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Study on the Properties of High Purity Germanium Crystals

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Abstract In the crystal growth lab of South Dakota University, we are growing high purity germanium (HPGe) crystals and using the grown crystals to make radiation detectors. As the detector grade HPGe crystals, they have to meet two critical requirements: an impurity level of $\sim 10^9$ to 10^{10} atoms/cm³ and a dislocation density in the range of $\sim 10^2$ to 10^4 /cm². In the present work, we have used the following four characterization techniques to investigate the properties of the grown crystals. First of all, an x-ray diffraction method was used to determine crystal orientation. Secondly, the van der Pauw Hall effect measurement was used to measure the electrical properties. Thirdly, a photo-thermal ionization spectroscopy (PTIS) was used to identify what the impurity atoms are in the crystal. Lastly, an optical microscope observation was used to measure dislocation density in the crystal. All of these characterization techniques have provided great helps to our crystal activities.

1. Introduction

In order to meet high-resolution requirements of radiation detectors, high purity germanium (HPGe) single crystals must have a net impurity level of $\sim 10^{10}$ /cm³ and a dislocation density between $\sim 10^2$ and $\sim 10^4$ /cm² throughout the entire crystal, which are two very challenging tasks [1-5].

In our lab, we are carrying out to grow this kind of HPGe crystals and using them to make radiation detectors. The detailed process is shown in Fig.1. Firstly, we used zone refining method to purify the raw germanium materials and then measured their electrical properties using van der Pauw Hall measurement system. If the impurity level of zone-refined ingots reaches 10^{10-11} /cm³, decreased by a factor of 3 from 10^{13-14} /cm³ of raw materials, then the purified ingots could be used to grow HPGe crystals. After a crystal was grown, the x-ray diffraction analysis, van der Pauw Hall measurement, PTIS and measurement of dislocation will be used to characterize grown crystals. Once as-grown crystals with an expected orientation have an impurity level 10^{9-10} /cm³ and dislocation density in the range of 10^{13-14} /cm², we will use them to fabricate the detector. Therefore, the characterization of grown crystals is an indispensable step during HPGe crystal growth.



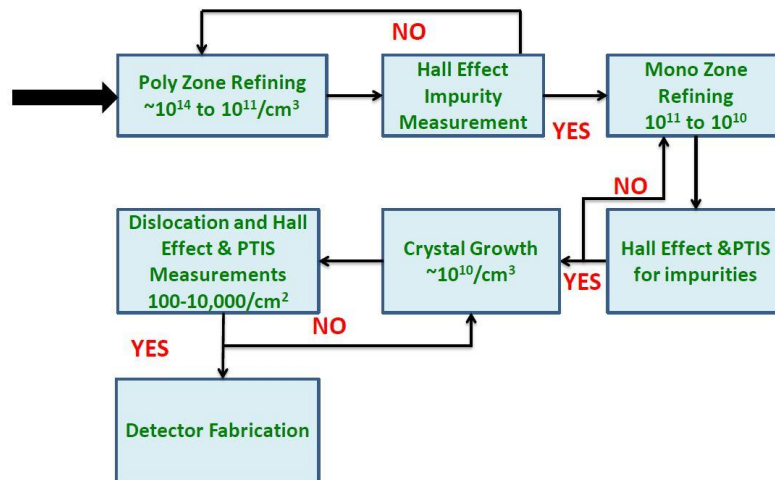


Fig.1 Flow chart of HPGe crystal growth and detector fabrication

2. XRD analysis

XRD analysis is a common and effective method to investigate the crystallographic orientation and structure of the crystals. Contrary to conventional powder measurements, where intensity is monitored in dependence of the diffraction angle 2θ , single crystals should be measured by means of rocking curves. The full width at half maximum (FWHM) of the peak can be used to characterize crystal quality. Since XRD results can provide the evidence about the quality of grown crystals, they can be used to improve crystal growth process. Fig.2 (a) is an x-ray crystal orientation instrument (XY-3, Dandong, China), which can be used to determine the crystal orientation, such as $\langle 100 \rangle$ - or $\langle 111 \rangle$ -oriented crystal. After the orientation of the grown crystal was determined, we cut crystal into slide on the diamond wire saw. Furthermore, XRD measurement were carried out to analyzed the crystal quality in the X-ray diffractometer (Rigaku Ultima IV, Japan.) (Fig.2 (b)) with monochromatic $\text{CuK}\alpha 1$ radiation (wavelength: $\lambda = 1.5406 \text{ \AA}$), working voltage of 40kV and working current of 44mA.

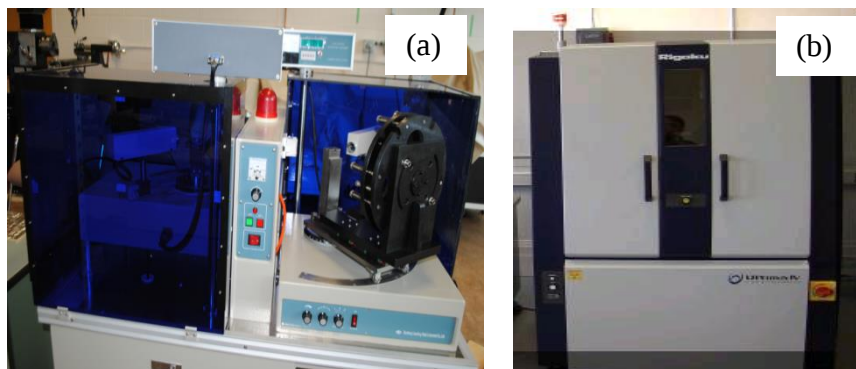


Fig.2 X-ray crystal orientation instrument (a) and x-ray diffractometer (b) at USD

XRD $\theta/2\theta$ scanning result of slides cut from the $\langle 100 \rangle$ -oriented crystal is shown in Fig.3. It is observed that there is an extremely strong (400) peak at 2θ of 66.15° on the XRD pattern of slide sample. Presence of 400 reflection indicates that the whole crystal has a very nice $\langle 100 \rangle$ orientation.

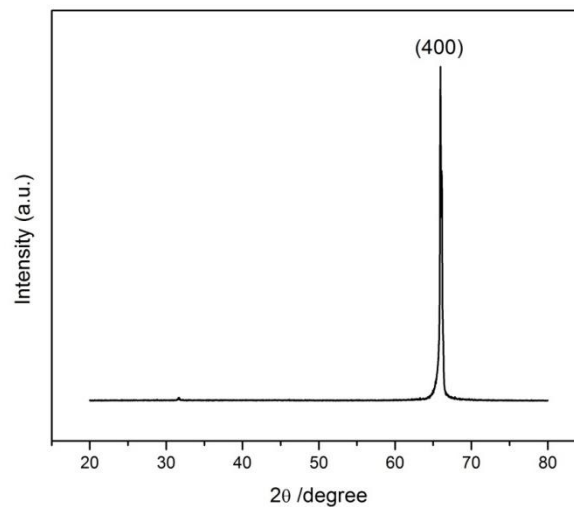


Fig. 3 XRD scanning pattern of $\langle 100 \rangle$ -oriented crystal of sample from the head of crystal

3. van der Pauw Hall measurement

van der Pauw Hall measurement is a standard measurement technique to characterize mechanical properties, such as carrier concentration, mobility and resistivity of semiconductors. From measured results, we can know the impurity level of semiconductors. In our lab, we used van der Pauw Hall method to measure the electrical properties of zone-refined ingots and crystals, which combines van der Pauw technique [6] for resistance measurement of thin sample and Hall effect technique [7] for mobility measurement of sample. Usually, we cut three slides from zone-refined one ingot and two slices from single crystals using diamond wire saw. The square samples with dimension of $15\text{mm} \times 1.5\text{mm} \times 1\text{mm}$ were prepared from slices, then polished and etched in $1\text{HF} + 3\text{HNO}_3$ solution, finally dried by nitrogen gas. The measurement was carried out at 77K on the HMS-3000 Hall Effect Measurement System (Ecopia, Korea.), shown in Fig.4. In Hall effect measurement, mobility characterizes the movement ability of charge carriers through a semiconductor under an electric field. At certain temperature, the movement of charge carriers will be scattered by ion impurity atoms, neutral impurity atoms and lattice. Therefore, total mobility is a combination of the mobility from all scattering processes.

Since the lattice will be frozen at 77K, the last two terms in the above equation have little influence on the total mobility. Therefore, the dominant factors should be scattering from neutral and ionized impurity atoms. For HPGe crystal, the mobility should be more than $26000 \text{ cm}^2/\text{Vs}$ [7].

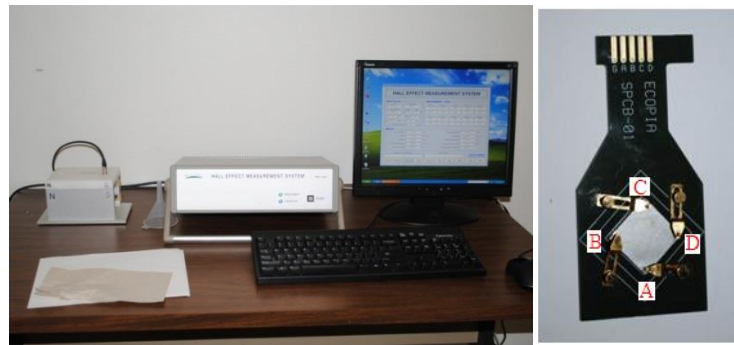


Fig. 4 XRD $\theta/2\theta$ scanning pattern of $\langle 100 \rangle$ -oriented crystal at USD

Table 1 Measured electrical properties of recent zone-refined ingot and crystal

Sample	Carrier Concentration /cm ³	Mobility(cm ² /V·s)	Resistivity($\Omega \cdot \text{cm}$)
Zone-refined Ingot			
ZR_S1	4.44×10^{11}	4.10×10^4	3.43×10^2
ZR_S2	2.08×10^{11}	4.67×10^4	6.41×10^2
ZR_S3	1.68×10^{11}	4.74×10^4	7.86×10^2
Single Crystal			
Crystal_S1	6.20×10^{10}	4.09×10^4	2.45×10^3
Crystal_S2	4.16×10^{10}	4.75×10^4	3.15×10^3

Table 1 shows the electrical properties of recent zone-refined ingot and crystal, which involves three samples cut from zone-refined ingot and two samples cut from the single crystal. ZR_S1, _S2 and _S3 represent samples cut from head, middle and tail parts, respectively. Crystal_S1 and _S2 represent samples cut from head and tail parts of crystal, respectively. It is shown that the entire zone-refined ingot has reached the level less than 5×10^{11} , while the crystal has reached the level of $\times 10^{10}$.

3. PTIS

As a unique technique for identification of residual impurities in high purity semiconductors, the photo-thermal ionization spectroscopy (PTIS) was discovered by T.M. Lifshitz and F. Ya Nad [8-10] when they studied photoconductivity of shallow hydrogenic impurities in germanium. The photoconductivity peaks in PTIS are produced by two-step excitation process. Initially, the electron (or hole) is ionized from the ground state to an excited state by absorption of a photon, and then further excited by a phonon into the conduction band to produce photoconductivity signal [11-12]. Fig.5 shows the two excitation steps of PTIS and setup in the lab.

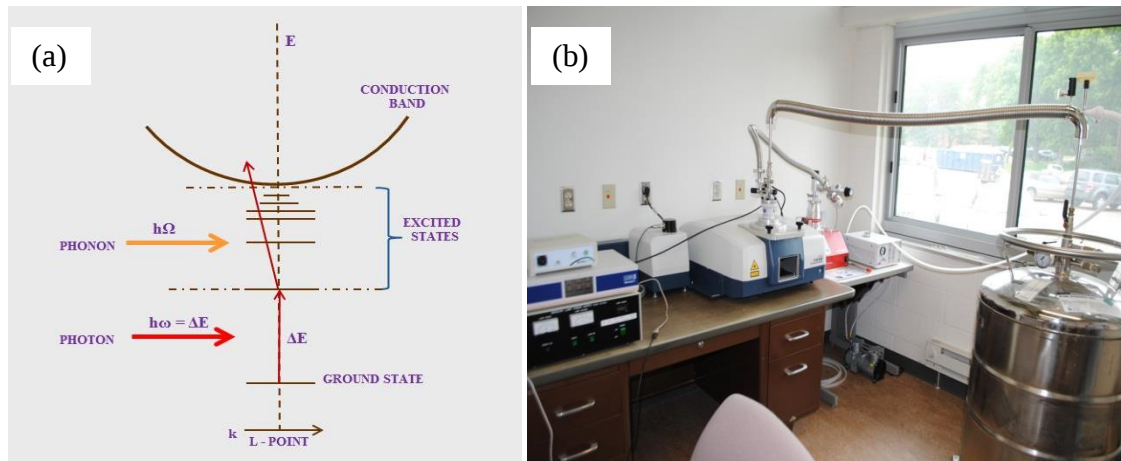


Fig.5 Two excitation of PTIS (a) [] and setup at USD (b)

For PTIS samples, we have prepared two samples with dimensions of $7\text{mm} \times 7\text{mm} \times 3\text{mm}$. Both were cut from the head section of the grown crystals. Before making contacts, the samples were etched for 3 minutes in $3\text{HNO}_3: 1\text{HF}$ solution. Since our PTIS equipment is not ready to use, so these samples were sent to the Leibniz Institute for Crystal Growth (IKZ), Berlin, Germany for the PTIS measurements. The samples were immersed in liquid helium and PTIS spectra were obtained at 7K. The results are shown in Fig. 6.

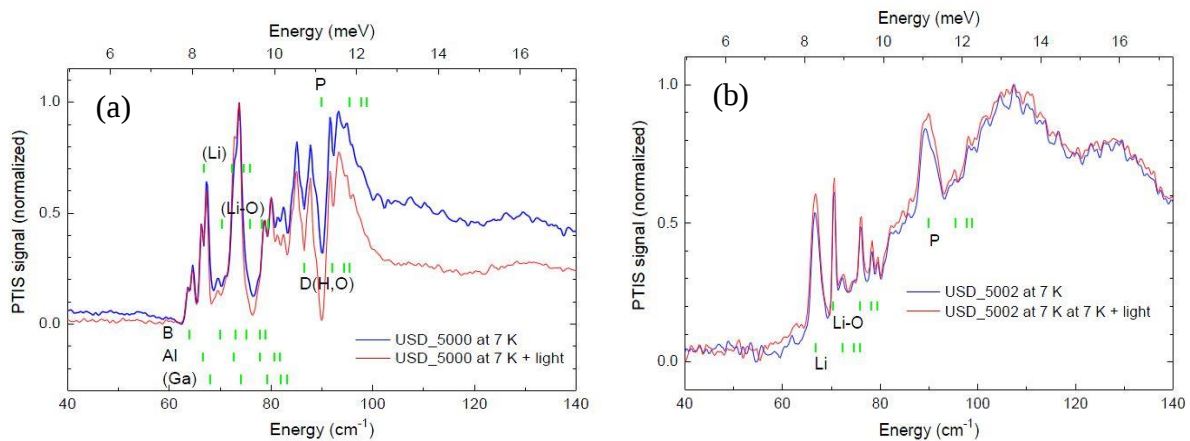


Fig. 6 PTIS spectra of p-type (a) and n-type (b) of two different germanium crystals

Fig.6(a) shows that the dominant impurities are boron and gallium, so the crystal is p-type semiconductor. The dominant impurity atom is phosphorus in Fig.6(b), which indicates that the crystal is n-type semiconductor.

3. Dislocation observation

As stated above, dislocation density in detector grade crystals must be controlled in the range of $\sim 10^2$ and $\sim 10^4$ /cm² throughout the entire crystal. Since occurrence of dislocations is directly related to distribution of residual stress in the crystals, which in turn is related to the thermal field in crystal growth, the dislocation density results can be used to improve the thermal field. The sample for dislocation observation was cut from the head part of the crystal. Prior to dislocation observation, the sample surface was polished to mirror-like surface, and then etched in a mixed solution of HF, HNO₃, and CH₃COOH. The dislocation was observed under Nikon Eclipse LV150L microscope (Fig.7(a)). Fig.7(b) shows the etched pits on one site on the slide sample, indicating a dislocation density of 2000/cm². The dislocation density on the entire slide is about 1.9×10^3 /cm², shown in Fig.7(c).

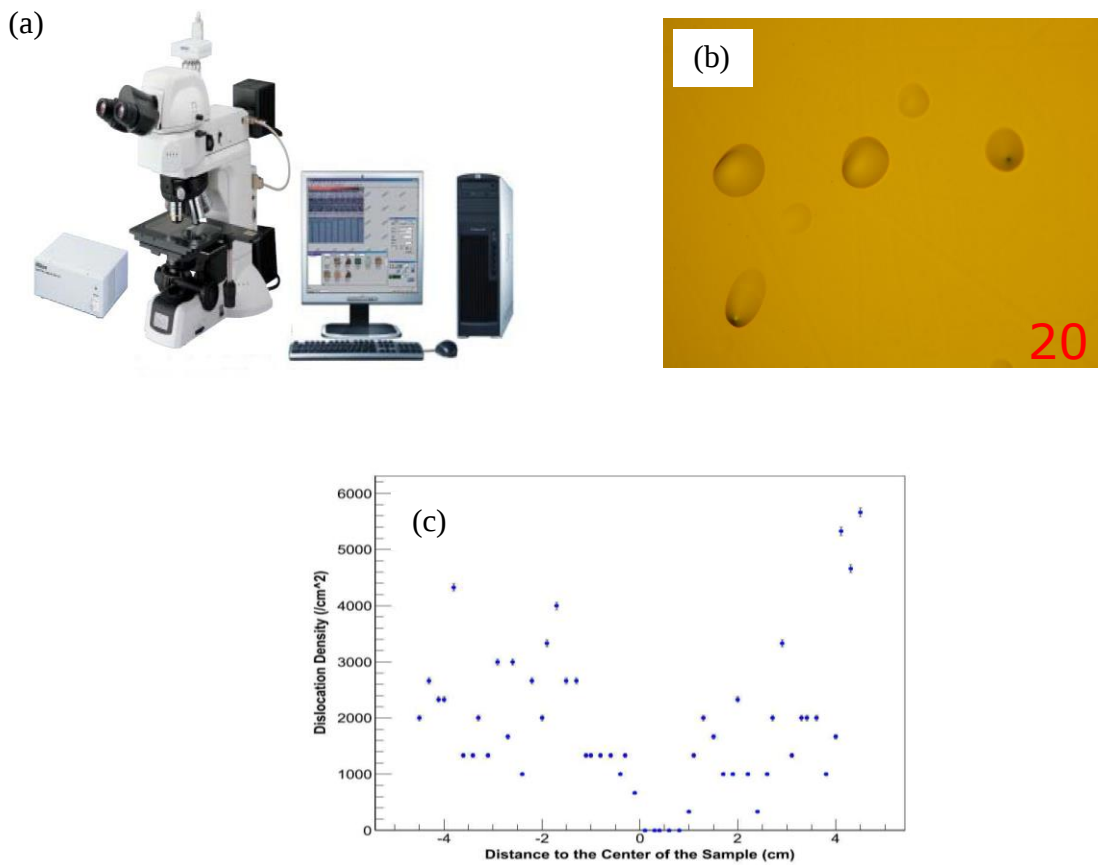


Fig. 7 Optical microscope (a) and dislocation density in germanium crystals (b)

4. Conclusions

In order to assure that the HPGe crystals we grow are detector grade crystals, we have used four kinds of techniques to characterize the grown crystals, such as XRD analysis, van der Pauw Hall

effect measurement, PTIS and dislocation observation. XRD technique can be used to grow crystals with the required orientation and high quality. Van der Pauw Hall measurement and PTIS can help us to improve the purification level of the grown crystals. Dislocation results can help us to optimize the thermal field in crystal growth process. With the help of those characterization methods, the grown crystals at USD have an impurity level of $\times 10^{10}/\text{cm}^3$ and an average dislocation density of about $2 \times 10^3/\text{cm}^2$, which meet the requirement for making radiation detectors.

Acknowledgements

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