High purity germanium crystal growth at the University of South Dakota

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Abstract. High-purity germanium crystal growth is challenging work, requiring the control of individual crystal properties such as the impurity distribution, the dislocation density, and the crystalline structure. Currently, we grow high-purity germanium crystals by the Czochralski method in our laboratory in order to understand the details of the growing process, especially for large diameter crystals. In this paper, we report the progress of detector-grade germanium crystal growth at the University of South Dakota.

1. Introduction

Recently, Germanium-based experiments have reported a possible dark matter signature (CoGeNT)[1] and the claimed discovery of neutrinoless double beta decay[2]. Therefore, the detectors made by high purity germanium (HP-Ge) crystals are preferred for use in future experiments. However, the commercially available germanium crystals will have to be customized to meet the sensitivity requirements set by next generation experiments, which prefer the crystals to be grown in an underground environment that minimizes the cosmogenic activation. It is almost impossible to request commercial companies to meet both production rate and sensitivity for next generation experiments according to our investigation. Thus, additional capacity for growing high-purity germanium crystals with a research entity is a key element in the success of these underground experiments. Motivated by large demands from ultra-low background experiments searching for dark matter and neutrinoless double-beta decay with germanium-based detectors such as Super-CDMS [3], CRESST [4], Majorana [5], GERDA [6], and CDEX [7], we are in cooperation with Sanford Underground Research Facility (SURF) to grow HP-Ge crystal and fabricate it into detectors underground. Without the effect of cosmic rays, our detector will fit the demands for germanium-based neutrinoless double-beta decay and dark matter experiments. We want to create state-of-the-art detectors to advance neutrinoless double-beta decay and dark matter exploration research and technology while simultaneously paving the way for infrastructure to support an underground laboratory for crystal growth, and detector. However, much R&D needs to be done on the surface to grow detector-grade crystals.

There are three challenges in crystal growth. Firstly, the impurity level should be lower than 10¹⁰ cm⁻³ for the requirement of detector fabrication with depletion region higher than one centimeter. The

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impurity concentration in germanium ingots should be purified by Zone Refining method down to \(10^{11}\) cm\(^{-3}\).

Secondly, the HP-Ge crystals must be grown in high purity hydrogen atmosphere to reduce the silicon oxide going into crystal to form trapping centers. Hydrogen has large thermal conductivity, convective heat transfer coefficient and lower viscosity. These make the thermal field difficult to be controlled. Therefore, it is a challenge for growing crystal to control the dislocation density in the range of 100 -10,000 cm\(^{-2}\) and make the dislocation uniformly distributed in the crystal.

In the end of crystal growth process, all the germanium melt should be grown out. The thermal expansion coefficient in quartz is much less than germanium. Therefore, even a drop of germanium melt will break the valuable quartz crucible.

Here, we report the current progress of HP-Ge crystal growth in our lab.

2. Experimental

2.1. Crystal growth

The HP-Ge crystals are grown by the Czochralski method [8, 9]. Before each crystal growth, the quartz crucible, the raw Ge rod and the Ge seed were cleaned by sequence of DI water (18M\(\Omega\)cm), acetone (A.R), methanol (A.R). Then the quartz crucible was etched by HF : HNO\(_3\) (1:3) solution for 8 minutes and the Ge rod and the Ge seed were etched by HF : HNO\(_3\) (1:3) solution for 4 minutes. Following the etching, the quartz crucible, the raw germanium rods and the germanium seed were rinsed by DI water and blown dry by nitrogen gas. The quartz crucible was located in a graphite crucible, which was used to transfer the high frequency electromagnetic field into heat to melt the germanium rods in the quartz crucible. The crystal growth was carried out in hydrogen atmosphere with flow rate 1.5 l/min. After the germanium rods are melted, the temperature of the melt is cooled down to the melting point (937\(^{\circ}\)C) of germanium. The seed is lowered to touch the melt and the crystal growth process is started. When a germanium crystal is pulled along \(\langle 1 0 0 \rangle\) direction, four \(\langle 1 1 1 \rangle\) planes are oblique to the pull axis [10]. Therefore, most of the dislocations with Burgers vectors of \((a/2)\langle 1 0 1 \rangle\) type will grow out and terminate at the crystal surface. Dash’s neck growth technique [11, 12] is introduced to reduce the dislocations generated in the seed through thermal shock. Then, the diameter is increased as the shoulder of the crystal is grown. The diameter is kept constant in order to grow the body of the crystal. During growth of the tail the diameter is decreased and the last remainder of the melt is used up to avoid breaking the quartz crucible [9]. Figure 1 illustrates the four processes of HP-Ge crystal growth. Figure 2 shows the grown crystals with different diameters: \(\varnothing 3.5, \varnothing 10.5\) and \(\varnothing 12.7\) cm. Currently, we can grow crystals with diameter from 3.5 to 12.7 cm and weight from 0.9 to 6.5 Kg.

![Figure 1. The processes of crystal growth, (a) Dash process, (b) Shouldering process, (c) Equal diameter growth, (d) Ending process.](image-url)
Figure 2. The grown crystals with different diameters: Ø 3.5 cm (left), Ø 10.5 cm (middle) and Ø 12.7 cm (right).

2.2. Characterization of grown crystals
The grown crystals are oriented and studied by X-ray diffraction using a Rigaku Ultima IV X-ray diffractometer. The Olympus BX40 microscope is used to count the dislocation density in the crystals. The net carrier concentration and material type of select samples are determined using Hall effect measurements. The samples are measured at 77 K using the Hall effect with the Van der Pauw geometry. An Ecopia HMS-3000 with a 0.55 T permanent magnet is used to make the measurements. For these measurements, square samples with dimensions of 1.5x1.5x0.16 cm$^3$ are cut from select wafers.

3. Results and discussion
Characterization of a grown crystal provides necessary feedback information to make improvements in the growth procedure. We use the standard characterization procedures adopted by the early pioneers in the field of germanium crystal growth [13]. Figure 3 shows the X-ray rocking curves from middle part of φ3.5, φ10.5, and φ12.7 cm crystals, respectively. It is observed that there is an extremely strong peak at $\omega$ of 29.99° on the XRD patterns of three samples with FWHM 0.035-0.038°. This diffraction peak is the reflection of (400) in germanium indicates that the whole crystal has a very nice <100> orientation. The FWHM of these peaks is from 0.035 to 0.038° confirming the high quality of the crystals.
HP-Ge crystals were grown in Hydrogen atmosphere. Hydrogen will form hydrogen di-vacancy (V$_2$H) in germanium crystal, which acts as a trap center in HP-Ge detector. Experience has shown that if the dislocation density in the crystal is more than 100 cm$^{-2}$, the V$_2$H trap concentration will be too low to influence radiation detector properties [14]. However, a high dislocation density results in too many defect states, which serve as generation/recombination centers or trap states for charge carriers. The defects lead to increased leakage current of the detector and hence result in reduced detector sensitivity. Deep defects also contribute to flicker noise in the detectors. The maximum dislocation density should not be higher than 10,000 cm$^{-2}$.

It was known that a high impurity concentration results in an excessively high depletion voltage and risk of breakdown. The net impurity concentration for the crystals is required to be controlled around $10^{10}$ cm$^{-3}$, depending on the size of the detectors. Figure 4 shows the typical etch pits for the top, middle and bottom slices samples cut from the Ø 3.5 cm crystal. There is no dislocation was found at the top sample. The dislocation density was counted, and found to be around 4,000 cm$^{-2}$ for the middle and bottom samples. Figure 5 presents the dislocation densities are 3,000 and 7,000 cm$^{-2}$ from top and bottom sample, respectively.
In HP-Ge crystal, the main donors are phosphorus, arsenic, and antimony and the main acceptors are aluminum, boron, and gallium. The net carrier concentration \( |N_A-N_D| \) depends on the resistivity \( \rho \) of germanium, as following:

\[
|N_A-N_D| = \frac{1}{(\rho e \mu)}
\]  

(1)

where \( \mu \) is mobility at 77K and \( e \) is the electron charge \((1.6 \times 10^{-19} \text{ coulombs})\).

Hall effect measurements are the effective method to measure such low impurity level \((10^{10} \text{ cm}^{-3})\) in HP-Ge. Hall coefficient \( R_H \) is measured in terms of the voltage produced across the Hall probes, per unit magnetic field \( B \) and current \( I \).
\[ R_H = \frac{C}{[N_A - N_D]e} = \frac{\Delta V t}{IB} \]  

where \( \Delta V \) is the Hall voltage, \( t \) the thickness of the plate along the magnetic field. The factor \( C \) depends on temperature, crystal type and crystal orientation and is always close to unity [14]. We used Van der pauw geometry for our Hall effect measurements [15]. Table 1 displays the Hall measurements for the grown crystals demonstrate that the impurity levels range from 2.9 – 5.3x10^{10}/cm^3 depending on the grown crystals with different diameter. For p type high purity germanium crystals, the Hall mobility is higher than 40,000 cm^2/V*S. However, the mobility for n type crystal No.23-14 is around 30,000 cm^2/V*S. At liquid nitrogen temperature, the lattice scattering was frozen and the impurity scattering is dominant. For hole and electron in germanium crystal, the values of drift mobility are 42,000 and 36,000 cm^2/V*S at 77 K [16], respectively. The ratio of Hall mobility to drift mobility is close to 1 at 77K [16]. It confirms the dominant carriers are holes for p type and electrons for n type. For detector fabrication, the Hall mobility of samples should be higher than 25,000 cm^2/V*S [13]. The detector fabrication from the grown crystals has been addressed in our lab [17].

| Crystal number | Net carrier concentration (10^{10}/cm^3) | Resistivity (\(\Omega\ast\)cm) | Mobility (\(10^4\)cm^2/V*S) | Type | Crystal diameter (cm) |
|----------------|----------------------------------------|-------------------------------|----------------------------|------|----------------------|
| 30-13          | 4.433                                  | 3184                          | 4.423                      | P    | 3.5                  |
| 20-14          | 2.917                                  | 4536                          | 4.718                      | P    | 10.7                 |
| 23-14          | 5.321                                  | 3892                          | 3.014                      | N    | 11.5                 |
| 24-14          | 3.673                                  | 3786                          | 4.489                      | P    | 11.5                 |
| 35-14          | 4.160                                  | 3158                          | 4.751                      | P    | 12.7                 |

The net impurity concentration and the dislocation density for the crystals are required to be controlled within a narrow range of 0.5 – 1.5x10^{10} cm^{-3} and 100 – 10,000/cm^2, respectively, depending on the size of the detectors. We demonstrate the required impurity as a function of the size of the detector in Figure 6. It was understood that too low of an impurity concentration results in a highly non-uniform electric field; too high of an impurity concentration results in an excessively high depletion voltage and risk of breakdown. Similar issues arise with the dislocation density. It is also demonstrated that dislocation-free crystals do not yield good detectors because dislocations serve as nucleation centers for vacancies and as traps for impurity ions, thus acting as “getters”, spatially isolating the defects that serve as traps to charge carriers. On the other hand, a high dislocation density results in too many defect states, which serve as generation/recombination centers or trap states for charge carriers. The defects lead to increased leakage current of the detector and hence result in reduced detector sensitivity. Deep defects also contribute to flicker noise in the detectors.
4. Conclusion

We have conducted intensive studies to address challenges in the detector-grade crystal growth and the correlation of these challenges to the use of various methods in the control process. This information allows us to reliably reduce impurity concentrations and dislocation density to acceptable levels on a consistent basis. Consequently, high quality crystals are being grown on a weekly basis at the surface facility located at USD. The grown crystals are in diameters from 3.5 cm to 12.7 cm due to the limitations of the current grower.

Acknowledgement

This work is supported by DOE grant DE-FG02-10ER46709 and the state of South Dakota.

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