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ZONE REFINING HIGH-PURITY GERMANIUM

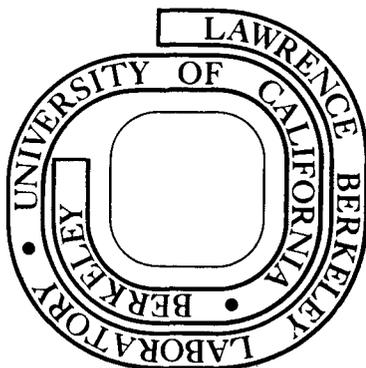
G. S. Hubbard, E. E. Haller, and W. L. Hansen

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### Abstract

The effects of various parameters on germanium purification by zone refining have been examined. These parameters include the germanium container and container coatings, ambient gas and other operating conditions. Four methods of refining are presented which reproducibly yield 3.5 kg germanium ingots from which high purity ( $|N_A - N_D| \leq 2 \times 10^{10} \text{ cm}^{-3}$ ) single crystals can be grown. A qualitative model involving binary and ternary complexes of Si, O, B, and Al is shown to account for the behavior of impurities at these low concentrations.

### Introduction

High purity ( $|N_A - N_D| \leq 2 \times 10^{10} \text{ cm}^{-3}$ ) single crystal germanium suitable for large volume radiation detectors has been produced in several laboratories for a number of years.<sup>1,2</sup> Once it was demonstrated by Haller, *et.al.*,<sup>3</sup> that the zone refined germanium was the source of all but one (P) of the impurities found in these crystals, a program to investigate the zone-refining process was begun.

The zone-refining process for germanium as described by Pfann and others in the 1950's<sup>4,5</sup> depends for its effectiveness on the nature of the equilibrium between the solid and liquid phases of germanium in which impurities are dissolved. This relationship is usually expressed as the segregation or distribution coefficient  $k$ ; a ratio between the impurity concentration in the solid phase to that in the liquid. Impurities with  $k > 1$  (B, Si) tend to remain in the solid phase and segregate in the opposite direction as zone travel. Most impurities in Ge, however, have  $k \sim 10^{-3}$  or less. They will move easily with the liquid zone and be deposited in the last Ge to freeze at the "dirty" end of the bar. A few elemental impurities from Groups III and V (Al, Ga, In, P) have segregation coefficients of about .1 and will be removed more slowly.

This simple model of the zone-refining process can be applied for impurity concentrations down to the intrinsic level ( $\sim 10^{13} \text{ cm}^{-3}$ ). At lower concentrations, the effective segregation coefficient of a number of impurities, (Al, B, Ga) does not remain constant, but approaches unity. Consequently, the impurity concentrations in our zone refined ingots do not reach the ultimate distributions predicted by Pfann.

Identifying those parameters of zone-refining which produce "anomalous" segregation coefficients has required the investigation of many possible conditions which are compiled in Table 1. The number of combinations of factors is quite large, so not all possibilities have been covered in detail.

\*This work was done with support from the U.S. Energy Research and Development Administration.

Table 1. Zone Refining Parameters

#### A. Container

1. Solid graphite
2. Carbon smoke from butane on quartz
3. Carbon smoke from butane plus pyrolytic carbon on quartz
4. Pyrolytic carbon on quartz
5. Silica smoke on quartz
6. Silica smoke plus pyrolytic carbon on quartz

#### B. Ambient Gas

1.  $\text{H}_2 + \text{N}_2$  (forming gas)
2.  $\text{H}_2$  only
3.  $\text{N}_2$  only

#### C. Crystallinity

1. Single crystal
2. Polycrystalline

#### D. Operating Conditions

1. Speed of zone travel
2. Ingot length/zone length ratio
3. Position of zone start

### Experimental

The primary measurement techniques used in this research were conductivity measurements at 77K, van der Pauw Hall effect,<sup>6</sup> Photoelectric Spectroscopy (PES)<sup>7</sup> and Czochralski growth of single crystals under controlled conditions.<sup>8</sup> Most of the time, Hall effect measurements were performed at 77K, but to verify that the result at 77K represented the shallow impurity concentration, several measurements were made from 300K to 5K. In addition to these primary techniques, important information was provided by scanning electron microscopy (SEM). With the exception of SEM, our methods have been detailed elsewhere and will not be discussed in this paper.

The application of these experimental techniques to zone-refined material was a problem in the early stages of this work since all the Ge was polycrystalline. It was demonstrated recently by Hubbard, *et.al.*,<sup>9</sup> that small single crystallites could be successfully located and removed from polycrystalline material and subsequently analyzed. Single crystal germanium grown from polycrystalline material demonstrated that impurity concentration values given by the crystallite measurements were representative. However, depending on random growth of sufficiently large crystallites for analysis proved risky in crucial experiments, so we found it necessary to return to the older techniques developed for zone-leveling. By providing a {111} seed at the zone start or "clean" end of an ingot, single crystal ingots were refined, thus simplifying the problem of analysis. Various

techniques for doing this seeding are described in the literature.<sup>4,5</sup> Of the 104 ingots which make up the data base for this paper, 20 have been single crystal. Refining single crystal ingots also allowed us to examine the question of whether impurities are trapped at grain boundaries in polycrystalline material, perhaps contributing to the non-segregating nature of major impurities. All other conditions being equal, no difference has been found in impurity distribution between single crystal ingots with 5 to 10 x 10<sup>3</sup> etch pits/cm<sup>2</sup> and polycrystalline germanium.

Care was still exercised in measuring even single crystal ingots since the crystallography occasionally became so severely disturbed that it affected the conductivity measurements. It was also found that lineages and high etch pit density could cause considerable difficulties in measuring the small (.7 x .7 x .2 cm<sup>3</sup>) samples used in our variable temperature Hall effect apparatus. A sample with poor crystallography would cease to give a meaningful measurement at a temperature of around 30K, probably due to the acceptor and donor bands created by dislocations.<sup>10</sup> Hall effect measurements performed over the whole temperature range showed no deep levels with the exception of occasional small amounts of Cu with an activation energy of 44 meV.

A typical zone-refined ingot measures about 60 cm in length including the seed (8 cm), and has a trapezoidal cross-section 2.5 cm high with a mean width of 3.2 cm. [The only exception are several ingots with a half-circular cross-section of diameter 4.5 cm--this special case will be discussed later.] During normal refining, our molten zone was about 3 cm long. Such a zone gives a ingot length (L) to zone length (ℓ) ratio of about 20:1. If  $k \leq 1$ , this ratio should have produced an ultimate impurity distribution with a very steep gradient after many passes. Because most techniques of zone refining high-purity Ge do not show strong segregation ( $k \approx 1$ ), little work has been done on the influence of the L/ℓ ratio. The speed of zone travel, recommended by Pfann and others to be .8 to 8.5 cm/hr for the best resistivity uniformity and crystal perfection, was usually 10 cm/hr in our work. Some refining was done at 3 cm/hr and while the crystallography of the ingot was much better no differences could be observed in the impurity distribution.

By far the most significant factor studied in our zone-refining research has been the influence of the material in contact with the germanium. The atmosphere during refining also plays a role, but unless stated otherwise, one may assume a "forming gas" mixture of 90% N<sub>2</sub> and 10% H<sub>2</sub>.

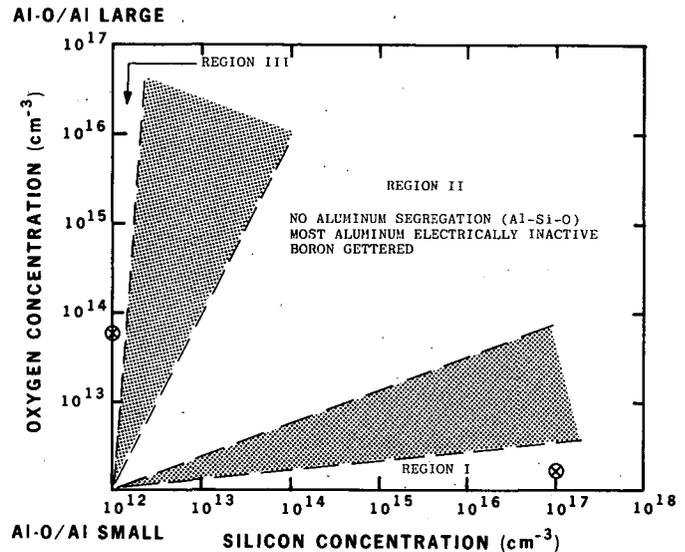
Since germanium wets quartz and will stick upon freezing, bare quartz containers cannot be used for zone refining as it can in crystal growing where the entire melt is removed as a crystal. The alternatives are to use a solid graphite boat or to coat the quartz.

The detailed preparation of the coatings as well as the cleaning of the germanium are given in the Appendix.

## Results and Discussion

### A Model of Complex Formation

Evidence provided by zone refining and crystal growth has led us to construct a model of impurity behavior which involves binary and ternary complexes of silicon, oxygen, boron, and aluminum. This model



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Fig. 1 Our tentative qualitative model of the effect of silicon and oxygen on aluminum and boron is shown. In Region I where silicon is dominant, the impurities segregate. Region II represents the conditions of crystal growth from quartz and silica zone refining. In Region III, oxygen is dominant and electrically active impurities segregate. As the amount of oxygen increases, more impurities become electrically inactive (Al-O, B-O).

is an extension and modification of that presented in an earlier paper.<sup>3</sup> For purposes of clarity, it is presented first (Fig. 1), and we shall see later how the results of zone refining and crystal growth experiments fit the picture.

In Fig. 1, the total concentration of aluminum or boron in a melt or zone is considered to be constant. The material in contact with the germanium is not directly relevant; although, as we shall see, each container considered may be represented by one of the regions.

Region I is characterized by an increasing silicon concentration and low oxygen concentration. At even very high silicon concentrations, normal segregation of aluminum and boron occurs and almost all of the aluminum and boron is electrically active. In Region III, the concentration of silicon is low and the amount of oxygen increases. Here the behavior of aluminum and boron is more complex, but in general the electrically active impurities still segregate normally. At very high concentrations of oxygen, B and Al completely disappear due to the creation of electrically inactive Al-O, B-O complexes. This was demonstrated by the work of Edwards.<sup>12</sup> At intermediate levels of oxygen, both electrically active and inactive impurities exist. The electrically active form segregates normally, whereas the electrically inactive impurity-oxygen complex seems to have  $k \approx 1$ . Most high-purity germanium crystals are grown under the conditions of Region II. In this region, silicon and oxygen are present in approximately equal quantities, creating Si-O-(Al, B) complexes. Electrically active aluminum does not segregate and a large fraction of aluminum is in the form of electrically inactive

complexes. Boron is largely gettered by complex formation.

Impurity Behavior During Single Crystal Growth

The importance of the container for high-purity single crystal growth was made clear by Hall<sup>1</sup> and Haller, et.al.<sup>3</sup> They showed that aluminum in the starting charge segregates normally when single crystals are grown from a graphite crucible or pyrolytic carbon coated quartz crucible but does not segregate in a bare quartz crucible. Furthermore, the electrically active aluminum concentration of a given crystal will appear to increase by about a factor of 6-10 if it is grown in a carbon container rather than quartz. This increase is reversible and demonstrates that most of the aluminum in a crystal grown from bare quartz is not electrically active.

Boron, which may be present at concentrations  $\sim 10^{11}$  cm<sup>-3</sup> in the starting material, will remain electrically active if the melt is contained in pyrolytic carbon but will largely disappear if the crystal is pulled from a quartz crucible. This reduction, which can be as much as a factor of 100, is irreversible in the sense that regrowing the quartz crucible crystal in carbon will not make the boron reappear.

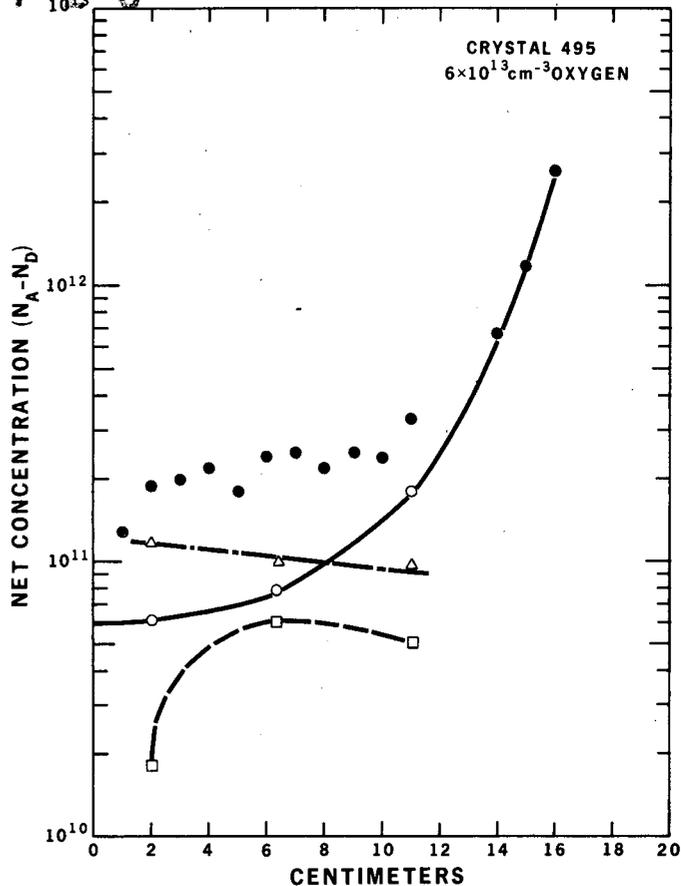
An explanation of such impurity behavior was suggested by the work of Edwards<sup>12</sup> when he demonstrated that electrically inactive complexes of Al and B with O<sub>2</sub> can be formed during crystal growth from graphite crucibles. At the time, however, the role of silicon was not fully appreciated except as a component which might explain the discrepancy between Edwards' observations of boron and our own.

It was shown<sup>3</sup> that at a level of  $\sim 10^{17}$  cm<sup>-3</sup> silicon in a single crystal grown from a Suprasil quartz crucible aluminum segregates. Aluminum also segregates in crystals containing oxygen at concentrations as high as  $6 \times 10^{13}$  cm<sup>-3</sup>\* as long as the quartz crucible is isolated from the Ge melt by a pyrolytic carbon layer. Such a case is shown in Fig. 2 (Crystal 495). The high level of oxygen can be accounted for by the non-reducing atmosphere of N<sub>2</sub> present during crystal

growth. These two results fall into Regions I and III, respectively, on Fig. 1 and are indicated by ⊗. They show that if one can shift the Si/O ratio very much in one direction, or the other, aluminum can be forced to segregate. At very high levels of oxygen alone, as in Edwards' case, B and Al disappear in electrically inactive binary complexes. However, as long as concentration of oxygen is about that commonly encountered during high-purity crystal growth ( $6 \times 10^{13}$  cm<sup>-3</sup>), and no silicon is present, segregation of electrically active impurities will occur. Once silicon is introduced, the impurity behavior switches to Region II where Si-O-(Al, B) complexes occur. Then, the electrically active aluminum ceases to segregate (one observes flat aluminum profiles) and boron is gettered.

The disappearance of boron when crystals are grown in quartz can be explained by the formation of glasses. Doremus<sup>14</sup> points out that boro-silicate systems can be formed at temperatures as low as 500-600°C, far below the melting point of germanium. By introducing silicon from a quartz boat, silica coating or crucible, an effective gettering mechanism could occur. Alumina-silicate systems such as ceramics occur at higher temperatures but may be similar to the

\*Oxygen concentration is measured by the lithium precipitation method.<sup>13</sup>



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Fig. 2 Grown from a pyrolytic carbon quartz crucible under a nitrogen atmosphere, Crystal 495 was determined to have  $6 \times 10^{13}$  cm<sup>-3</sup> oxygen by a lithium precipitation measurement. Points marked with ● represent net acceptors, ○ indicates aluminum, △ is acceptor A<sub>4</sub> and □ is acceptor A<sub>5</sub>. A<sub>4</sub> and A<sub>5</sub> disappear upon annealing and appear to be related to the presence of nitrogen. The activation energies are very close to those of boron and gallium, respectively.

type of complex formed in the Region II of Fig. 2. The optimum conditions for segregation and zone purification should then be a low oxygen, low silicon environment such as a graphite container with hydrogen.

Zone Refining in Graphite and Carbon Coated Quartz

Early germanium zone refining was done in solid graphite boats and today such containers are routinely used by commercial suppliers of "intrinsic" grade germanium. Analysis of test crystals\*\* grown directly from Eagle-Picher 40 Ω cm intrinsic germanium showed that boron and phosphorous were usually quite high, with both in the range of  $10^{11}$  to  $10^{13}$  cm<sup>-3</sup>. The

\*\*Unless otherwise stated, it will be understood that all single crystals are grown by the Czochralski method from a Suprasil quartz crucible under a pure H<sub>2</sub> atmosphere using cleaning procedures and techniques described in previous publications.<sup>8</sup>

aluminum content varied but in the test crystals it was observed to be  $3 \times 10^{10} \text{ cm}^{-3}$  to  $\sim 10^{11} \text{ cm}^{-3}$ . When such intrinsic grade starting material was further refined in solid graphite boats at our laboratory, an impurity distribution such as that of Ingot 90 (Fig. 3) was observed. The impurity seen segregating toward the zone start and maintaining the high ( $\sim 5 \times 10^{11} \text{ cm}^{-3}$ ) background is boron. The constant level of boron seen in graphite boats and carbon coated quartz boats indicates that carbon is a source of boron. However, the low silicon, low oxygen environment of the graphite boat allowed the aluminum in the intrinsic material to segregate. As a result, crystals subsequently grown from material refined in graphite were low in Al but the boron contamination was too great to be adequately gettered by complex formation.

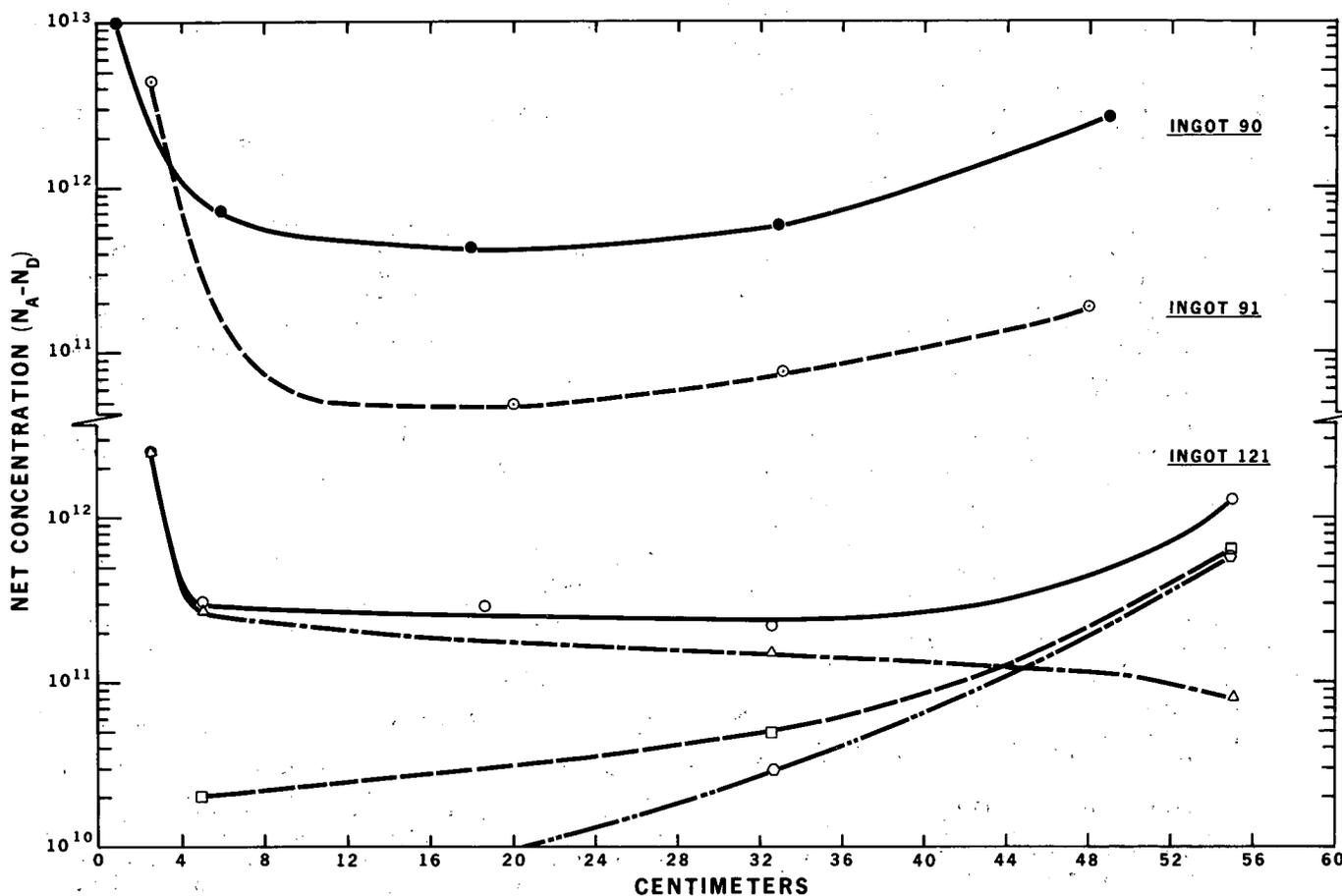
Ingot 91, (Fig. 3), was first refined in a solid graphite boat then placed in a butane smoked quartz boat for about 20 passes. Single crystal growth and electrical measurements have demonstrated that both Ingots 90 and 91 contain about the same amount of aluminum though Ingot 90 seems to have substantially less boron. The factor of 10 difference in impurity concentration can be explained by complex formation involving boron, oxygen, and silicon as demonstrated for single crystals.

We assume that the amorphous carbon smoke, in contrast to the much denser pyrolytic carbon, did not prevent the liquid germanium zone from interacting with the quartz boat. Silicon and oxygen contributed from the quartz then combined with the boron to form boro-silicates.

SEM has provided proof of the porousness of these smoke coatings. An examination of coatings of pyrolytic carbon on smoke (either silica or carbon) showed that a pyrolytic coating on the surface of the quartz boat nearest the germanium can be formed through the smoke layer.

"Double" zone refining was then found to produce acceptable starting material. By first refining under low oxygen, low silicon conditions to make aluminum segregate and then refining in some environment where boron could be gettered by Si-O complexes all impurities could be reduced to low levels.

Ingot 121, refined in a coating of pyrolytic carbon and carbon smoke bears a striking resemblance to Ingot 90, again demonstrating that when one separates the germanium from quartz so that Si-O complexes cannot form, boron is not gettered and aluminum segregates. The distribution of all p-type impurities as



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Fig. 3 Ingot 90 has been refined in a solid graphite boat. Ingot 91 has been first refined in solid graphite then in a quartz boat smoked with carbon from burning butane. Ingot 121 was refined in a boat coated with carbon smoke then pyrolytic carbon.  $\odot$ ,  $\bullet$  and  $\circ$  represent net acceptors,  $\triangle$  indicates boron,  $\square$  aluminum and  $\circ$  gallium. All ingots are polycrystalline.

determined by PES and Hall effect is shown for Ingot 121. As with Ingot 90, boron segregates towards the zone start and also has an almost constant residual concentration of  $\sim 2 \times 10^{11} \text{ cm}^{-3}$ . Aluminum segregates into the "dirty" end of the ingot but the distribution in the bulk of the ingot does not follow the ultimate distribution given by Pfann. We explain this by a high-oxygen concentration in the absence of silicon which creates an electrically inactive, non-segregating Al-O complex. Crystals grown from Ingot 121 under low oxygen, low silicon conditions show that most of the aluminum is electrically inactive, indicating that the concentration of oxygen is at least  $6 \times 10^{13} \text{ cm}^{-3}$  or higher.\*

Since we believe that during single crystal growth from a pyrolytic carbon quartz crucible under hydrogen atmosphere, there is very little oxygen and probably no silicon present, the obvious extension would be to refine under such conditions. The technological difficulty is that molten germanium wets pyrolytic carbon coated quartz, allowing the solidified germanium to adhere to the walls of the boat. If the germanium cannot slide in its container as the thermal expansions and contractions occur, the boat will break as the germanium pushes against one end. Recently, we have found that by selecting very smooth quartz tubes with uniform inner diameter (45 mm), closing off the ends by rounding, then slicing lengthwise, half-cylinder boats can be made in which refining can be done. The glassy pyrolytic carbon on smooth quartz with no constriction in diameter allows just enough slippage in short "jumps" to keep the boat from breaking. Experiments with boats of this type are in the initial stages so results are still forthcoming.

During each zone pass through Ingot 121, the electrically active portion of the aluminum segregated but the Al-O/Al ratio re-established in the frozen germanium behind the moving zone left some new fraction of electrically active aluminum. Thus, the impurity profile did not reach the ultimate distribution. Refining with pyrolytic carbon/amorphous carbon coated quartz under a pure hydrogen rather than forming gas atmosphere has not yet proved successful in reducing the concentration of aluminum to lower levels. This may be due to oxygen in the amorphous carbon smoke.

Zone Refining in Silica Coated Quartz

Another approach to the search for effective zone refining has been the use of silica smoke as a boat coating. Made by burning silane as described in the

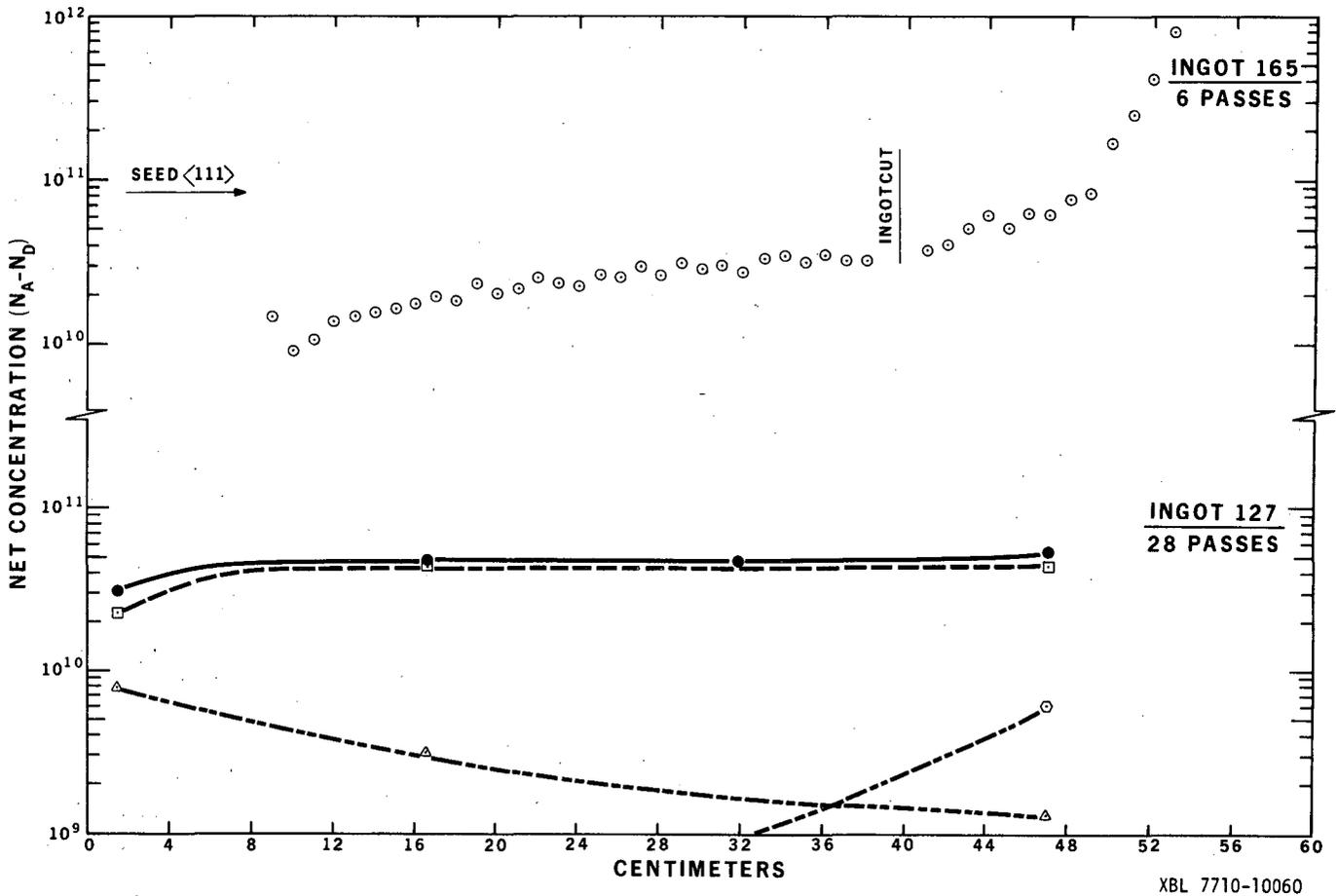


Fig. 4 Ingot 165 is single crystal, refined in a silica smoked quartz boat.  $\odot$  represents net acceptors as measured by conductivity. Ingot 127 is polycrystalline, refined in a silica smoked quartz boat.  $\bullet$  indicates net acceptors,  $\square$  represents aluminum,  $\triangle$  boron, and  $\circ$  gallium.

\*Attempts to measure the oxygen in samples taken from polycrystalline material have yielded inconsistent results, possible due to poor crystallography.

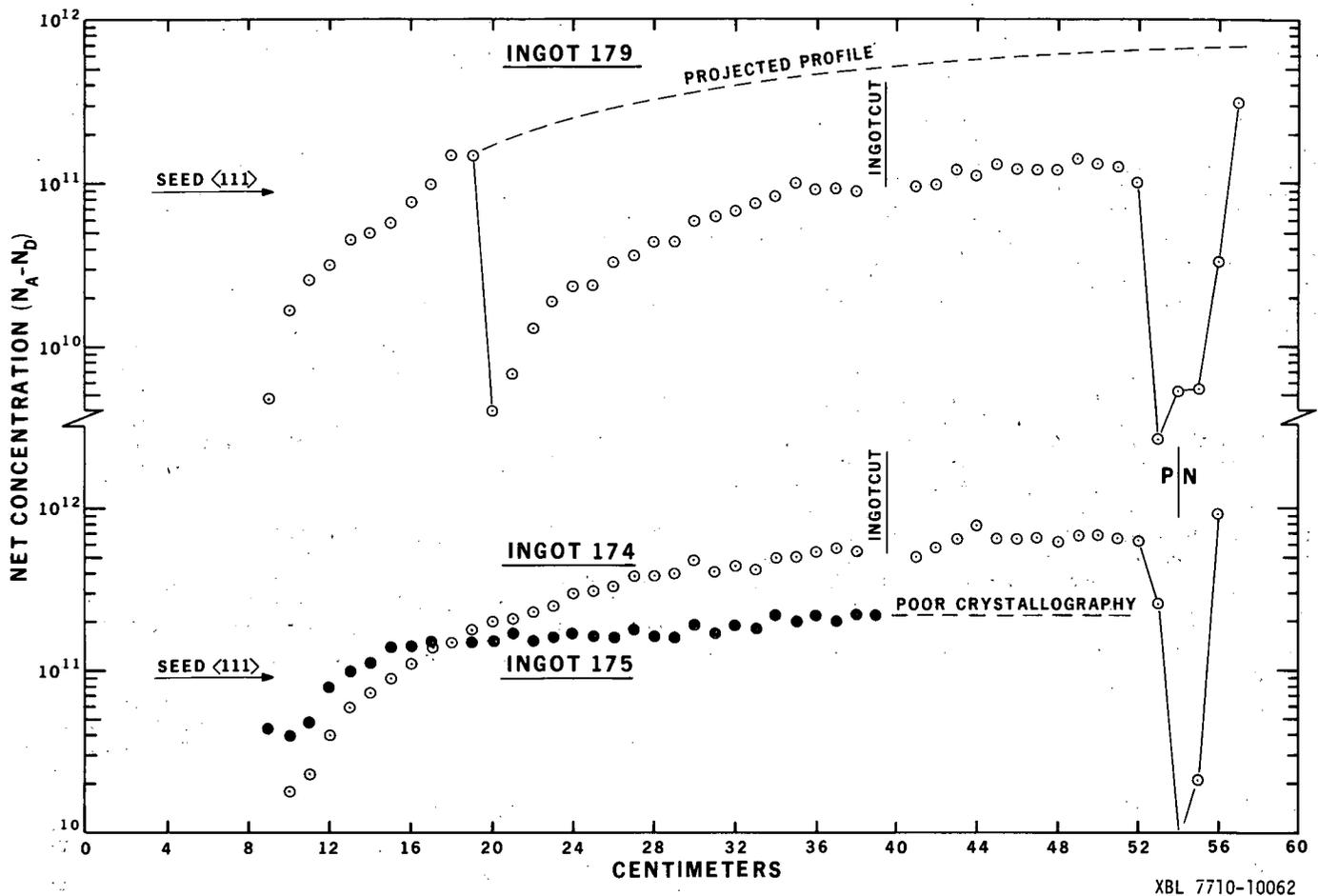


Fig. 5 All ingots are single crystals.  $\odot$  and  $\bullet$  both represent net acceptors. Ingot 179 was given five passes in a silica smoked boat, removed, the silica replaced and given five more passes from 20 cm to the end. Ingot 174 was given five passes in a silica smoked boat, removed, analyzed, etched, and replaced into the same silica coating. After five more passes, the ingot, now called 175, was removed and measured to the point where poor crystallography began to disturb the measurement.

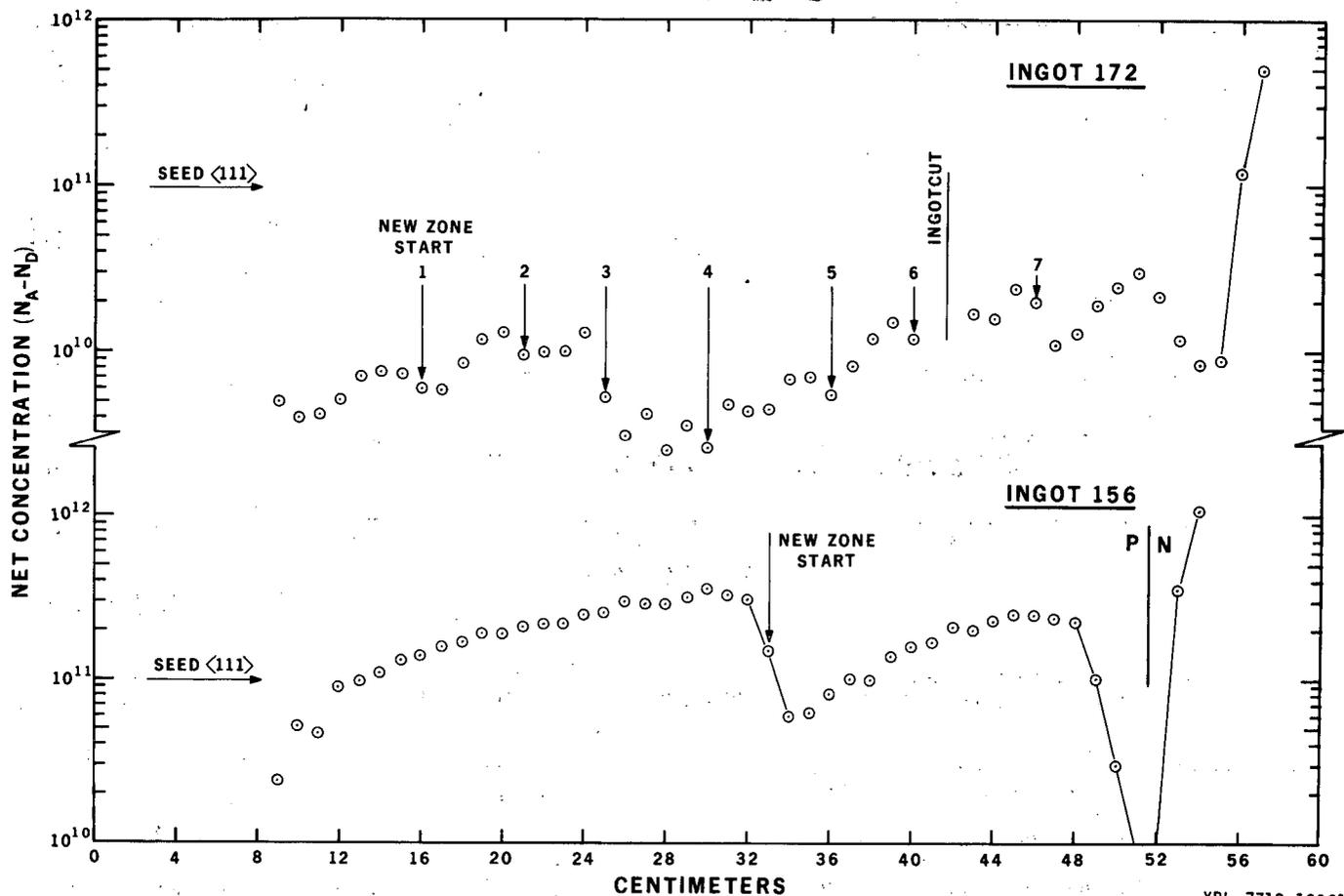
Appendix, the smoke consisted of Si and  $\text{Si}_x\text{O}_y$ . Most likely the Si/O ratio is slightly in favor of the silicon, i.e., the impurity behavior should be in Region II but nearer the x-axis and Region I. Considerable work has been done with this coating for two reasons: 1) Ease of analysis: The white coating gave a small thermal gradient at the melt/solid interface in the zone refiner, yielding large crystallites in polycrystalline ingots and facilitating seeding in single crystal ingots. 2) High purity: This coating has yielded consistently high-purity ingots, although single step zone refining is not always sufficient.

Figure 4 shows two typical ingots, 127 and 165, refined from the less pure sections of other ingots. There is little difference in impurity concentration between the single crystal and polycrystalline material or between 6 and 28 passes of the molten zone. Ingot 127 has a "flatter" impurity profile while 165 shows a slightly "sloping" profile with some accumulation in the tail end. From PES data, we found the major impurity in the silica smoke ingots to be aluminum with small amounts of boron and gallium. PES measurements have also determined that slight segregation of aluminum in Ingot 165 makes the impurity profile rise slowly in concentration. This effect is consistent with the hypothesis that the presence of excess silicon allows some segregation. However, most purification takes place in a few passes

so a mechanism such as gettering by complex formation rather than segregation must be dominant.

Figure 5 shows a cast ingot (174) of intrinsic grade commercial germanium refined for five zone passes. After removing the ingot and measuring the concentration it was etched, exposing a new surface. The ingot was returned to the same coating for five more passes and a further reduction of 2.5 in impurity concentration was achieved (Ingot 175). Ingot 179 was also a cast ingot of 40  $\Omega$  cm germanium refined for five passes. The ingot was carefully removed but not etched and only the silica smoke coating replaced. By moving the position of zone start, enough of the initially refined germanium could be preserved to determine the profile after the first five passes. The balance of the ingot, unetched but in contact with a fresh coating exhibited a dramatic 5-fold drop in impurity concentration. Taken together, these two experiments demonstrate that a vigorous gettering by complex formation occurred at the germanium/silica coating interface. No change in the shape of the impurity profile was noted, as would be the case with segregation, but etching the ingot and replacing the silica coating effected large reductions in the impurity concentration.

Using this gettering action, one can consistently produce germanium of sufficiently high purity for detector grade crystals to be made in a single pull.



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Fig. 6 Both ingots are single crystal.  $\odot$  indicates net acceptors. Ingot 156 was refined eight passes in a silica coated boat, then a new zone was begun at 33 cm and passed to the end. Ingot 172 was refined four passes in a silica coated boat then a sequence of seven new zones were passed to the end. Each new zone was begun about 5 cm closer to the end.

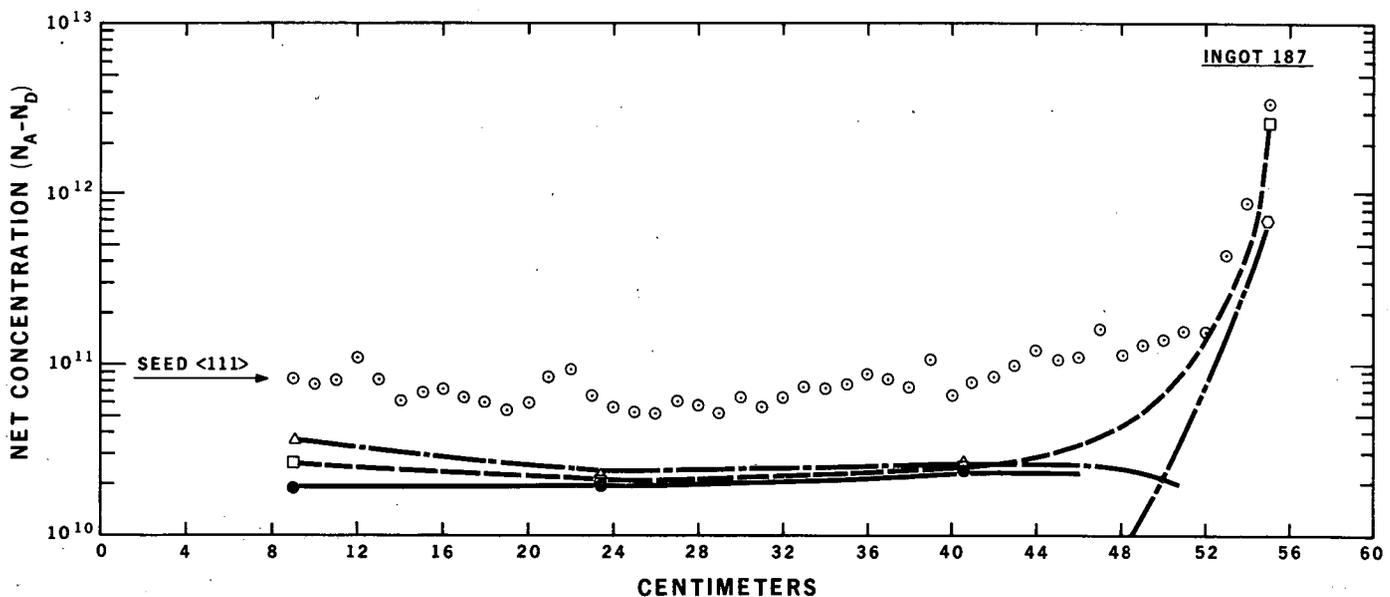
If one begins with intrinsic grade germanium, the process requires two separate refinings in which the ingot is etched and the silica coatings replaced. A final equilibrium between electrically active and complexed impurities appears to be established at a measured impurity concentration of 1 to  $4 \times 10^{10} \text{ cm}^{-3}$ . As a result more etching and new coatings do not further improve the impurity concentration. If the ingot has been first refined in a graphite or pyrolytic carbon/carbon smoke environment, a subsequent refining in silica smoke usually easily removes the boron in a few passes.

While investigating the silica coating, it was observed that all such ingots had a characteristic "dip" in concentration wherever a zone was begun. This effect is shown in Fig. 6, Ingot 156. The "dip" was observed only when hydrogen (either as pure  $\text{H}_2$  or forming gas) and silica smoke were both present. No dip was seen with pure nitrogen or when one refined with one of the carbon coatings. Furthermore, just stopping the zone travel in the middle of an ingot did not produce a dip. A new zone had to be started in solid germanium. The difference between a "starting" zone and a "moving" zone depends on the fact that some segregation occurs when a zone begins, but an equilibrium between impurity complexes in the melt and the coating is soon reached. No further gettering and little segregation then occurs as the zone moves to the end of the ingot.

By restarting the zone in a different place, the impurities in the melt had a chance to segregate before a new equilibrium was established.

Ingots such as 172 Fig. 6 were then produced by making many zone starts. The majority of the ingot is in the range of  $5 \times 10^9 \text{ cm}^{-3}$  to  $1 \times 10^{10} \text{ cm}^{-3}$ ; the dominant impurities still being aluminum and some boron. Crystals grown from this type of material have not consistently reflected such extremely high purity, however. A few crystals have been nearly all n-type, indicating that residual acceptor impurities are compensated by the phosphorous from the Suprasil crucibles. Other crystals have not been substantially purer than those grown from germanium refined in silica smoke without the extra zone starts. It may well be that the multi-start technique increases the degree to which the impurities are complexed beyond the point that can be sustained during final crystal growth.

Figure 7 displays Ingot 187, refined in a pyrolytic carbon/silica smoke coating which combines the aluminum segregating environment of carbon refining with the boron gettering property of silica. This coating has allowed us to successfully purify the commercial germanium in one step. From analyzing ingots and studying the coating with SEM, it appears that: 1) the presence of the pyrolytic carbon reduces the silicon contribution by covering the quartz boat walls and surrounding the silica smoke with carbon. This effectively moves the refining environment near Region III



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Fig. 7 Ingot 187 is a single crystal, refined 12 passes in a pyrolytic carbon/silica coated boat.  $\odot$  represents net acceptors,  $\triangle$  indicates boron,  $\square$  represents aluminum,  $\bullet$   $A_6$  and  $\diamond$  gallium.

where segregation can occur. 2) The intimate contact between the silica and carbon makes possible borosilicate formation, effectively removing most of the boron contributed by the carbon.

The starting material for Ingot 187 was intrinsic grade germanium whose aluminum content can be seen segregating into the end of the ingot as in Ingot 121. The major difference is that the presence of the silica smoke has kept the boron to a level easily removed in final crystal growth. A new acceptor, identified by Haller<sup>15</sup> as  $A_6$ , also contributes to the measured impurity concentration. This acceptor, which is seen quite often in the presence of pyrolytic carbon and hydrogen, will disappear during single crystal pulling. Its presence is a reminder to not assume that all observed impurity concentrations are related to the common substitutional elements and points out again the power of PES as an analytical tool for semiconductors.

Crystals grown from Ingot 187 have been p-type and consistently in the range of  $1-3 \times 10^{10} \text{ cm}^{-3}$  at the seed end with a junction of 30% to 50% of the melt frozen. Refining similar ingots under a pure hydrogen atmosphere has been recently attempted but the results are still forthcoming.

#### Summary and Conclusion

A qualitative model (Fig. 1) involving ternary and binary complexes of silicon, oxygen, boron, and aluminum has been presented to account for most of the behavior of the impurities observed during single crystal growth and zone refining of high purity germanium. At least four different methods of refining commercial  $40 \Omega \text{ cm}$  to sufficient purity for detector grade single crystals have been found:

- 1) Refining in a solid graphite boat followed by refining with amorphous carbon smoke on quartz.
- 2) Pyrolytic carbon/carbon smoke refining

followed by silica smoke refining.

3) Silica smoke refining repeated.

4) Pyrolytic carbon/silica smoke refining alone.

Further areas for investigation involve reducing the oxygen content during refining so that higher levels of purity can be reached and attempting to understand the nature of the new acceptors such as  $A_6$  which have appeared in both zone refined and single crystal material. We feel that the understanding of high-purity germanium is now at the point where the consistent production of large amounts is feasible.

#### Acknowledgments

We would like to thank P. L. Richards, University of California at Berkeley and Materials and Molecular Research Division, LBL for the use of the Fourier Transform Spectrometer in our PES studies. We also would like to thank F. S. Goulding for his continuous interest in this work.

#### Appendix

##### I. Cleaning of quartz boats and ingots:

Prior to applying any new coating, the quartz boat is first etched by spraying a mixture of 3:1,  $\text{HNO}_3:\text{HF}$  to remove any residual germanium as well as the old coating. Following a distilled deionized water (DDW) rinse, the boat is then etched with HF alone, rinsed again with DDW and then dried with a boil off  $\text{N}_2$  jet.

The ingot is treated much as in the preparation for growing a final crystal. First, the charge is spray etched with 3:1 as above to polish any sawed areas, rinsed with DDW, then etched again

with 5:1:1; DDW:HCl:H<sub>2</sub>O<sub>2</sub>. Another DDW rinse follows, then the ingot is blown dry with N<sub>2</sub>. Any subsequent handling is usually done with clean, dry filter paper.

## II. Quartz boat coatings:

### A. Carbon smoke

An etched boat is inverted and placed in a dust free enclosure while a flame of butane from a Bunsen burner is passed underneath. If one positions burner and boat so that the tip of the flame just touches the quartz, a coating of smoke should be produced. It is important to continuously move the burner with respect to the boat to assure the uniformity of the coating. One drawback of this type of coating is that the deposition is done in room air which could result in organic compounds and particulates being deposited along with the amorphous carbon.

### B. Pyrolytic carbon

The production of a pyrolytic carbon layer is utilized for a number of coatings: pyrolytic carbon on bare quartz, on butane smoke and on silica smoke. A quartz boat, etched or suitably coated is placed into a quartz tube surrounded by a resistance heated furnace. The tube is evacuated and pumped continuously as the temperature is brought to 1100°C. This procedure was instituted in an attempt to remove any outgassing oxygen or other volatiles.

After stabilizing the temperature, pumping is discontinued and methane is introduced to a partial pressure of .7 atm. The decomposition of CH<sub>4</sub> at 1100°C for 1/2 hour coats the boat with a pyrolytic carbon. Only one or two such treatments are necessary to produce a satisfactory coating--further applications tend to increase the amount of amorphous carbon created at cooler spots in the furnace. This additional amorphous carbon is the most pernicious problem in producing a truly pyrolytic coating. Scanning electron microscope studies of multiple layer coatings such as pyrolytic carbon on silica smoke indicate that the methane penetrates the silica smoke and forms a pyrolytic carbon on the hot quartz boat as well as encapsulating the silica smoke. In addition, a layer of amorphous carbon is deposited on top of the existing layers which then appears to act as a source of additional boron and possibly oxygen. One cure for this difficulty may be to introduce the methane in much smaller quantities.

A pyrolytic carbon coating can be removed by: 1) Etching: (This requires that the coating be underetched and floated away since few etchants will attack the carbon directly.) 2) Burning: (A gas/oxygen torch in air will heat the carbon sufficiently that it will oxidize--though this risks contamination of the boat from the torch.) 3) Oxidation in the furnace: (By placing the used boat back into the furnace heating and introducing air or O<sub>2</sub>, the carbon can be oxidized as with the torch.)

### C. Silica smoke

As described in an earlier paper,<sup>3</sup> silica smoke is produced by burning silane (5% SiH<sub>4</sub> in hydrogen) using a triaxial

quartz burner which mixes SiH<sub>4</sub> and O<sub>2</sub>, using Ar as a separating gas blanket to keep the flame away from the burner tip. As in applying the butane smoke, the tip of the orange flame should just touch the bare quartz boat. If one is too close yellow-brown spots of silicon will form; too far away and no smoke will be deposited. Constant motion is also required to avoid overheating any one spot and to ensure a uniform coating of 20-50 μ thickness.

The use of a laminar flow hood for this type of coating has been employed to reduce the likelihood of contaminating dust particles being incorporated into the silica smoke. The hood and protective clothing such as long rubber gloves and particulate filtering mask are also necessary to ensure the safety of the person doing the coating. Silane itself is quite poisonous and the silica smoke produces in the process can cause extreme lung damage if inhaled.

A used silica smoke coating is easily removed by etching with 3:1; HNO<sub>3</sub>:HF.

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