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ORIGIN AND CONTROL OF THE DOMINANT IMPURITIES IN HIGH-PURITY GERMANIUM*

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SUMMARY

Techniques have been developed to consistently purify germanium to the 10^{10} atoms/cm³ range.

The major impurities are the acceptors boron and aluminum and the donor phosphorous. Formation of non-segregating compounds of boron and aluminum make these elements difficult to remove by conventional zone refining whereas phosphorous and all other electrically-active impurities segregate normally and are therefore removed in the zone refining process. The only significant impurity introduced in our Czochralski crystal puller is phosphorous whose source has been traced to the quartz crucible.

To reliably reduce impurity concentrations to acceptable levels it has been necessary to develop techniques for determining the types and concentrations of impurities in both the final single crystals and in the polycrystalline zone-refined ingots and to relate these results to the use of various boat and crucible materials. Photothermal Ionization Spectroscopy and electrical measurements have been used to identify and measure the impurities.

INTRODUCTION

High-purity germanium single crystals suitable for large-volume thick radiation detectors have been grown in two laboratories over the last few years.^{1,2} Experience in our laboratory is that purification, and to some degree crystal growth, have not hitherto been well controlled processes. Spontaneous appearance of contaminants, lack of purity of the starting material and deviation from 'normal' segregation of some impurities are serious problems. While we have reduced spontaneous contamination by maintaining a clean small working area and by working quickly with standardized procedures, the removal of impurities contained in the starting material has presented difficulties. Unfortunately, the quality of raw germanium as purchased from supplies is not under our control, and maximum impurity levels are not specified even in 'high-grade' material. It has therefore been necessary for us to adopt extra purification steps to reduce all impurities to the necessary low levels.

The well-established multi-pass zone purification³ method is therefore used on germanium prior to our growing single crystals by the Czochralski technique. However, we have found that zone-purification using standard techniques rarely achieves the desired purity levels in the refined material that is to be used for crystal pulling. This failure of zone refining has led to our detailed studies of the segregation behavior of impurities in Czochralski single crystal growth in a very clean crystal puller. These studies have elucidated the mechanisms responsible for the

poor results in zone-refining and have suggested better techniques which we are able to apply successfully.

IMPURITY SEGREGATION DURING CZOCHELSKI SINGLE CRYSTAL GROWTH

General Observations

The value of the segregation coefficient K of an impurity (K = concentration in solid/concentration in liquid) tells directly how easily an impurity can be removed from a semiconductor by melting and recrystallization. Most impurities in Ge have a value of K between 10^{-3} to 10^{-5} (i.e. a very small number). Such impurities are easily removed. Some elements of the third and fifth group of the periodic table of the elements have a value of K close to 0.1. Many zone passes or multi-generation crystal growth can move these impurities to one end of a bar. Boron and silicon have a value of $K > 1$ which means that they congregate at the opposite end of the bar compared with other impurities. The end of a refined polycrystalline or single crystal bar of Ge which contains all impurities with $K < 1$ will be referred to as the 'dirty' end in the following text (this is the end that freezes last). Boron and silicon collect at the 'clean' end. Our experiments indicate that neither of the acceptor elements boron or aluminum follow the expected behavior under our typical refining and growing conditions. In this paper we show that this complication is caused by these elements forming complexes with oxygen which do not segregate (i.e. $K = 1$).

Using a Czochralski crystal puller⁴ together with analytical methods such as conductivity, Hall-effect measurements and Photothermal Ionization Spectroscopy (PTIS)⁵ we have studied the formation of these complexes and have found ways to reduce their effect.

Segregation and Complex Formation of Aluminum in Germanium

In the early work on high-purity germanium, Hall, et al.⁶ observed a non-segregating acceptor. Later work, using PTIS, showed that this acceptor was aluminum. A typical plot of net-concentration versus solidified fraction of melt profile is shown in Fig. 1. This crystal (#384) has a net-acceptor concentration of $\sim 5 \times 10^{10}$ cm⁻³ over 70% of its volume. The segregating donor phosphorous causes the change to n-type material in the tail section of the crystal.

Since tests have shown that aluminum segregates normally in crystals grown from a graphite susceptor it is clear that the quartz crucibles used in high-purity germanium crystal growth are in some way involved in causing the non-segregating behavior of Al.

* This work was performed under the auspices of the United States Energy Research and Development Administration.

One of the mechanisms suggested by Hall⁶ is based on the assumption that most of the Al in the Ge-melt is absorbed in a thin surface layer of the crucible which then acts as a constant source of Al. If this hypothesis were correct, regrowing a crystal in the same crucible, but with its surface etched off after the first growth, should reduce the Al concentration considerably. Figure 2 shows that this is not the case. Crystal #399 was grown using crystal #398 as starting material. The net-concentration in both crystals is almost the same and the small difference can easily be explained by a slightly higher phosphorous concentration in crystal #399. The possibility that the crucible or the crystal puller is the source of the Al is excluded by the fact that much purer crystals were grown under the same conditions. We conclude that the Al was introduced in the original starting material and was carried from one crystal to the next in an inactive form.

Edwards⁷ showed in 1963 that, under suitable conditions, Al can form an electrically inactive complex with oxygen. In his work, carbon crucibles were employed and the oxygen was introduced in the ambient gas. In our case, we believe that the quartz crucible releases oxygen at the melt-crucible interface. An oxygen concentration of $\sim 5 \times 10^{13} \text{ cm}^{-3}$ as determined by Li-precipitation experiments⁸ is typical in crystals grown from quartz crucibles. We will call such Ge 'oxygen-rich'. The mechanism proposed by us to explain our results involves the formation of the Al-O complex in the melt in the 'oxygen-rich' situation. We postulate that this Al-O complex does not segregate between the liquid and solid Ge, so its concentration is the same in the solid and liquid. In the final crystal a small fraction of the Al-O complex is assumed to dissociate to provide the elemental Al observed by electrical or PTIS measurements.

Since no obvious method gives a direct measurement of the Al-O complex we have devised and carried out experiments in which the oxygen level is substantially reduced or in which an oxygen scavenger is added to the Ge-melt. Since the main oxygen source in our system is the quartz crucible, avoiding the use of quartz is an obvious step. Unfortunately, growing crystals directly from any high-purity graphite susceptor leads to high boron and phosphorous concentrations. However, coating the quartz crucible with a pyrolytic-carbon layer (Appendix I) has proved to be a possible way to avoid contact between the Ge-melt and the quartz crucible, thereby excluding most of the oxygen from the Ge-melt. Figure 3 shows profiles of crystals grown from such a crucible. A segregation coefficient of 0.20 to 0.25 fits the profiles very well. This is consistent with the expected values of K for Al under our crystal growth conditions (pulling speed = 2 mm/min, rotation = 15 rpm). Li-precipitation measurements show that the oxygen content of these crystals is much lower than that of crystals grown in quartz crucibles.

If normal segregation can be achieved in this manner, it should be possible to purify Ge by growing successive generations where each crystal is grown from the purer fraction of earlier crystals. Such a result is also shown in Fig. 3. Crystal #438 was grown from the upper halves of crystals #434 and #435. Since we know from PTIS measurements that the donor concentration is much smaller than the acceptor concentration we can conclude that improvement in purity is only due to segregation. The reduction factor of about 4.0 agrees with the segregation coefficient. In addition this experiment shows that the pyrolytic-carbon layer does not introduce significant amounts of impurities.

Quite a different way to suppress the influence of the oxygen is to add a strong scavenger of oxygen to the Ge-melt. Doping the 810 g Ge-melt in a quartz crucible with 25 mg of pure Si (20 K Ω cm) led to crystal #436 with a profile shown in Fig. 4. PTIS indicates the presence of some boron near the head end while aluminum is the main impurity over the whole length of the crystal. The Al-segregation coefficient is again in the range that indicates 'normal' segregation. Li-precipitation tests on a sample from this crystal indicate an extremely low oxygen concentration. That the silicon is actually incorporated in the Ge has been shown by Spark Source Mass Spectrography measurements executed by Tavendale, et al.⁹ Their result shows a Si-concentration of $3.7 \times 10^{17} \text{ cm}^{-3}$ at 18% solidified fraction of the melt and $1.4 \times 10^{17} \text{ cm}^{-3}$ at 90% which indicates the correct segregation direction for silicon (K = 1.5).

To obtain a more quantitative picture of the Al-O interaction, a series of crystals were grown from well characterized polycrystalline germanium. The starting material was evaluated by selecting small single crystals with the method recently developed by Hubbard, et al.¹⁰ and by using PTIS and Hall-effect measurements to determine the species and concentration of the dominant impurities. Small crystals were taken from a number of points along the length of the polycrystalline bars and were evaluated. Usually sets of two or three crystals were grown from each zone-refined Ge bar. Each set contains at least one crystal grown in a quartz crucible (oxygen rich) and one grown in a pyrolytic carbon-coated quartz crucible (oxygen poor). Figure 5 shows two crystals grown from portions of the same bar of oxygen rich starting material (in this case a quartz boat was used in the refiner). The measured net-acceptor concentration in Ge starting material used for both charges was $\sim 5 \times 10^{10} \text{ cm}^{-3}$. Crystal #488 was grown under oxygen poor conditions. The observed Al-concentration of $\sim 10^{11} \text{ cm}^{-3}$ at the seed end, assuming a segregation coefficient of 0.25, indicates that the concentration of free Al in the melt was $\sim 4 \times 10^{11} \text{ cm}^{-3}$. Since the measured free Al concentration in the starting material was $5 \times 10^{10} \text{ cm}^{-3}$ the ratio R of the Al-O complex concentration to that of free Al in the starting material must have been about 8 ± 2 (assuming that all the Al-O complexes dissociate in the melt in the absence of oxygen). Growing under oxygen rich conditions, as in #487, we obtain a crystal with a junction. The compensating, segregating donor phosphorous is believed to be introduced by the Suprasil-quartz crucible since no donors could be detected in the starting material. Extrapolating from the tail end of the crystal, the donor concentration near the seed end of the crystal is $\sim 2 \times 10^{10} \text{ cm}^{-3}$. Taking this into account we find for the Al concentration $\sim 5\text{-}6 \times 10^{10} \text{ cm}^{-3}$ near the seed end-nearly the same number as was measured in the starting material! This means that R must be very similar in the starting material and in this single crystal. This result is standard for all the crystals grown or bars refined under oxygen rich conditions.

As suggested by the effect of silicon as an oxygen scavenger in crystal growing, a further possibility for accomplishing Al segregation is to add silicon to the starting material during zone-purification. Figure 6 shows profiles of crystals grown from Ge bars that contained 10^{17} to 10^{18} Si/cm^3 . Whereas crystal #440 was grown in a pyrolytic carbon-coated quartz crucible (i.e. oxygen poor conditions), crystal #441 was grown in a bare quartz crucible (i.e. oxygen rich conditions). The concentration profiles of the two crystals are practically equal. This nicely confirms our earlier result which showed that silicon

at high concentrations ($\geq 10^{17} \text{ cm}^{-3}$) scavenges the free oxygen thereby suppressing Al-O complex formation and permitting normal segregation of aluminum.

Segregation and Complex Formation of Boron in Germanium

The behavior of boron in Ge also depends very much on the presence of oxygen as was shown by the investigations of Edwards.¹¹ We have not studied boron to the same extent as aluminum since it is not usually present at high concentrations in our starting material. In contrast to Al, we find a reduction of the boron concentration during multi-generation crystal growth in bare quartz crucibles that are etched in between successive use. Regrowing an oxygen rich boron-contaminated crystal under oxygen poor conditions does not significantly increase the boron concentration. This observation is in contrast to the results obtained by Edwards, who, after leaching oxygen from his system, found that the boron dopant again became an electrically active acceptor. The conflict can be resolved by assuming that the quartz crucibles in our experiments form stable boron-silicate glass layers at the melt-crucible interface. The etching of the crucible between successive crystal growing operations then removes the boron-contaminated layer and leads to a reduction in concentration. Edwards' experiments were carried out in graphite susceptors where no glass formation takes place.

Figure 7 shows the concentration profile of crystal #466 grown in a quartz crucible from a zone-refined polycrystalline Ge bar with an average boron concentration of $2.3 \times 10^{11} \text{ cm}^{-3}$. Using an effective segregation coefficient of ≈ 6 one would expect a boron concentration near the seed end of the crystal of approximately 10^{12} cm^{-3} . PTIS measurements give a boron to aluminum ratio of 1:3 at 5% of solidified melt, so the boron concentration is $\sim 10^{10} \text{ cm}^{-3}$ which is 100 times smaller than would be expected but for the capturing of boron by the quartz.

IMPURITY SEGREGATION DURING ZONE PURIFICATION OF GERMANIUM

The experiments discussed in the previous section show that formation of an Al-O complex and the associated non-segregating behavior of Al can be circumvented by using oxygen poor conditions or by the addition of an appropriate oxygen getter (e.g. silicon). The next logical step in the development of a purification process is the application of these results to zone purification. The selection of a clean container for the germanium bar is more difficult than for the crystal puller since a material must be found to which Ge does not adhere*. Tests with bare carbon boats and carbon boats coated with pyrolytic carbon showed that boron and phosphorous, in substantial quantities, were present in the refined bars. These impurities appear to be contributed by the carbon boats. Leaching impurities from the carbon by refining many bars in the same boat is not a feasible approach for small-scale operations. Therefore, a better choice for a boat material seems to be quartz with a carbon smoke layer providing a suitable

sliding surface. Tests show that such boats are satisfactory only if the Al concentration in the initial material is very low. For typical initial material, which contains high levels of Al, an almost constant Al concentration is observed along the length of the refined polycrystalline bar. This is similar to the situation in single crystals grown from quartz crucibles. Li-precipitation measurements on material refined in such boats indicate oxygen concentrations of around 10^{14} cm^{-3} , a level which is consistent with formation of the Al-O complex.

In an attempt to improve the barrier between the quartz boat and the molten zone, and thereby to reduce the oxygen concentration, we have coated quartz boats with a pyrolytic-carbon film on top of the smoke layer (see Appendix II). Bars refined in such boats exhibit some Al segregation but the effective segregation coefficient is still rather close to 1. We postulate that residual oxygen in the zone refiner atmosphere (forming gas) might be responsible for the poor segregation. Despite this poor segregation, refining in boats coated with pyrolytic carbon is effective in removing Al (see +s in Fig. 8) but we observe that the pyrolytic carbon layer may itself be a source of boron (□'s in Fig. 8) causing an average boron concentration $\approx 10^{11} \text{ cm}^{-3}$. Due to segregation it rises at the 'clean end' to over 10^{12} cm^{-3} (see Fig. 8). Experiments show that the boron source is not depleted by many zone passes. We have not yet isolated the origin of the boron, but it seems unlikely that the argon-methane mixture, which is thermally decomposed to produce the carbon film, is the source since the same gas mixture is used for coating crucibles which do not produce B-contaminated crystals. The most likely source is the vacuum system used in the furnace employed in the formation of the pyrolytic-carbon coating on boats (e.g. flux residues and pump oil).

The failure of pyrolytic-carbon coatings to provide the ideal oxygen poor conditions required in the zone refiner and their effect in introducing boron led to a search for alternatives. The best solution has proved to be a quartz smoke layer on the quartz boat produced by burning silane (SiH_4)*. The results obtained with this type of coating are striking, the impurity concentration being in the low 10^{10} cm^{-3} range over 90% of the polycrystalline bar. The dominant impurity is Al. Very little boron can be detected even when initial material containing boron is used. Phosphorous appears only in the very tail of the bar. The flat concentration profile suggests oxygen rich conditions and complex formation. This is confirmed by growing crystals from this starting material under oxygen rich and oxygen poor conditions.

When the Al concentration exceeds 10^{13} cm^{-3} before the zone purification, we observe a slight Al concentration increase towards the 'dirty end' of the bar. The results obtained from refining in boats coated with quartz smoke can be explained in two ways:

1. Because the probability that the Si is not totally oxidized in the silane-burning process is high, it is possible that the molten Ge zone picks up elemental silicon or silicon monoxide. These then scavenge oxygen and suppress impurity complex formation so that normal segregation initially takes place.

* The difference in thermal expansion coefficients demands that the Ge bar be allowed to slide in its container.

* A triaxial burner is used for the application of the quartz smoke coating. 5% SiH_4 in hydrogen is fed through the center pipe. Argon fed down the intermediate pipe protects the burner tip from the flame which occurs in oxygen fed through the outer most pipe.

After many zone passes the scavenging materials will be used up by combining with oxygen from the forming gas or the quartz boat. Complex formation then takes place leading to the final flat profile.

2. The large surface area of incompletely oxidized quartz smoke getters all complex-forming impurities by forming boro- and alumina-silicates.

Silicon concentrations between 10^{16} and 10^{17} cm^{-3} and low oxygen concentration values near the 'clean end' of the bar obtained from Li-precipitation support the first suggestion. On the other hand, the very low concentration of free boron in Ge bars refined in these boats tends to support the formation of boro-silicate glass. We therefore assume that both mechanisms work simultaneously. A plot of the concentration versus bar length for a typical bar refined in this manner is shown in Fig. 9.

Single crystals grown from such polycrystalline germanium usually have net-impurity concentrations below 2.5×10^{10} cm^{-3} in more than 80% of their volume (see Fig. 10). An obvious concern is that the presence of silicon or Si_xO_y in the germanium might cause trapping in detectors. However, 1 cm thick detectors fabricated from these single crystals exhibit no visible trapping in ^{60}Co spectra indicating that the effect of the silicon is negligible.

CONCLUSIONS

These experiments with single crystal growth and zone purification show that it is possible to create conditions which substantially reduce the levels of electrically-active impurities in germanium. An oxygen poor environment or the addition of silicon as an oxygen getter prevents complex formation with the associated non-segregating behavior (particularly of Al).

We have shown that zone-refining carried out in quartz boats coated with quartz-smoke produced adequate low impurity levels. If the raw germanium is very impure a two step process, first zone-refining in a quartz boat coated with pyrolitic carbon or in a raphite boat, and then refining in a quartz boat coated with quartz smoke, will reduce all impurity concentrations to low levels. Using this method it is possible to use any commercially available intrinsic ($40 \Omega \text{ cm}$) germanium for starting material which means a substantial reduction in initial material cost.

The lower limit of the impurity concentration in our high-purity single crystals is set by the phosphorous released from quartz crucibles. Suprasil crucibles contribute the lowest phosphorous contamination* (about 2×10^{10} cm^{-3} near the seed end of the crystal). Detector-grade single crystals can be grown in one pull from suitably zone-refined material and no compensating impurities need be added to the melt.

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APPENDIX I

PREPARATION OF A PYROLITIC CARBON COATING ON QUARTZ CRUCIBLES

The following preparation steps lead to a tenacious, impermeable pyrolitic carbon layer on quartz crucibles:

1. Etch the crucible in HF (48%) for 2-5 min, rinse with distilled and deionized water, blow dry with N_2 .

Figure 11 illustrates the following steps:

2. Preheat the crucible under flowing argon ($600 \text{ cm}^3/\text{min}$).
3. Formation of the pyrolitic carbon layer by decomposition of 6% CH_4 in argon ($400 \text{ cm}^3/\text{min}$) for 30 minutes at 950°C .

* As compared to General Electric #204 or Spectrosil quartz.

4. Cool down to room temperature under pure argon ($600 \text{ cm}^3/\text{min}$).

With the gas flow geometry shown in Fig. 11 one obtains a shiny coating which covers the inside and some of the outside of the quartz crucible.

APPENDIX II

PREPARATION OF A PYROLITIC CARBON COATING ON QUARTZ BOATS USED FOR ZONE PURIFICATION OF GE

The following steps are involved in the preparation of a tenacious, impermeable pyrolitic carbon layer on quartz boats:

1. Etch boat with HF (48%) for 1-2 minutes, washing with distilled and deionized water; blowing dry with a N_2 jet.
2. Deposition of a carbon smoke layer on the inside of the boat by burning C_3H_8 .
3. Preheat in a 3 foot tube furnace inside a quartz tube under argon to 950°C .
4. Evacuate and fill with $1/2 \text{ atm}$ of CH_3 .
5. Decomposition of CH_3 (pressure rise!) for 30 minutes.
6. Repeat Steps 4. and 5. two times.
7. Cool down to room temperature.

The type of coating obtained with Steps 1. through 7. allows the Ge-bar to slide, a necessary requirement in zone-purification.

FIGURE CAPTIONS

- Fig. 1. A typical profile of the net-impurity concentration versus the solidified fraction of the melt showing the non-segregating acceptor aluminum. The segregating donor is phosphorous.
- Fig. 2. Net-impurity profiles of a first ($X = \#398$) and a second generation crystal ($\square = \#399$). The small difference in net-acceptor concentration is most probably due to a slightly higher phosphorous concentration in crystal #399. The quartz crucible (Suprasil) clearly did not remove aluminum from the melt.
- Fig. 3. Net-impurity profiles of three crystals grown in pyrolitic carbon coated quartz crucibles. The 'clean' 50% of crystals #434 and #435 were used to grow crystal #438. The improvement in purity in #438 indicates normal Al segregation and negligible impurity contribution from the crucible. No donors could be detected using PTIS and intraband light.
- Fig. 4. Crystal #436 was grown in a Suprasil quartz crucible and doped with $\sim 10^{17}$ Si cm $^{-3}$. The segregating acceptor is aluminum. Some boron can be detected near the seed end of the crystal.
- Fig. 5. Crystals #487 and #488 were grown from 'oxygen-rich' polycrystalline germanium exhibiting a net-acceptor concentration of $\sim 5 \times 10^{10}$ cm $^{-3}$. In crystal #487, grown in a quartz crucible, the aluminum stays mostly oxidized and phosphorous from the quartz makes the material turn n-type at about 50% of the melt. Crystal #488 was grown in a quartz crucible coated with pyrolitic carbon. It exhibits normal Al segregation.
- Fig. 6. The starting material used to grow crystals #440 and #441 was highly doped with Si. Under these conditions the same results occur whether the quartz crucible is bare (#441) or coated with pyrolitic carbon (#440) because the silicon in the melt scavenges oxygen. As expected crystal #441 exhibits a slightly higher donor concentration due to phosphorous dissolved from the quartz crucible.
- Fig. 7. Crystal #466 was grown in a quartz crucible from highly boron-contaminated starting material ($\approx 10^{12}$ cm $^{-3}$). The boron concentration near the seed end of the crystal is surprisingly low ($\sim 10^{10}$ cm $^{-3}$), probably due to formation of a boro-silicate glass at the melt-crucible interface.
- Fig. 8. Net-impurity concentration profile of polycrystalline germanium bar #121. The quartz boat was coated with pyrolitic carbon. The melted zone length was $\sim 4\%$ of the bar length and it traversed the bar 37 times. The net profile is indicated by X, boron by $\square$, aluminum by + and gallium by *. All impurities are segregating but the Al segregates only slowly. No donors could be detected with PTIS over 95% of the bar length.
- Fig. 9. Net-impurity profile of polycrystalline Ge bar #127 refined in a quartz boat coated with quartz smoke. The molten zone (4% of the bar length) traversed the bar 28 times. The net impurity concentration is indicated by X, aluminum by $\square$, boron by + and gallium by *. The Al exhibits a low level and a flat profile.
- Fig. 10. A typical net-concentration profile of a crystal (#483) grown in a quartz crucible using quartz-smoke refined starting material. Over 80% of the volume is below 2.5×10^{10} cm $^{-3}$. Detectors prepared from this crystal have exhibited excellent performance.
- Fig. 11. Furnace used for pyrolitic carbon coating of quartz crucibles. A = quartz crucible, B = ground quartz base plate, C = modified large quartz crucible with ground base. D = circle where modified quartz crucible and base plate form a seal. E = ground quartz joint. F = furnace kept at 950°C. G = weight which keeps ground joints tight.

XBL 7511-9011

Fig. 1

Fig. 2

XBL 7511-9012

XBL 7511-9008

Fig. 3

XBL 7511-9013

Fig. 4

Fig. 5

XBL 7511-9014

XBL 7511-9009

Fig. 6

XBL 7511-9015

Fig. 7

XBL 7511-9016

Fig. 8

Fig. 9

XBL 7511-9017

XBL 7511-9010

Fig. 10

XBL 7511-8935

Fig. 11

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