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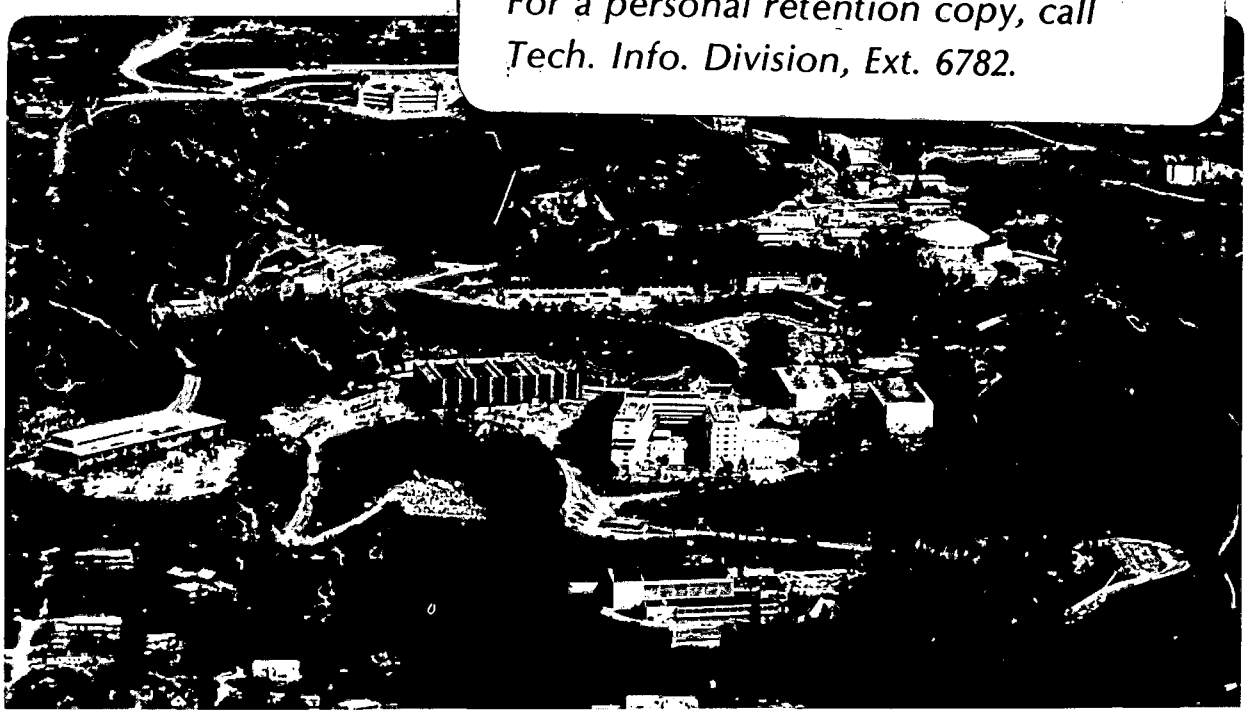

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ABSTRACT

The germanium crystals used for the fabrication of nuclear radiation detectors are required to have a purity and crystalline perfection which is unsurpassed by any other solid material. These crystals should not have a net electrically active impurity concentration greater than $10^{10}cm^{-3}$ and be essentially free of charge trapping defects.

Such perfect crystals of germanium can be grown only because of the highly favorable chemical and physical properties of this element. However, ten years of laboratory scale and commercial experience has still not made the production of such crystals routine. The origin and control of many impurities and electrically active defect complexes is now fairly well understood but regular production is often interrupted for long periods due to the difficulty of achieving the required high purity or to charge trapping in detectors made from crystals seemingly grown under the required conditions.

The compromises involved in the selection of zone refining and crystal grower parts and ambients is discussed and the difficulty in controlling the purity of key elements in the process is emphasized. The consequences of growing in a hydrogen ambient are discussed in detail and it is shown how complexes of neutral defects produce electrically active centers.

INTRODUCTION

High-purity germanium was developed as a material for fabricating nuclear radiation detectors to be used principally as high resolution γ-ray detectors. A semiconductor nuclear radiation detector [1] is a reverse biased p-n junction with a region depleted of mobile charges to a width sufficient to stop a significant fraction of the radiation of interest. For the case of a detector made of germanium and for the detection of nuclear γ-rays (MeV energy range), this width must be of the order of centimeters. The width of the depleted region is related to the net electrically active impurity concentration by the expression:

$$W^2 = \frac{2\varepsilon V}{q|N_A - N_D|} \qquad (1)$$

where W is the width of the depleted region in cm, ε is the dielectric constant of the semiconductor ($\varepsilon = \varepsilon_r\varepsilon_0$; $\varepsilon_r = 16$ for Ge, $\varepsilon_0 = 8.85 \times 10^{-4}Fm^{-1}$), q is the unit electron charge in (1.6×10^{-19} As), V is the applied reverse voltage and N_A and N_D are the ionized acceptor and donor impurity concentrations per cm^3. For V = 1140 volts and W = 1cm,

$$|N_A - N_D| = 2 \times 10^{10} cm^{-3}. \quad (2)$$

Purity in the range of $10^{10} cm^{-3}$ was not thought to be attainable and for a number of years Ge detectors were made only by using lithium ion drift compensation [2] of $10^{14} cm^{-3}$ p-type doped crystals. Dissatisfaction with the ion drift compensation technique led to a proposal by Hall [3] in 1966 that attempts should be made to achieve the required purity directly. Less than four years after Hall's proposal, crystals of the requisite purity were being grown.

The procedure which has been developed for growing crystals of high-purity germanium consists of zone refining the polycrystal in carbon or silica smoked silica boats [4] and subsequently growing single crystals by the Czochralski [7] method from synthetic silica crucibles in a hydrogen atmosphere [5,6]. All commercial high-purity germanium single crystals are produced by this method because it is a good compromise between process complexity, purity and cost and gives a moderate yield of acceptable product. However, this process is not optimium for the production of high purity material in a chemical sense and it involves the acceptance of fairly high concentrations of silicon, oxygen and hydrogen [17]. These impurities can combine to produce electrically active centers or charge traps [12].

Single crystals of germanium cannot usefully be grown by the float zone technique which has been so successfully applied to silicon because the ratio of the melt surface tension to density is too small to support a floating zone of more than 1cm diameter. Initial attempts to grow detector grade germanium by the horizontal boat technique were abandoned because of difficulties encountered in achieving high purity; experimenters objected to the trapezoidal shape of detectors thus grown. The ability to grow crystals with circular cross-sections and arbitrarily selected diameters were among the important factors in dictating that all of the development of high-purity germanium crystal growth be done using the Czochralski technique.

On presenting the current state-of-the-art of high-purity germanium crystal growth, the crystal growers' point of view will dominate. A discussion of the growth parameters which affect crystalline perfection will be followed by a discussion of typical impurity distributions and the kinds of information which can be abstracted from these distributions. The origin and control of the important impurities found in high-purity crystals introduces the problem of aluminum removal. It is next shown how growing out of silica in a hydrogen atmosphere leads to significant concentrations of neutral impurities, complexes and possibly precipitates. The stability of precipitates and their interaction with aluminun is examined using thermochemistry. The discussion section leads to a suggestion for improving the method of growing high-purity germanium crystal in the future.

CRYSTAL GROWTH

Crystal perfection and defect thermodynamics

Crystal perfection is of much greater importance for nuclear radiation detectors than for other semiconductor devices. Transistors, diodes, etc., have electrically functional regions with volumes often less than $10^{-9} cm^3$ whose operation is controlled by added chemical impurities. In radiation detectors, chemical impurities are minimized so as to produce large sensitive regions and the functional volume of the device can exceed $100 cm^3$. Therefore, charge trapping and recombination effects due to native defects (dislocations, vacancies, interstitials) which would be unnoticed in other types of devices, can be the dominant cause limiting the performance of detectors.

It is known from thermodynamics that it is not possible at any finite temperature to grow a crystal free of defects [8]. A crystal in equilibrium with its melt is in a state of minimum free energy F with respect to the concentration of native defects, so that:

$$F = E - TS, \tag{3}$$

where E is the energy needed to create a defect and S is the entropy gained from the defect. Restricting the discussion to vacancies, for n vacancies in a crystal of N atoms, the entropy gained by the generation of vacancies is the logarithm of the number of combinations of ways of removing the n atoms so that:

$$F = E - TS = nE_v - kT \log \frac{N!}{(N-n)!n!} \tag{4}$$

where E_v is the energy needed to create a vacancy. If the factorials are simplified by Stirling's approximation ($\log N! = N \log N - N$) and knowing that at equilibrium $(\partial F/\partial n)_T = 0$, we have for $n \ll N$:

$$n = N \exp(-E_v/kT). \tag{5}$$

For germanium at its melting point, $E_v \simeq 2$eV and T = 1200K,

$$n \simeq 10^{14} cm^{-3}. \tag{6}$$

Using the appropriate energy of formation, the same basic argument holds for interstitials and for vacancy-interstitial pairs (Frenkel defects) [8]. Because germanium crystals have very strong, covalent molecular bonds, the native defect concentrations are extremely low compared with metals, for example, where $n_v = 10^{17}$ to $10^{19} cm^{-3}$ [31].

Because of the exponential dependence of native defect concentration on temperature, a cooling crystal becomes highly supersaturated in defects which tends to condense on lower energy state sites such as impurities, the surface, dislocations or on each other. Vacancies and interstitials tend to annihilate each other and the remaining dominant species is the result of complicated precipitation kinetics and is different for each semiconductor. In high-purity dislocation-free germanium, the remaining species is vacancy precipitates (voids) [9,18]. (It might be noted that in silicon it is interstitials (swirl defects) [10]). So much energy is required to nucleate dislocations that they cannot form in thermal equilibrium--this is the reason why dislocation-free crystals can be grown. Dislocations, if present, can consume an unlimited number of vacancies and interstitials by translation or climb.

Dislocation-free high-purity germanium grown in a hydrogen ambient has turned out to be unsuitable for detector fabrication because of a deep level at $E_v + 0.072$eV with a concentration of about $10^{11} cm^{-3}$ [11,18]. This center has been identified as a divacancy-hydrogen complex (V_2H) [12]. Experience has shown that if the crystal contains at least 100 uniformly distributed dislocations cm^{-2}, the V_2H trap concentration will be too low to influence radiation detector properties. It has further been shown that if the local density of dislocations exceeds $10^4 cm^{-2}$, the dislocations themselves begin to act as charge trapping centers [13]. Meeting the requirement that the dislocation density must be everywhere between 10^2 and $10^4 cm^{-2}$ over volumes that can exceed $100 cm^3$ has proved to be the greatest challenge to the art of crystal growing.

A simplified schematic of apparatus typically used to grow high-purity germanium crystals is shown in Fig. 1. The design goal in a Czochralski

growth apparatus is to establish a one-dimensional thermal gradient so that finite growth will occur and, at the same time, to minimize radial gradients which give rise to thermal stresses in the growing crystal. In Czochralski growth, thermal stresses have their origin in differential thermal expansion that the growing crystal may encounter as the newly formed solid moves away from the melt-solid interface. That is, away from the melt boundary the crystal experiences a three-dimensional thermal gradient instead of the one-dimensional gradient that exists at the boundary. Thermal stress provides the only means of accumulating enough energy to launch a dislocation, since the thermal energy at the melting point is insufficient.

A crystal growing from a melt can never be completely free of thermal stress because this implies zero thermal gradient and, therefore, zero growth rate. The best that can be done is to arrange the thermal environment so that an accepable growth rate is achieved while keeping the stress in the grown crystal below the level required to multiply a dislocation. One criterion for low thermal stress is that the growing interface be flat and normal to the growth direction. A flat interface can be approximated by arranging the thermal environment so that when the crystal is growing slowly at full diameter, the melt-solid interface is convex when viewed from the melt. The pulling rate is then increased until the heat of crystallization balances the radial heat loss from radiation and convection. Because Czochralski growth is a dynamic process, there is only one "right" set of conditions for each part of the crystal and the axial and radial gradients are locked to a precise growth rate.

To initiate crystal growth, a low dislocation density seed is selected and it is "necked down" [14] by fast pulling until only very few dislocations remain. The diameter is then increased under conditions of moderate thermal stress until the proper number of dislocations is obtained. A great deal of experience is required to successfully achieve these conditions. Flat interface growth is maintained for the bulk of the crystal but the interface shape near the end of the crystal is generally neglected as this portion will be discarded. A typical evolution of the melt-solid interface shape during Czochralski growth is illustrated in Figure 2.

The proper control of dislocation density and distribution is also sensitive to crystallographic growth direction. Diamond lattice crystals such as germanium grow isotropically except for the (111) surface which is growing more slowly. Because of this, (111) crystals tend to develop a "facet" [15] which causes a flat interface growth even under conditions of considerable isothermal curvature and, as a result, they may have the thermal stress frozen in. For any other growth axis, interface curvature will lead to stresses which cause dislocation multiplication which has the effect of "decorating" the stress distribution. Pure edge dislocations in crystals grown along the (100) direction tend to line up with the crystal growth axis and can often be followed through the entire length of the crystal. This propagation habit makes dislocation counting very reliable in (100) crystals because chemical etches preferentially decorate dislocations which intersect the surface nearly normally. For all other growth directions, the dislocations propagate by kinks and jogs so that only a small fraction meet any surface in a way that leads to chemical decoration. The (113) growth direction has proven to be useful in that the dislocations are much less effective as charge traps and thus greater dislocation densities can be tolerated [16].

The preferred cross-sectional shape of detector crystals is circular. However, this can only be achieved with a strong axial thermal gradient, otherwise the shape will tend to be dictated by the isothermal condition: triangular for (111), square for (100) and rectangular for (110) growth axes. Once a growing crystal acquires pronounced side facets, growth stability is threatened because the facets increase thermal radiation due to increased

surface area which, in turn, enhances facet growth and may lead to dendritic growth. All of these restraints become more severe as larger cross section crystals are grown. For particular crystal grower designs, the thermal environment can lead to conflicting demands such as increased axial gradient to improve growth stability and decreased axial gradient so that some combination of radial gradient and growth rate can produce a flat interface. This can happen, for example, when after-heaters are used to lower radial gradients; the condition of flat interface may need a melting rather than a growing crystal.

It is unreasonable to expect that the production of the required high quality crystals will ever become routine, especially when the demands of chemical purity are added.

Net impurity profiles

After the above review of basic intrinsic defects and before going into the details of impurity chemistry and purification, let us examine "typical" high-purity germanium crystals which have been grown under typical conditions.

An impurity profile is a plot of the net electrically active impurity concentration $|N_A - N_D|$ against % of the melt crystallized. The measurement of $|N_A - N_D|$ is performed at 77K because at room temperature the generation of electron-hole pairs across the band gap exceeds $|N_A - N_D|$ by several orders of magnitude in typical radiation detector crystals. At 77K the free carrier concentration will be very nearly $|N_A - N_D|$.

The $|N_A - N_D|$ profile is found by soldering wires to the ends of the crystal with indium, immersing it in liquid nitrogen, passing a constant current through it (e.g. 100μA) and recording the voltage drop at predetermined intervals. At high purities there is negligible impurity scattering so that the carrier mobility μ is a constant with constant temperature. For germanium, the mobility of both electrons and holes is 44000 cm^2/Vs at 77K. The measured resistivity ρ and the net impurity concentration are related by:

$$\rho = \frac{V}{I} \cdot \frac{A}{l} = \frac{1}{|N_A - N_D| \; e\mu}$$

where e = charge of the electron (= 1.6×10^{-19}C), A is the cross-sectional area of the crystal and l = length of the interval between voltage contacts (in our case 1cm). We find:

$$|N_A - N_D| = \frac{I}{e\mu V} \; \frac{l}{A} \qquad (7)$$

Experience with a particular crystal growing furnace has shown that a casual inspection of the impurity profile can usually indicate the identity and concentration of the dominant impurities and often reveals defect complexes and radial impurity gradients. As a result of many analyses by photothermal ionization spectroscopy (PTIS) [17], deep level transient spectroscopy (DLTS) [17] and low temperature Hall effect [17], which indicate the identity and distribution of the impurities it has been found that the important ones have a characteristic signature in the impurity profile. The impurity profiles are a reflection of the real impurity segregation during growth.

The impurity segregation coefficient K is the ratio of the solubility of the impurity in the solid to the solubility in the melt and unless otherwise stated, refers to the equilibrium value. As an example of a signature in an impurity profile, for a single impurity with $K < 1$, the profile will show a constantly increasing impurity concentration from seed end to tail due to accumulation of impurity in the remaining melt.

Typical impurity profiles for germanium crystals grown in hydrogen out of silica crucibles are shown schematically in Fig. 3. The most common profile is that of Fig. 3a. It is dominated by non-segregating aluminum acceptors and segregating phosphorus donors. Figure 3b illustrates boron contamination; boron is the only electrically active element in germanium with a segregation coefficient greater than one. Figure 3c shows a dislocation-free crystal with divacancy-hydrogen acceptors (V_2H) dominating the profile. Under our crystal growing conditions, the V_2H concentration lies always between 1 and $3 \times 10^{11} cm^{-3}$. Figure 3d is the profile of a crystal which is mostly dislocation free at the seed end and is, therefore, dominated by (V_2H) acceptors in the first part of the crystal only.

Whenever the crystal has a radial impurity gradient, the test current is inhomogeneous and the impurity profile is distorted. Hall effect measurements by the Van der Pauw method on slices cut from crystals with so-called "coring" yield greatly reduced average Hall mobilities when the free carrier concentration at the periphery is much larger than at the center. The signature of radial impurity gradients or "coring" is shown in Fig. 3e where the dotted lines show more distortion for greater degrees of coring. These coring profiles are sometimes indicative of copper contamination.

The impurity profiles show several general characteristics: 1) they are dominated by the residual chemical impurities B, Al, P and by the complex V_2H; 2) under normal growing conditions, i.e., no air leaks, B and P segregate normally and Al and V_2H do not segregate; and 3) condition 2 automatically leads to the observation that whenever the crystal contains a p-n junction, it is always p-type at the head and n-type at the tail, never the reverse.

Purification and impurity control

Elemental impurities. Aluminum, an acceptor, is by far the most troublesome impurity to remove because it does not seem to segregate. It appears that the aluminum is bound to a dispersed stable phase which survives both zone refining and crystal growth and that the electrically active Al concentration is a result of the equilibrium constant for the reaction:

$$Al\text{-}X \leftrightarrows Al_{(1)} + X_{(1)} \qquad (8)$$

where X is almost certainly SiO_2. This point will be discussed again later.

Phosphorus, a donor, is a ubiquitous impurity which is best reduced by good housekeeping and particulate control. Phosphorus does not form compounds that are stable at the melting point of germanium and it is readily removed by zone refining. Experience suggests that synthetic silica crucibles are the principal source of phosphorus. Because it segregates normally during crystal growth, phosphorus is not usually the dominant cause for rejection of a crystal, at least not for the first half grown.

Boron, an acceptor, forms a very stable oxide and if its presence is suspected, it can be removed by oxidation and precipitation of the oxide rather than by segregation. One zone pass under slightly oxidizing conditions [19] removes boron effectively. The segregation coefficient for boron is >1 so that it is not easily removed by zone refining.

Copper behaves in a peculiar way in germanium. On the one hand, it has a very small segregation coefficient (10^{-5}) and very low solubility so that it should be easily removed, but on the other hand, it has a very high diffusion coefficient at relatively low temperatures so that it is easy to recontaminate the crystal. Copper is a deep level multiple acceptor in germanium and is a strong hole trap at 77K.

One signature of copper contamination in germanium can be a radial impurity gradient. The small segregation coefficient of copper seems to make it almost

impossible to contaminate the crystal through the melt. It is more likely that the crystal is contaminated through the gas phase. Measurements show the copper distribution in the crystal is strongly influenced by the time-temperature history of the growing crystal. Figure 4 illustrates this kind of distribution in a copper contaminated crystal which would be otherwise high-purity n-type. The resultant distribution is described as "coring" It depends on where in the crystal the sample is cut and on the underlying shallow impurity concentration and type.

Copper forms many high vapor pressure, low stability compounds [CuOH, $Cu(OH)_2$, $Cu_2(OH)_3Cl$, $CuCl_2 \cdot 3CuO \cdot 4H_2O$, etc.] and care must be exercised in excluding it from the crystal grower environment. We have found that rubber gaskets can be an important copper source. Problems with copper contamination are variable from facility to facility. In our laboratory, copper is not normally present in the as-grown cyrstals when measured with a sensitivity of $\leq 10^8 cm^{-3}$ (DLTS). When copper contamination tends to occur, it can usually be suppressed by cleaning the crystal grower parts.

Neutral impurities, complexes and precipitates

The concentration of neutral impurities in high-purity germanium far exceeds the concentration of the impurities P, Al, B and Cu so far discussed. This is, in part, a result of growing in hydrogen out of silica which has been chosen to reduce the electrically active impurity concentration. In crystals which have had no further thermal treatment after growth, the known neutral impurities appear in the following concentrations: $H \simeq 10^{15} cm^{-3}$ [20], $Si \simeq 10^{14} cm^{-3}$ [21], $O \simeq 10^{14} cm^{-3}$ [22] and $C \simeq 10^{13} cm^{-3}$ [23]. All of these elements are expected to remain electrically neutral in germanium. However, it has been discovered that complexes [24] between these elements and precipitates [25] can have electrical activity. The shallow centers which are formed by complexes of these elements and which are well understood are A(H,Si), A(H,C) and D(H,O) [17]. Further centers are the acceptors A_3, A_4, A_5, A_7 and several donor [17]. All of these centers are shallow (~ 10meV) and thus do not act as trapping centers at 77K but they may change $|N_A - N_D|$ to unacceptably high levels. Most of these centers are very weakly bound and dissociate or interconvert [26] at detector processing temperatures. The presence of these shallow complexes makes $|N_A - N_D|$ and with it the depletion voltage of detectors unpredictable. An originally excellent piece of ultra-pure germanium may turn out to be useless after inappropriate medium temperature processing such as n^+-contact formation with lithium diffusion. These complexes together with any copper can be removed by long time annealing in contact with liquid metal getters [27]. Such a process to be avoided, however, as gettering is costly and time consuming. Proper temperature time sequences during processing greatly reduce complex formation.

Another important center which leads to charge trapping is associated with "smooth pits" [25] as revealed by chemical etching. Whenever chemical etching shows a significant concentration ($> 100 cm^{-2}$) of smooth pits, charge trapping is observed in detectors even in the absence of all the other well-known traps (Cu, V_2H, etc.). The smooth pits are always due to excess oxygen during growth due, for example, to air leaks or impure hydrogen. There are good intuitive and thermochemical arguments to support the suggestion that these pits have their origin in SiO_2 precipitates [25]. It is likely that the charge trapping is associated with the local lattice strain that accompanies the precipitation. DLTS analysis of crystals with smooth pits does not reveal any discrete levels. In this characteristic they are similar to crystals with a high density of dislocations. Both kinds of crystals have excessive local lattice strain, as revealed by chemical etching. In high-purity materials, chemical etchants do nothing more than decorate local variations in the chemical potential which can result from lattice strains.

EQUILIBRIUM THERMOCHEMISTRY

In a carefully reasoned and thorough study, Darken [28] applied the principles of equilibrium thermochemistry to the problem of stability of precipitated oxide phases in liquid germanium with special emphasis on SiO_2 precipitates and their interaction with aluminum. One of the central conclusions of this study was that under normal crystal growing conditions the reaction:

$$SiO_{2(l)} \rightleftharpoons Si_{(l)} + O_{(l)} \tag{9}$$

is proceeding to the right because of the extremely low oxygen partial pressure. In another paper, Darken [29] showed that the oxygen in the melt will be in equilibrium with the oxygen in the vapor phase. These conclusions can be combined to show that if sufficient oxygen is added to the gas phase (leaks, impure H_2), reaction (9) will be driven to the left and SiO_2 precipitation can occur. This result is in accord with the experimental observation that SiO_2 precipitates (smooth pits) only occur in the presence of excess oxygen. Darken further shows that Al has a great chemical affinity for binding to SiO_2 but that the oxygen concentration in the melt will never be high enough for this reaction to proceed to form the aluminum silicate $Al_6Si_2O_{13}$ (mullite).

The behavior of SiO_2 in germanium as deduced from equilibrium thermochemistry still leaves unclear the process by which aluminum survives zone refining. It has been tacitly assumed that the aluminum survives zone refining by being absorbed on an external phase; namely, aluminum is associated with suspended particles of SiO_2 which do not agglomerate. This model was proposed because, among other reasons, it was thought highly unlikely that a dissolved chemical species would be non-segregating. Table I is an attempt to list some of the conflicting observations concerning Al survival. While equilibrium thermochemistry analysis has introduced some much needed limits to speculation by demonstrating which reactions cannot occur, there are still basic conflicts between proposed explanation and experimental observation.

TABLE I

Precipitate theory of aluminum survival

Factors Favoring Theory	Factors Against Theory
1) Al does not seem to segregate in zone refining.	1) Thermal chemistry shows that SiO_2 is a dissolving species during crystal growth.
2) K=1 is improbable for any dissolved species.	2) No smooth pits observed if grown under dry conditions.
3) Al has great affinity for SiO_2.	3) Zone refiner is "dryer" than crystal grower so SiO_2 dissolution should be more effective.
4) ^{14}C tracer studies [23] show that stable precipitates can survive generations of growth.	4) Al is not effectively removed by zone refining in C.
5) Al segregates normally if crystal is grown in C [32].	5) Reactions during crystal growth are near equilibrium as shown by equilibrium between O in gas and O in liquid.
6) Al segregates if excess Si is available [32].	

Possible Scenarios

1) C is always contaminated with Al and precipitate theory is correct.
2) Al is already in Ge in particulate form but more stable than SiO_2, e.g., some precipitate of the form $Al_n(SiO_2)_m$.
3) There exists a dissolved chemical species of the form $Al_xGe_yO_z$ or $Al_xSi_yO_z$ which does not segregate and is stable in dry H_2 at 1200K.
4) SiO_2 precipitates do not dissolve during zone refining because of some peculiarity of kinetics during refining.

DISCUSSION

It turns out that the impurities Al, P and Cu are most often the cause for rejection of germanium crystals in the making nuclear radiation detectors. Cu does not form stable oxides and is easily removed from germanium. However, its fast diffusion in germanium and the possibility of the formation of volatile compounds requires careful attention to the purity of crystal grower parts, even those remote from the hot zone, and the purity of the H_2 gas. We found high Cu contamination in a closed-loop crystal grower used for tritium doping [20]. Insertion of a liquid nitrogen trap in the recirculating gas line solved the problem, leading to the conclusion that volatile Cu compounds were being transported by the hydrogen.

Phosphorus compounds are unstable and ubiquitous. We have found occasional P contamination of the crystal grower which is persistent until a general superficial cleaning. The P concentration in germanium crystals can often be correlated with the use of a particular silica crucible and it is suspected that the crucible is the principal source in such cases. Use of synthetic silica crucibles from different manufacturers do not lead to consistent results except for crucibles made by fusing natural quartz crystals (G.E.204) which always contain excessive P.

The chemistry of Al in germanium is very complicated and the mechanism by which Al survives zone refining is still in doubt. Equilibrium thermal chemistry analyses give valuable insights into how Al may react with Si-O-H in a Ge melt. However, its conclusions may be in conflict with observation. The theory may be correct if some peculiar kinetics of zone refining prevent SiO_2 precipitates from dissolving, e.g., if the RF-induced stirring rapidly transfers particles from the melting to the freezing interface with minimal contact with the melted zone.

By deduction, it is concluded that the main Al source is not the silica crucible. When the starting polycrystal does not contain electrically active Al (as measured by PTIS), the grown crystal will be essentially free of Al. The Al in the crystal appears to be proportional to the electrically active Al in the zone refined bar and is usually higher. SiO_2-Al complex formation is strongly supported by the observation that when Si is added to the melt, consequently pushing reaction (9) strongly to the left, Al segregates and has a higher concentration than in the zoned bar. One problem with this analysis is that the silica crucible itself is a strong getter for Al. This can be shown by attempting to grow Al-doped crystals in a silica crucible. A zone-leveled charge containing $10^{17}cm^{-3}$ electrically active Al produced a crystal with $2 \times 10^{12}cm^{-3}$ Al showing no segregation, i.e., of constant Al concentration.

When germanium is grown in carbon, Al segregates normally. It was not known initially whether the Al was coming from the carbon or from residual SiO_2-Al complexes in the germanium charge. In order to determine if Al was coming from the carbon crucible, two crystals were grown in carbon which showed normal Al segregation. The upper, seed end halves of these crystals were combined and a third crystal was grown. The resulting crystal showed normal Al segregation and precisely the Al concentration predicted from the now known Al concentration in the starting material. This means that for this particular crucible, there was no detectable Al contribution from the carbon.

The purity of the carbon and silica crucible materials is known only to the extent of general emission spectroscopy data on typical unfabricated materials from the manufacturers. The range of speculation about the mechanism of phosphorus and aluminum transport could be greatly limited by good analytical data on the actual or closely similar crucibles. Data from spark source or secondary ion mass spectroscopy could prove very useful.

Thermochemical analysis can be used to limit the number of reactions which can take place during crystal growing, but to be usefully applied, its limitations should be strictly observed. Aside from the problem of treating the kinetics of crystal growth as stated by Darken [28], there is an additional problem with the idealization of external phases. In the analysis of the system SiO_2-Ge-H_2, it was assumed that the external phases (SiO_2 and H_2) were in their pure states and would only be modified by reactions between them. But the SiO_2 is not a pure phase and contains about 1000ppm H_2O as measured by the OH content. The availability of this oxygen during crystal growth is completely unknown and may strongly modify the partial pressure of oxygen in the hydrogen ambient.

It is apparent now that most of the residual impurities present in ultrapure germanium crystals for detector applications arise from growing out of silica in hydrogen. These problems are the result of the added elements Si, O and H and their interactions with each other and with native defects and with any remaining electically active impurities. The selection of this crystal growing environment arose naturally as a solution to early purity problems. Crystals grown in vacuum were found to contain copper, so a high-purity gas was needed to shield the growing crystal. Crystals grown in carbon were found to have a high concentration of acceptor impurities, so carbon was replaced by synthetic silica. Crystals grown from silica in inert gas were found to contain precipitates (SiO_2) which caused carrier trapping, so the shield gas must be hydrogen. Dislocation-free crystals grown in hydrogen contained a deep trap, so crystals grown in hydrogen from silica must contain dislocations.

Although the above scenario results from a logical series of observations, subsequent knowledge suggests that this crystal growing method makes the production of the largest, highest purity crystals unreasonably difficult. Now that the dominant sources of impurities have been identified, re-examination of the original compromises made in selecting hydrogen-silica may make other methods attractive.

One of the first crystal grower environments tried for high-purity germanium was growing out of carbon in vacuum. This system eliminates all the problems related to H_2-silica (V_2H, SiO_2 precipitates, hydrogen complexes) and has additional benefits. However, the original reasons for abandoning carbon-vacuum become prominent, namely, copper from vacuum and shallow acceptors from carbon. It is now virtually certain that the acceptors come from Si-O-Al complexes in the germanium and not from the carbon. But even if the carbon is found to contain aluminum, it could likely be removed using <u>in situ</u> chlorine etching, as has been so successful when applied to cleaning silica in silicon MOS technology [30]. According to Darken's analysis [28], any SiO_2 precipitates should dissolve in refining under the same conditions--provided that carbon is not the source of the aluminum. In any event, the aluminum problem is now better defined so that it can be attacked directly.

Copper contamination while growing in vacuum must still be solved. Experience suggests that the proper choice of crystal grower materials may suppress this contamination. A great advantage of growing under vacuum is the elimination of the V_2H center. This means that dislocation-free crystals could probably be used for making detectors if no other deep vacancy level appeared. Once dislocation-free crystals are suitable, the thermal constraints during growth are greatly relaxed and large diameter crystals are more easily grown. The great resistance to the formation of the first dislocation is shown by the routine production of large diameter, dislocation-free silicon crystals, even under the very poor thermal conditions of floating zone growth.

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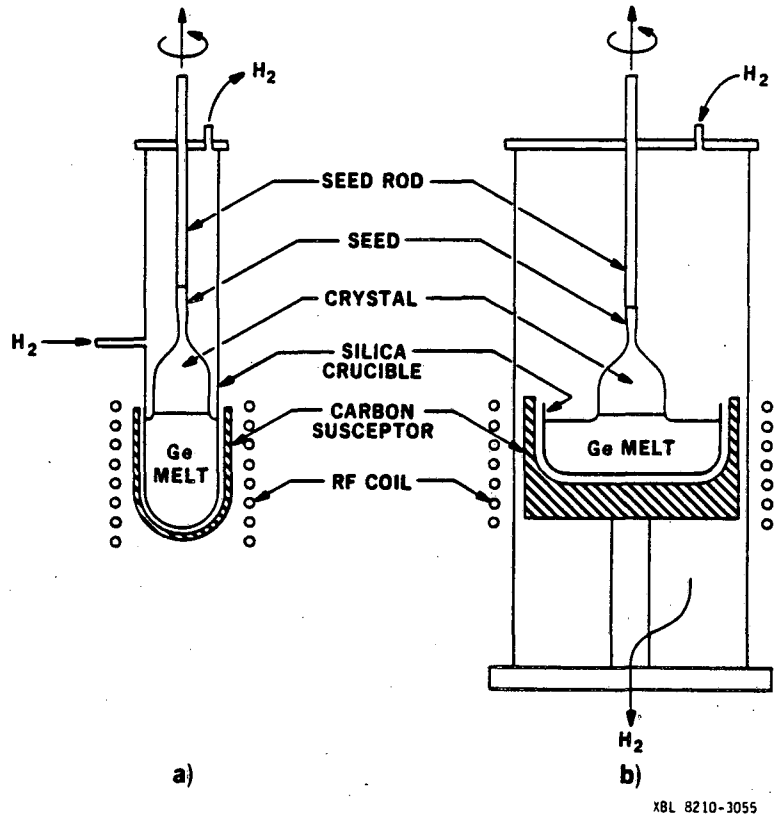

Fig. 1. Simplified illustrations of crystal grower designs currently used for high-purity germanium. Design (a) [5] uses an external carbon susceptor and a crucible which closely matches the crystal diameter. The shape of the melt-solid interface is probably dominated by heat radiation from the crystal. Design (b) [6] uses an internal susceptor and a large melt diameter. The shape of the melt-solid interface for this design is probably dominated by heat transport by hydrogen gas convection.

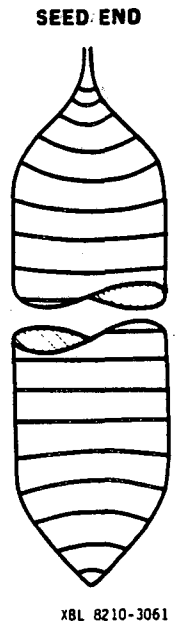

Fig. 2. The desired evolution of the melt-solid interface during crystal growth to minimize thermal stress so as to achieve a uniform dislocation concentration. This is a necessary but not sufficient condition for low thermal stress because the crystal can still experience a large radial thermal gradient after it is grown but while it is still hot.

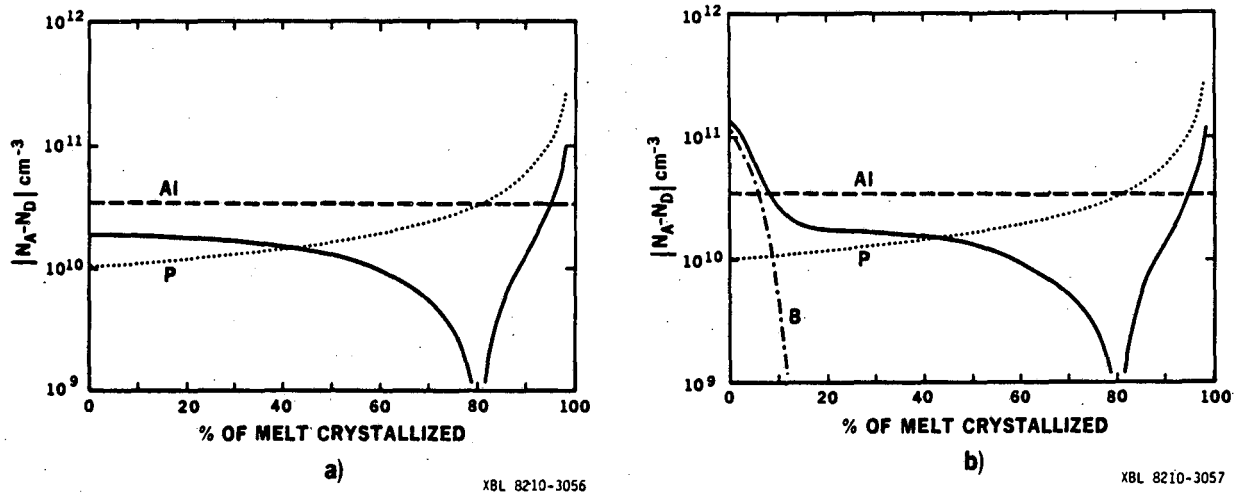

Fig. 3. (a) The solid line shows a common type of impurity profile for high-purity germanium. This profile results from equal concentrations of Al and P in the melt of 3 x 10^{10}cm^{-3}. The Al is non-segregating and the P has an effective segregation coefficient of 0.3 at our growth rate. (b) This profile is a result of the same P and Al impurity concentrations as 3a with the addition of some boron. Boron disappears faster than its segregation coefficient would predict due to oxidation by the silica crucible.

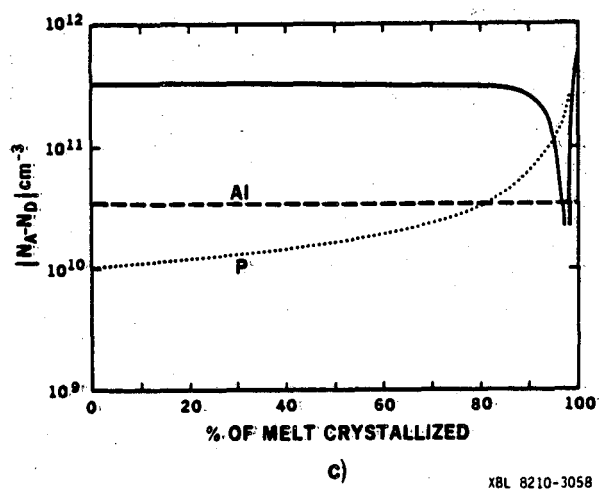

Fig. 3(c) A crystal with the same impurities as 3a but dislocation free. The constant acceptor concentration of 3 x 10^{11}cm^{-3} is due to (V_2H) complex formation.

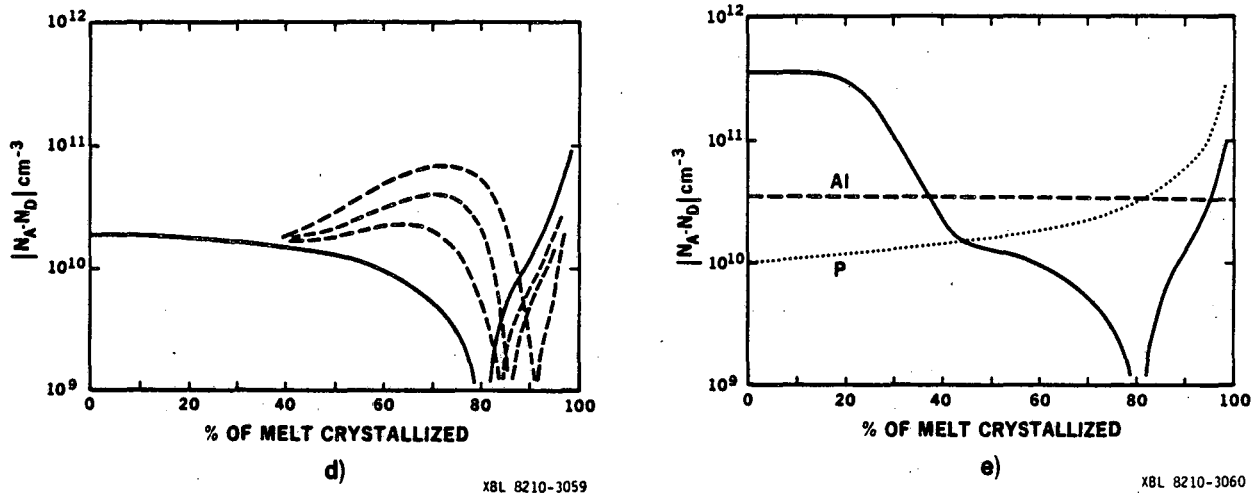

Fig. 3(d) Profiles of crystals with the same impurities as 3a but which have "coring". Coring is a radial impurity gradient which distorts the resistivity measurement. This radial impurity gradient is always more strongly p-type toward the outer surface and less p-type or n-type toward the center. (e) A more complicated profile which is the result of the same impurities as 3a but which is dislocation free for the first 20% of growth. Dislocations which appear in the last 80% act as sinks for excess vacancies which prevents (V_2H) formation.

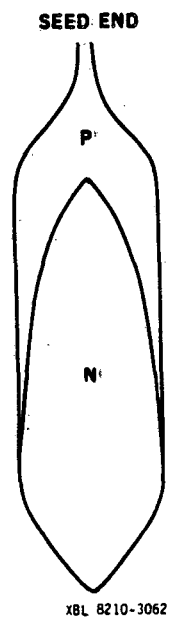

Fig. 4. The apparent impurity distribution inside a crystal which shows "coring" and which would be otherwise high-purity n-type. The coring phenomenon is often the result of copper contamination of the growing crystal through the gas phase. The shape of the acceptor distribution is due to the time-temperature history of the copper diffusion.

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