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Zone Refinement of Germanium Crystals

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Abstract Purification of commercial germanium with an impurity level of $\sim 10^{13-14} \text{ cm}^{-3}$ was successfully conducted in two-step zone refining process under an undiluted high-purity hydrogen gas atmosphere. Results for the first step conducted in graphite boats yielded ingots with an impurity level of $\sim 10^{12} \text{ cm}^{-3}$ near the center of the 60 cm long ingots. These center portions were collected and subsequently zone refined in a high purity quartz boat to reach a purity level of $\sim 10^{11} \text{ cm}^{-3}$. The best material achieved in a one step process employing a carbon-coated quartz boat yielded material of purity $8 \times 10^{11} \text{ cm}^{-3}$.



1. Introduction

Dark matter and neutrino physics are currently topics of great interest in modern physics. Unknown are such properties as the neutrino's absolute mass and magnetic moment as well as the Dirac or nature of the particle. The Neutrino Science Advisory Group and the Dark Matter Science Advisory Group encourage investigation into the better understanding of both dark matter and neutrinos. The MAJORANA and GERDA experiments plan to use high-purity germanium detectors to investigate neutrino properties [1]. They intend to base their work on the neutrinoless double-beta decay event to determine neutrino properties. Very high resolution and very low noise is required for double-beta decay searches using Ge detectors, because of the low event rate of double-beta decay. A high-purity germanium detector is one of the best candidates for such a detector. To satisfy the high resolution requirements, a germanium (HPGe) single crystal detector must have a net impurity level of $\sim 10^{10} \text{ cm}^{-3}$ and a dislocation density between 10^2 cm^{-2} and 10^4 cm^{-2} throughout the entire crystal. Production of such crystals is a very challenging task as described by Hansen and Haller [2]. The zone refinement of commercial germanium ingots to $\sim 10^{11} \text{ cm}^{-3}$ level is an essential precursory step to produce detector grade germanium crystals.

The zone refining technique was developed at Bell Telephone Laboratories in the early 1950s. It is a fractional solidification technique based on the separation of impurities through crystallization of a liquid without adding a solvent. Impurities have segregation coefficients across the liquid-solid interface that can differ by an order of magnitude, or more. A long germanium ingot is refined by repeatedly moving an inductively-melted liquid zone from one end of the ingot (head) to the other (tail). After multiple zone-refining passes, the impurities will accumulate at the ends of the ingot depending on whether the segregation coefficient is less than or greater than unity; thus, the middle part of the ingot becomes increasingly purified [3-4].

2. Zone-refining equipment

The two commercial zone refining units shown in Figure 1 were acquired and used to refine germanium at the University of South Dakota (USD). They are designated A (ZRA) and B (ZRB). They were able to handle ingots of 4 kg and 16 kg, respectively. Both have two tubes to simultaneously accommodate two ingots. Each tube has single induction coil for heating. The heating power is supplied by a 200 kHz induction generator [5]. A third zone refiner unit shown in Figure 2 was used for zone refining at the South Dakota School of Mines and Technology (SDSM&T). This zone refining unit was designed and built at SDSM&T.

3. Experimental procedure

Commercially pure germanium ingots with a purity level of 99.999% and specific resistance of $47 \Omega \cdot \text{cm}$ were purchased for subsequent zone refining purification. The electrical properties of the starting material were measured at room temperature and 77 K. The resistivity of the commercial ingot was approximately $50 \Omega \cdot \text{cm}$ at room temperature and the impurity level was

measured to be $(10^{13}$ to $10^{14})$ cm^{-3} at 77 K. The main impurities existing in the starting germanium were identified by photothermal ionization spectroscopy (PTIS) to be boron, phosphorous, and aluminum [5].

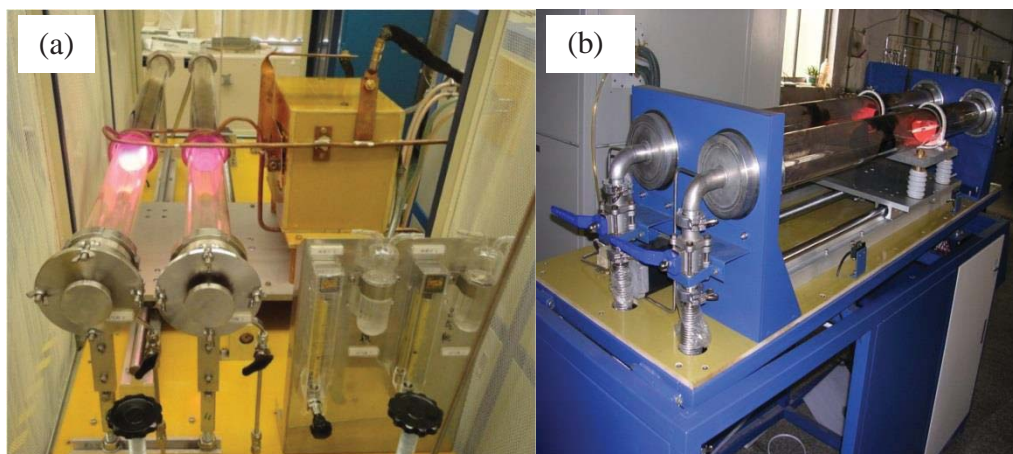


Fig. 1 USD zone refining units a) A and b) B.



Fig. 2 SDSM&T zone refining unit.

Refractory boats used to hold the germanium during zone refining were made of either very high-purity graphite or ultra-high purity quartz formed from the combustion of high purified silane. Both types of boats were obtained from commercial vendors. Both types of boats were used at USD while only quartz boats were used at SDSM&T. The ingots processed by USD A and SDSM&T zone refining units were 60 cm long with a cross sections of (6 to 12) cm² depending on the mass charge (2 to 4) kg. The ingots from USD Unit B were 60 cm long with a cross section of (20 to 40) cm².

All germanium, tubes, and boats used in zone refining were very strictly cleaned [5]. Outer quartz tubes were washed using a hydrogen peroxide solution, then washed using distilled deionized water. Graphite boats were cleaned using polyethylene cleanroom wipes. Germanium and quartz boats were etched in a 1 HF: 3 HNO₃ mixture solution to remove any contamination on the surface, then rinsed with distilled and deionized water multiple times, and dried by nitrogen gas. Finally, the quartz boats were coated using high-purity ethylene (99.999%) in a Class-100 clean room.

Once the boat was charged with germanium and secured in the zone refining unit, the enclosed volume of the zone refining unit was evacuated and sealed to verify that there were no leaks. At USD the pumps consisted of high-speed turbo pumps, which typically achieved 1×10^{-5} torr. At SDSM&T the pump was a mechanical pump capable of achieving 2×10^{-4} torr fitted with a molecular sieve trap to prevent oil vapor back streaming. Multiple evacuation and high-purity argon backfill cycles assured adequate removal of oxygen and water vapor from the SDSM&T system before commencing zone refining. The zone refining melt pool for the two 4 kg units was typically (2 to 3) cm wide and was driven the length of the ingot over an eight hour period. The melt pool width was somewhat larger on the 16 kg refining unit and the time somewhat longer so as to keep the velocity of the zone refining the same as for the 4 kg units. The atmosphere above the germanium was ultra-high purity hydrogen. At USD the hydrogen was produced by electrolysis followed by cryogenic condensation of residual water vapor and dryers while at SDSM&T the hydrogen was supplied from ultra-high-purity cylinders. In both locations, the hydrogen passed through a final heated Pd-foil purifier immediately before entering the zone refining units.

The electrical properties such as carrier concentration, mobility and resistivity of ingots were measured at 77 K using van der Pauw Hall measurement [6] system (HMS-3000, Korea). Samples for the Hall measurement were taken from the ingot head, middle and tail; made into square samples; etched in a 1 HF: 3 HNO₃ solution; washed using distilled and deionized water; and dried by nitrogen gas.

4. Results and discussions

The USD zone refining strategy was to initially zone refine in the graphite boat followed by further zone refining in the high-purity quartz boat. The main purpose of zone refining in

graphite boat was to remove aluminum. The graphite boat created a reducing environment, which according to Hubbard, Haller, and Hansen [7] promotes the removal of aluminum under what they called Region III conditions: low silicon and low oxygen. Without this step, aluminum does not segregate well in carbon-coated quartz boats (Hubbard, et al Region II: moderate oxygen and moderate silicon). Subsequent zone refining in a quartz boat under hydrogen atmosphere removes boron probably by the formation of silicon-oxygen-boron complexes and phosphorous (Region I: low oxygen and high silicon). Figure 3 shows the photographs of zone-refined ingots in graphite and quartz boats.

After zone refining in the graphite boat, the impurity level of the ingot was $\sim 10^{12} \text{ cm}^{-3}$, which was an improvement by factor of about 100 compared to the raw materials. The resulting material was p-type material as shown in Fig. 4a. After zone refined in quartz boat, the impurity level of all of samples reaches $\sim 10^{11} \text{ cm}^{-3}$ as shown in Fig. 4b, which was a further improvement by a factor of about 10 compared to the zone-refined ingots in the graphite boat alone. Because boron and aluminum are acceptor impurities, while phosphorous is a donor impurity, p-type material means that the dominant impurities after zone refining were boron and aluminum.



Fig. 3 Zone-refined ingots from quartz (top) and graphite (bottom) boats.

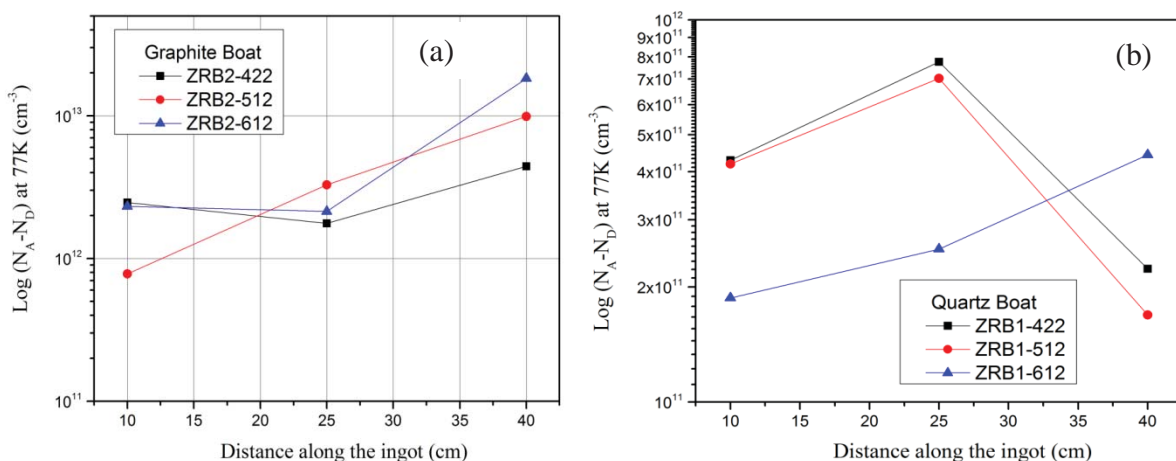


Fig. 4 Net carrier concentration as a function of distance along the ingots at 77 K, from a) graphite boat and b) quartz boat.

Zone refining at SDSM&T was conducted only in high-purity quartz boats coated with carbon under an ultra-pure and undiluted hydrogen atmosphere. Initially carbon was placed with a paraffin flame subsequently replaced with commercial butane and finally very high-purity (>99.9995%) ethylene. The initial carbon coating resulted in ingots ranging from no improvement to levels reaching the (2×10^{12} to 6×10^{12}) cm^{-3} impurities. As the purity of the carbon coating source was improved, purity levels generally improved finally reaching a result of 8×10^{11} cm^{-3} with the high-purity ethylene. In some runs, an attempt was made to purify the carbon coating by holding the coated boat at 1273 K in a high-purity argon-chlorine mixture for several hours followed by several additional hours in only flowing high-purity argon. The results of such attempted purification were no better than those obtained using ultra-pure ethylene for carbon coating.

5. Conclusions

Commercial germanium ingot ($\sim 10^{13}$ to $\sim 10^{14}$) cm^{-3} may be zone refined in a two-step process: graphite boat followed by high-purity quartz boat. The first step removed and segregated aluminum reaching $\sim 10^{12}$ cm^{-3} impurities while the second step segregated phosphorous and boron achieving $\sim 10^{11}$ cm^{-3} impurities as determined by the van der Pauw Hall effect measurements at 77 K. Single-step germanium purification in a process involving a quartz boat coated with very high-purity carbon under ultra-high purity hydrogen proved less successful than the two-step process reaching impurity levels of 8×10^{11} cm^{-3} and having p-type impurities. Zone refined germanium was produced that was suitable for growing HPGe single crystals for detectors.

Acknowledgements

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