high as they are in good melt-grown Ge. Etching characteristics of the deposited Ge using the standard etches and procedures are quite similar to etching melt-grown Ge, with two exceptions. First, there is the interface boundary between seed and deposit already mentioned; and, second, extensive etching with white etch shows a stratification effect on the edges of some deposited samples. Figure 4 is a photomicrograph of such a sample; these {111} plane strata are similar to those often seen on very heavily doped, melt-grown Ge monocrystals, although this deposited sample was not heavily doped. H. Ingham, of this laboratory, suggested that under certain conditions of stepwise growth,[21] the number of impurities being trapped at the lower portion of the advancing step is greater than at the upper portion, and that the higher doped layers etch faster. Various electrical tests, including making alloy junctions in the planes and perpendicular to the planes of the strata, have not indicated any inhomogeneity on the scale of the strata spacing.

The standard etches for revealing dislocations in melt-grown Ge also show them in deposited Ge. On the other hand, no new kind of defect has been observed in vapor-grown Ge, except for the occurrence of bundles of dislocations in the axes of {111} pyramids.[14]

The electrical properties of the vapor-grown Ge were measured by the standard procedures normally used on melt-grown Ge samples. The investigation consisted of two studies:[22] first, the purity of the vapor-grown Ge, and second, the incorporation of donors and acceptors in the vapor-grown Ge.

In undoped runs the source Ge was zone purified, polycrystalline, and nominally 40 ohm-cm; it was used just as it came from the vendor (Eagle-Picher Company). All in all, the purity of the deposits was quite good, especially in view of the fact that only simple cleanliness precautions had been observed. The lowest value of $N_D - N_A$ observed was $9 \times 10^{11}/\text{cm}^3$; values of 10^{12} to $10^{13}/\text{cm}^3$ for $N_D - N_A$ and with apparently low compensation are quite usual. The values of $N_D + N_A$ were very nearly the same as those of $N_D - N_A$. Room temperature electron mobilities were about 4000 cm^2/volt-sec, and lifetimes were in tens of microseconds. In this high-purity range, one of the major impurities seems to be the center which gives rise to the deep donor level observed in Ge deposited by the "open-tube" process.[2,11,13,19] However, the concentrations are widely different: in the "open-tube" process, concentrations were of the order of $10^{17}/\text{cm}^3$: in this "closed-tube" process they usually are about $10^{12}/\text{cm}^3$. At these low concentrations, not much could be done in the way of establishing the nature of these centers. The centers disappear with heat treatment in air in the 500° to 600°C range at a rate roughly comparable to that in "open-tube" material. Sixteen hours at 540°C lowers

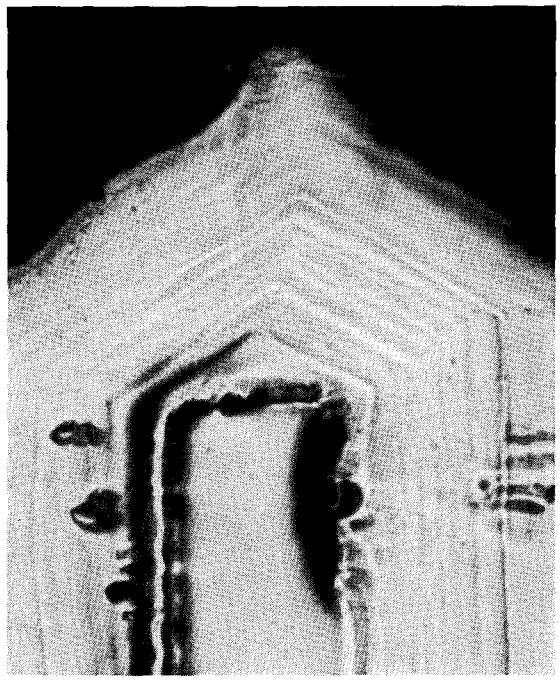


Figure 4 **Lapped and etched edge of vapor-grown wafer. Strata are in {111} planes. (~250×)**

their concentration by at least an order of magnitude; samples which had barely detectable concentrations before heat treatment no longer had detectable concentrations following the heat treatment.

The activation energy of the donor was measured on one sample and found to be about 0.27 ev below the conduction band. There have been some indications that another level, perhaps an acceptor, exists below the middle of the forbidden band, but because of a lack of suitable samples, this has not been verified. Unfortunately *p*-type material of very high resistivity, which is needed for this verification, is difficult to produce by this process.

As stated in the section on apparatus, the sealed tube can be left evacuated at $< 10^{-5}$ mm or can be backfilled with ~ 300 mm of H_2, Ar or He. These different ambients had no detectable effect on the purity of the vapor-grown Ge.

Another paper in this issue[10] treats of the incorporation of I_2 in the depositing Ge. It might be said here that I_2 in concentrations of roughly $10^{15}/\text{cm}^3$ or less does not seem to be electrically active in Ge. However, the possibility that some particular configuration of I_2 in the Ge lattice accounts for the deep donor level has not been entirely excluded.

Introduction of the impurities was effected in two ways. First, melt-grown Ge doped with the desired impurity was used as the source. Second, intrinsic Ge plus the elemental impurity was used as the source. It was found that the ease with which a particular element could be incorporated in the depositing Ge was approximately proportional to its electronegativity, as shown in Table 2. This

Table 2 **Lowest resistivity achieved for various doping elements.**

Element	*Electronegativity* $[ev/mole]^{\frac{1}{2}}$	*Lowest resistivity in deposit, ohm-cm*	*Doped source Ge, ohm-cm*	*Intrinsic Ge plus elemental source*	*Remarks*
P	2.1	0.001	0.001 and lower	not used	0.001 ohm-cm very reproducible
Au	2.1	0.4	not used	used	pptd Au in deposit
As	2.0	0.03	0.003 and lower	used	Elemental As deposits before Ge
Sb	1.9	degenerate <0.002	~ 0.003	used	Elemental source gave degenerate material
B	1.8 - 2.0	0.004	~ 0.001	used	Most often 0.01-0.09 ohm-cm
Ga	1.6	0.009	0.0005	not used	Most often 0.03 ohm-cm
In	1.5	~ 5-10	<0.1	not used	
Al	1.5		not used	used	Al stopped deposit

implies that the less electronegative the element, the more difficult it is to decompose. Only preliminary experiments have been performed so far to determine how the doping depends upon seed zone temperature and growth rate.

Using the standard deposition conditions shown in Fig. 1, the maximum doping (lowest resistivity) achieved for various doping elements are tabulated in Table 2.

It was established that alternate *p*- and *n*-type layers could be deposited successively by putting the seeds in the middle of a somewhat longer tube and oppositely doped source Ge at either end. By adjusting the temperature profile, either *p*- or *n*-type material could be deposited. Using sources doped below the maximum yielded more lightly doped vapor-grown Ge, when such was desired.

Discussion

It has been established that the "closed-tube" process utilizing the disproportionation reaction is capable of producing Ge of a purity comparable to that of the best melt-grown Ge. The lattice defects observed so far in vapor-grown Ge are of the same nature as those found in melt-grown Ge.

Either *p*-type or *n*-type Ge can be produced by this process, and a rather crude hypothesis has been made which estimates the ease with which a particular impurity can be incorporated in the depositing Ge. Also, alternating *p*-type and *n*-type layers can be produced successively.

Although the work reported in this paper has been mostly of a preliminary nature, it has been sufficiently encouraging to have warranted further investigation of the vapor-growth process. Recently, G. A. Silvey of this laboratory has grown gallium arsenide single-crystal material on a (111) germanium surface. Small gallium arsenide crystals have been grown previously by this process[23] at 1030°C. In the case of the epitaxial growth reported here, the growth temperature was 600°C.

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