Thermal stability of the properties of germanium crystals for IR optics

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Abstract. Both Sb-doped Germanium and Ge-Si solid solution single crystals with resistivity from 1.5 to 7 Ω·cm were grown using the Czochralski method. The optical transmission of single crystals and the stability of their optical properties were studied by infrared Fourier spectroscopy at a wavelength of 10.6 μm and temperature range from 25 to 60 °C. It was found that decreasing the background impurities concentration leads to the reduction of the infrared absorption at room temperature while not affecting the thermal stability of the optical properties. Thermal stability of the optical properties of Sb-doped germanium single crystals increases by adding from 0.2 to 0.8 at % of silicon.

1. Introduction
Infrared (IR) optics production is the largest sphere of germanium single crystals consumption. The crystals used for production of the high-quality optics are required to have the following [1, 2]:
– structural perfection, the dislocation density is less than 10⁴ cm⁻²;
– high optical uniformity, refractive index spread is less than 10⁻⁴;
– minimal birefringence, less than 1 μm/cm;
– low absorption coefficient α, it should not exceed 0.02 cm⁻¹ in the wavelength range from 2.5 to 11 μm and room temperature.

Absorption coefficient α in the transparency region can be defined as below:

\[
\alpha = \alpha_n + \alpha_p + \alpha_s + \alpha_{ad},
\]

where \(\alpha_n\) and \(\alpha_p\) – characteristics of the free carrier absorption, \(\alpha_s\) – absorption coefficient due to the defects presence, \(\alpha_{ad}\) is the contribution of impurity absorption.

The free carrier absorption is predominating in Ge and has a special property, that the cross section for the absorption of photons by holes is much higher than by electrons, thereafter \(\alpha_p >> \alpha_n\) [3-4, 6]. In this connection, to avoid the influence of holes generated by background impurities of the acceptor type, doping of germanium with donor additives, mostly by antimony, is used. Sb-doped germanium with resistivity (\(\rho\)) from 3 to 40 Ω·cm is widely used in the production of optical elements – lenses, windows, filters, etc. This single-crystal material with a dislocation content of less than 10⁴ cm⁻² has a high transparency of about 46.0 % in the working wavelength range. The absorption coefficient \(\alpha\) at a
wavelength of 10.6 μm has a value from 0.015 to 0.035 cm\(^{-1}\) depending on the value of the electrical resistivity \([1, 4-6]\).

The important disadvantage of optical germanium is the thermal instability of its properties which appears as a significant IR transmission decrease at temperatures above 45 °C. According to works \([4, 6-9]\), crystals with resistivity of 3 Ω·cm are characterized by maximum thermal stability. The IR absorption coefficient of these crystals increases from 0.015 to ~ 0.065 cm\(^{-1}\) with increasing the temperature from 25 °C to 60 °C. The absorption coefficient becomes even higher at higher values of \(\rho\).

The purpose of this research is to study the influence of background impurities content and silicon additions on the optical properties of Sb-doped germanium single crystals and their thermal stability.

2. Experimental methods

Both Sb-doped Germanium and Ge-Si solid solution single crystals were grown using the Czochralski method with a quartz crucible in the Redmet unit in an argon atmosphere under 0.02 MPa overpressure. The raw material used for the growth of single crystals was polycrystalline zone-refined germanium with resistivity of more than 47 Ω·cm. The net carrier concentration in raw germanium was determined on single-crystal samples by the voltfaradic characteristics (CV measurements) method using the QuadTech QT7600B LCR meter.

The charge mass was from 4 to 18 kg. The diameter of the resulting crystals was from 60 to 100 mm. The crystallographic growth direction was [111], the crucible rotation speed was 4 rpm, the seed rotation speed was from 0.1 to 0.5 mm/min. The antimony was introduced into the melt in the form of a Ge-Sb ligature and silicon was added in pure form by the method proposed in [10].

The measurements of electrical resistivity of germanium single crystals were carried out at a room temperature by a four-probe method.

Additional germanium refining was performed in order to obtain single crystals meeting high requirements for the impurities content. The refining was conducted by the zone melting method in the "Crystal" unit in a hydrogen atmosphere using fused quartz containers coated with high-purity amorphous silica. Experimental Sb-doped single crystals from additionally refined raw germanium were grown by Bridgman method in hydrogen atmosphere.

The dislocation density of all the investigated crystals was less than 10\(^4\) cm\(^{-2}\).

Plane-parallel polished samples with 1.0 cm thickness were prepared from the experimental crystals in order to determine the optical characteristics. The IR spectrum was recorded at a wavelength in the range from 2.5 μm to 16.6 μm (wavenumber range 4000-600 cm\(^{-1}\)) using a SPECTRUM BXII IR Fourier spectrometer. The optical transmission accuracy was ± 0.1%. Heating attachment was used for performing measurements at the temperature increased to 60 °C which ensured a stable sample temperature control with an ± 0.1 °C accuracy.

The optical transmission T was determined at a wavelength of 10.6 μm using the obtained spectra. The absorption coefficient was calculated from the formula

\[
\alpha = -\frac{1}{t} \ln \left[ \left( \frac{1 - r}{4r^2 T^2} + \frac{1}{r^2} \right)^\frac{1}{2} - \left( \frac{1 - r}{2r^2 T} \right)^2 \right],
\]

where \(t\) is the test sample thickness (cm), \(\alpha\) is the absorption coefficient, \(r\) is the reflectance.

3. Results and discussion

Figure 1 shows the IR spectra of Sb-doped germanium with resistivity of 3 Ω·cm at temperatures of 25 and 60 °C in the wavenumber range from 600 to 1500 cm\(^{-1}\). The presented data shows that the optical transmission of the experimental crystals at room temperature is 46.10 % at a wavenumber of 943 cm\(^{-1}\).
which corresponds to a wavelength of 10.6 μm. Transmission is decreasing while temperature is growing. At a temperature of 60 °C the transmission at 10.6 μm is 43.10 %.

The transmission at room temperature varies only slightly with the increase of the sample resistivity to the 7 Ω·cm due to decrease of Sb amount in the crystal. At the same time, the transmission decreases to 42.80 % at an elevated temperature of 60 °C, i.e. it becomes significantly lower than for a sample with resistivity of 3 Ω·cm. In this connection, studies of crystals with a resistivity of equal to or greater than 7 Ω·cm were not carried out.

The IR absorption coefficients of the experimental crystals with resistivity of 3 Ω·cm were calculated according to equation (2) using the experimental data shown in figure 1. Their values were 0.015 and 0.065 at room temperature and at 60 °C, correspondingly.

![Figure 1. IR spectra of Sb-doped germanium crystal with a resistivity of 3 Ω·cm. 1 – 20 °C; 2 – 60 °C.](image1)

![Figure 2. Absorption coefficient of single crystals with the net carrier concentrations in the raw material \(n_{net} \leq 10^{12} \text{ cm}^{-3}\) (1 and 3) and \(\sim 10^{13} \text{ cm}^{-3}\) (2 and 4), as a function of the resistivity at 25 °C (1 and 2) and 60 °C (3 and 4).](image2)

The results of experiments performed in this study correlate with the known data reported in the works [8-9]. However, it was reported that the decrease of ρ below 3 Ω·cm leads to a sharp decrease of transmission both at room temperature and at 60 °C [8-9]. For example, the values of \(\alpha\) for crystals with resistivity of 1.5 Ω·cm at temperatures 25 and 60 °C are 0.045 and 0.075 cm⁻¹, respectively [8-9]. The investigation results of the optical properties of SB-doped germanium single crystals with ρ values from 1.5 to 5.0 Ω·cm are demonstrated in Table 1. It could be seen that results for the crystals with ρ values less 3.0 Ω·cm are different from data reported in the works [8-9].

| Resistivity at 25 °C, Ω·cm | Transmission, % at 10.6 μm | Absorption coefficient, cm⁻¹ at 25 °C | Transmission, % at 10.6 μm | Absorption coefficient, cm⁻¹ at 60 °C |
|---------------------------|--------------------------|---------------------------------|--------------------------|---------------------------------|
| 1.5                       | 45.60                    | 0.024                           | 43.60                    | 0.056                           |
| 2.0                       | 46.00                    | 0.017                           | 43.30                    | 0.062                           |
| 2.5                       | 46.00                    | 0.017                           | 43.10                    | 0.065                           |
| 3.0                       | 46.10                    | 0.015                           | 43.10                    | 0.065                           |
| 5.0                       | 46.10                    | 0.015                           | 43.10                    | 0.065                           |
According to the data (Table 1), the absorption coefficient for crystals with resistivity of 1.5 $\Omega\cdot cm$ at room temperature and at 60 °C is 0.024 and 0.056 cm$^{-1}$, respectively, which is much lower than reported in the works [8-9].

The discrepancy between the experimental data and the results of [8-9] can be explained as follows. The background acceptor impurities concentration ($N_a$) in a single crystal is not known in advance and, first of all, depends on the efficiency of raw material refining that is used for growing. The amount of the compensating donor additive ($N_d$) is chosen experimentally for obtaining the crystal with $n$-type conductivity and desired resistivity. The value of $\rho$ can be the same for a different total impurities content $N_{ad} = (N_d + N_a)$. At the same time, the absorption coefficient $\alpha_{ad}$ in the equation (1) depends on the total impurity concentration. Obviously, a lower absorption should correspond to a lower content of impurities in the raw material at the same value of the electrical resistivity.

In this case, the zone-refined germanium with a total background impurity content of ~ 3.0 ppm was used as raw material for growing the crystals. The content of the main impurities is given in Table 2.

| Element | ppm   | Element | ppm   | Element | ppm   |
|---------|-------|---------|-------|---------|-------|
| H       | < 0.03| Zn      | < 0.03| Pr      | < 0.02|
| Li      | < 0.0006| Ga      | < 0.04| Nd      | < 0.05|
| Be      | < 0.001| Ge      | rest  | Sm      | < 0.10|
| B       | < 0.002| As      | < 0.04| Eu      | < 0.04|
| C       | 0.3   | Se      | < 0.02| Gd      | < 0.20|
| N       | 1     | Br      | < 0.06| Tb      | < 0.03|
| O       | 1     | Rb      | < 0.03| Dy      | < 0.10|
| F       | < 0.05| Sr      | < 0.02| Ho      | < 0.03|
| Na      | < 0.01| Y       | < 0.03| Er      | < 0.04|
| Mg      | < 0.02| Zr      | < 0.05| Tm      | < 0.03|
| Al      | 0.02  | Nb      | < 0.10| Yb      | < 0.10|
| Si      | 0.04  | Mo      | < 0.04| Lu      | < 0.05|
| P       | < 0.01| Ru      | < 0.08| Hf      | < 0.10|
| S       | 0.02  | Rh      | < 0.04| Ta      | –      |
| Cl      | –     | Pd      | < 0.08| W       | < 0.20|
| K       | < 0.05| Ag      | < 0.05| Re      | < 0.10|
| Ca      | 0.06  | Cd      | < 0.20| Os      | < 0.20|
| Sc      | < 0.007| In     | < 0.03| Ir      | < 0.10|
| Ti      | < 0.009| Sn     | < 0.10| Pt      | < 0.20|
| V       | < 0.009| Sb     | < 0.05| Au      | < 0.10|
| Cr      | < 0.006| Te     | < 0.10| Hg      | < 0.30|
| Mn      | < 0.008| I      | < 0.05| Tl      | < 0.05|
| Fe      | 0.03  | Cs      | < 0.05| Pb      | < 0.10|

The net carrier concentration ($n_{net} = n_d - n_a$) of the order of $10^{13}$ cm$^{-3}$ corresponds to a given content of background impurities.

It was determined (Table 1) that $\alpha$ is less for a crystal with resistivity of 1.5 $\Omega\cdot cm$ than for a crystal with $\rho$ equal to 3 $\Omega\cdot cm$ at an elevated temperature and the values of $\alpha$ are 0.056 and 0.065 cm$^{-1}$, respectively. The comparison of the values of $\alpha$ shows a higher thermal stability of crystals with resistivity of 1.5 $\Omega\cdot cm$ which probably corresponds to a higher content of Sb donor impurity which participates in the compensation of thermally generated intrinsic holes. On the other hand, a decrease in the optical transmission at room temperature to 45.60 % ($\alpha = 0.024$ cm$^{-1}$) is observed for crystals with a minimum resistivity, as a consequence of an increase in absorption on impurity atoms $N_{ad}$. For this reason no studies were carried out at lower values of samples resistivity.
Experimental Sb-doped crystals obtained from additionally zone-refined germanium were studied. The net carrier concentration values $n_{\text{net}} \leq 10^{12}$ cm$^{-3}$ were achieved during refining which indicates a lower background of impurity level.

The comparison of the optical properties of experimental germanium crystals with different background impurities contents is shown in figure 2.

It was found that in the range of resistivity from 1.5 to 5 Ω·cm the IR absorption decreases at room temperature with increasing germanium refining efficiency (the shaded region). The properties of samples with different background impurities contents basically do not differ at elevated temperature, probably due to the relatively low concentration of Sb, necessary for the compensation of acceptor impurities in crystals with increased purity. In this way, the purification efficiency does not affect the thermal stability of optical properties.

The decrease of the optical properties of Sb-doped germanium single crystals at elevated temperature is reasoned by the physical nature of Ge and determined by its small band gap width (0.72 eV at absolute zero temperature) because the absorption at thermally generated holes predominates in IR transparency range [3-4, 6].

Hence, one of the ways to improve the temperature stability of the operating characteristics of germanium-based IR optics is to make the band gap of the semiconductor material wider by adding an isovalent element – silicon. The band-gap width of the Ge-Si solid solution increases from 0.72 (Ge) to 1.2 eV (Si) at absolute zero.

It is known that single crystals of Ge-Si solid solution are used in micro- and optoelectronics. They are used in solar cells, photodetectors, X-ray and neutron monochromators, gamma detectors, thermoresistors and high-temperature thermoelectric generators manufacturing. At the same time, the data on the effect of Si additives on the thermal behavior of the optical properties of germanium is limited and mostly has a qualitative nature [11-12].

In this connection, the effect of silicon additions in amount of 0.2 to 0.8 at. % on the optical properties of Sb-doped germanium single crystals [13] was studied.

The boundaries of the concentration ranges of silicon are determined by the fact that there is no positive effect at lower values, and at concentrations exceeding these limits, the structural perfection of single crystals deteriorates because of the large difference between the ionic radii of germanium and silicon [13].

The obtained results in analyzing the optical characteristics of the experimental samples at room temperature and under heating to 60 °C are presented in Table 3.

| Table 3. Optical properties of Sb-doped Ge-Si solid solution single crystals |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| No. | Si content, at.% | Resistivity, Ω·cm | Temperature 25 °C | | Temperature 60 °C | |
| | | Transmission, % | Absorption coefficient, cm$^{-1}$ | Transmission, % | Absorption coefficient, cm$^{-1}$ |
| 1 | 0.0 | 3.0 | 46.10 | 0.015 | 43.10 | 0.065 |
| 2 | 0.2 | 3.0 | 46.10 | 0.015 | 43.30 | 0.062 |
| 3 | 0.3 | 3.0 | 46.20 | 0.013 | 43.50 | 0.058 |
| 4 | 0.8 | 2.0 | 45.60 | 0.024 | 43.80 | 0.053 |
| 5 | 0.6 | 2.0 | 45.40 | 0.027 | 43.70 | 0.054 |
| 6 | 0.6 | 3.0 | 46.20 | 0.013 | 43.60 | 0.056 |

It was found that the optical transmission of a Sb-doped Ge-Si crystals with a silicon content of 0.6 at % and a resistivity of 3 Ω·cm is 46.20 % at room temperature. This value of $T$ corresponds to absorption coefficient of 0.013 cm$^{-1}$. As the temperature rises to 60 °C, the transmittance decreases to 43.55 % and the absorption coefficient increases to 0.057 cm$^{-1}$ accordingly. The value of $\alpha$ at 60 °C is 0.008 cm$^{-1}$.
less than the absorption coefficient of the crystal with resistivity of 3 Ω·cm, which contains no silicon additions.

For the samples with a resistivity of 2 Ω·cm at a silicon content of 0.6 at.% the absorption coefficient at high temperature decreases even more - up to 0.054 cm⁻¹. At the same time, as ρ decreases from 3 to 2 Ω·cm, the optical transmittance of the crystal at room temperature decreases from 46.20 to 45.4 %. The minimum measured absorption coefficient corresponds to the upper limit of the range of silicon concentrations under study. For the sample with resistivity of 2 Ω·cm and 0.8 at.% Si, the value of α is 0.053 cm⁻¹.

4. Conclusion
It was experimentally proved that Sb-doped germanium crystals in the range of resistivity from 1.5 to 3 Ω·cm have the maximum thermal stability of optical properties. The absorption coefficient at a wavelength of 10.6 μm increases from 0.015 to 0.065 cm⁻¹ in Sb-doped germanium single crystals with resistivity of 3 Ω·cm with an increase in temperature up to 60 °C. It was established that the background impurities concentration decrease does not affect the thermal stability of the crystals optical properties. The thermal stability increases with the addition of silicon. The optical absorption coefficient decreases from 0.065 to 0.057 cm⁻¹ at 60 °C with the increase of the silicon concentration to 0.6 at. %.

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