ISSN 1063-7826, Semiconductors, 2018, Vol. 52, No. 2, pp. 264–267. © Pleiades Publishing, Ltd., 2018.
Original Russian Text © A.F. Shimanskii, T.O. Pavlyuk, S.A. Kopytkova, R.A. Filatov, A.N. Gorodishcheva, 2018, published in Fizika i Tekhnika Poluprovodnikov, 2018, Vol. 52, No. 2, pp. 276–279.

FABRICATION, TREATMENT, AND TESTING OF MATERIALS AND STRUCTURES

Effect of the Addition of Silicon on the Properties of Germanium Single Crystals for IR Optics

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Submitted March 13, 2017; accepted for publication March 15, 2017

Abstract—Homogeneous Sb-doped single crystals of Ge–Si solid solutions are grown with a silicon content of 0.2 to 0.8 at %. The optical absorption of single crystals with a resistivity of (2–3) Ω cm is studied by IR Fourier spectroscopy at a wavelength of 10.6 μm in the temperature range from 25 to 60°C. It is found that the introduction of silicon into antimony-doped germanium improves the temperature stability of the optical properties of the crystals.

DOI: 10.1134/S1063782618020161

1. INTRODUCTION

The first publications concerned with the optical properties of germanium appeared in the 1970s [1, 2]. The patent [3] proposed the use of *n*-type germanium crystals as lenses for the infrared (IR) spectral range. At present, Sb-doped germanium is the main material serving as the optical medium in different devices operating in the IR spectral range from 3 to 12 μm [4, 5]. The given material with a resistivity of 3 to 40 Ω cm and dislocation density of $<10^4$ cm^{-2} is highly transparent at room temperature, which varies from 46.1 to 45.2% near the transmission-band edge at a wavelength of 10.6 μm, depending on the resistivity of the crystal. The corresponding values of the absorption coefficient α are in the range from 0.015 to 0.030 cm^{-1} [1, 2, 6].

It was noted in [3, 7] that the main disadvantage of optical germanium is that the transmittance in the transparency range decreases and the absorption coefficient increases with increasing temperature. For example, the absorption coefficient increases from 0.015 to 0.1 cm^{-1} as the temperature is raised from room temperature to 77°C for crystals with a resistivity of 3 Ω cm, which have the highest temperature stability. At 60°C, α is ~0.065 cm^{-1}, which corresponds to the data reported in modern sources [8, 9].

The decrease in transparency is due to the physical nature of germanium and is determined by its small band-gap width (0.72 eV at absolute zero temperature). In the IR transparency range of Ge, absorption at free thermally generated carriers, which are mostly holes, is predominant. [3, 10, 11].

One of the ways to improve the temperature stability of the operating characteristics of germanium-based IR optics is by making wider the band gap of the semiconductor material via the introduction of an isovalent element, i.e., silicon, into Ge. The band-gap width in the Ge–Si system increases from 0.72 to 1.2 eV at absolute zero [12].

It is known that single crystals of Ge–Si solid solutions are used in micro- and optoelectronics, they are used to fabricate solar cells, photodetectors, X-ray and neutron monochromators, γ-detectors, thermal resistors, and high-temperature thermoelectric generators. At the same time, data on the influence exerted by the addition of Si on the temperature behavior of the optical properties of germanium are scarce, being mostly of a qualitative nature [12, 13].

Practical applications require Ge–Si crystals with a low dislocation density, but growth of these crystals is a complex task because the constituents have significantly different lattice constants and melting points. A method for improving the crystal quality of single crystals of solid solutions in the germanium–silicon system was suggested in [14]. The problem can be solved by continuous replenishment of the germanium melt with silicon via the dissolution of Si rods mounted in a special holder parallel to the growth axis. The rods start to dissolve only after the germanium crystal is nucleated and reaches a prescribed diameter upon their being brought in contact with the melt surface.

In [15], we suggested a way to improve the temperature stability of the optical properties of optical germanium single crystals by introducing into the ini-

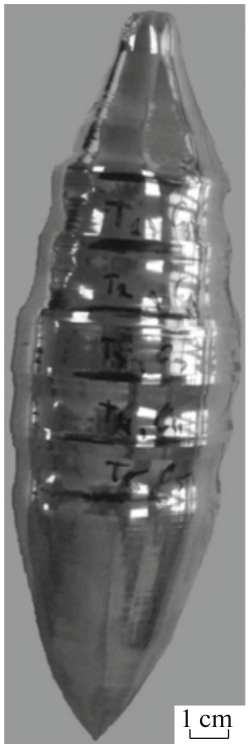

Fig. 1. Ge–Si crystal with a Si content of 0.6–0.8 at %.

tial charge silicon and additionally tellurium, together with the main doping additive, tellurium. The maximum effect of doping is observed in crystals with a resistivity of 3 Ω cm. In the case of triple doping for crystals with 0.05 to 0.15 at % silicon and ~5 × 10^{13} cm^{-3} tellurium concentration, an optical absorption coefficient at a wavelength of 10.6 μm and 60°C has values of 0.060 to 0.058 cm^{-1}, which is smaller than the corresponding value for single crystals doped with only antimony (0.065 cm^{-1}).

The boundaries of the concentration ranges of silicon and tellurium are determined by the fact that there is no positive effect at smaller values, whereas at concentrations exceeding these limits, the crystal quality of single crystals deteriorates because of the pronounced difference between the ionic radii of germanium and the doping component, which refers to a greater extent to tellurium. Moreover, the high volatility and toxicity of tellurium create additional technological difficulties in the growth of single crystals. Therefore, the present study is aimed at improving the temperature stability of the optical properties of crystals by raising their content of silicon and retaining single-crystallinity by excluding tellurium from among the doping additives.

The goal of our study is to examine the effect of silicon added in amounts exceeding 0.15 at % on the optical properties of antimony-doped single crystals of germanium.

2. EXPERIMENTAL

Single crystals of Ge–Si solid solutions were grown by the Czochralski method from a quartz crucible using a Redmet installation in an atmosphere of argon under an excess pressure of 0.02 MPa. The charge mass of GPZ-1 zone-refined germanium (germanium polycrystalline zone-refined) was 4 kg, and the diameter of the resulting ingots was 40–60 mm. The crystallographic growth direction was [111], the crucible rotation speed was 4–6 rpm, and the rotation rate and ascent speed of the seed were 20 rpm and 0.1–0.5 mm/min, respectively. The main doping additive (antimony) was introduced into the initial charge as a Ge–Sb alloy. When silicon was introduced into the charge in the necessary amount calculated from its prescribed content in the crystal (>0.15 at %) and from the effective distribution coefficient [16], the single-crystallinity of the resulting material was violated. The structural quality of the crystals was raised by using the method of gradual saturation of the melt, with silicon introduced by the technique suggested in [14].

The crystals were used to fabricate polished samples in the form of 1.0-cm-thick plane-parallel plates serving to determine the optical characteristics. The optical transmission spectrum was recorded at wavelengths in the range from 2.5 to 16.6 μm (wave numbers 4000–600 cm^{-1}) using a SPECTRUM BXII IR Fourier spectrometer. The accuracy in determining the optical transmittance was ±0.1%. Measurements at temperatures raised to 60°C were performed with a heating attachment that provided stable thermostating of the sample with an accuracy of ±0.1°C.

The resulting spectra were used to find the optical transmittance T at a wavelength of 10.6 μm, and the absorption coefficient was calculated by the formula

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

where t is the thickness of the sample under study; α is the absorption coefficient; and r is the reflectance.

3. RESULTS AND DISCUSSION

Homogeneous single crystals of Ge–Si solid solutions with a silicon content of 0.2 to 0.8 at % were grown. The crystals were doped with antimony to a resistivity of 2–3 Ω cm. A photograph of a crystal containing 0.6–0.8 at % Si is shown in Fig. 1.

The dislocation density in the experimental crystals with a Si content of 0.2 to 0.8 at % is ~5 × 10^3 cm^{-2}. With the fraction of silicon increasing to 1.5 at %, the dislocation density sharply grows. A sector structure and a microsegregation inhomogeneity are formed in ingots containing 2.0 to 2.5 at % silicon, as shown in Fig. 2a.

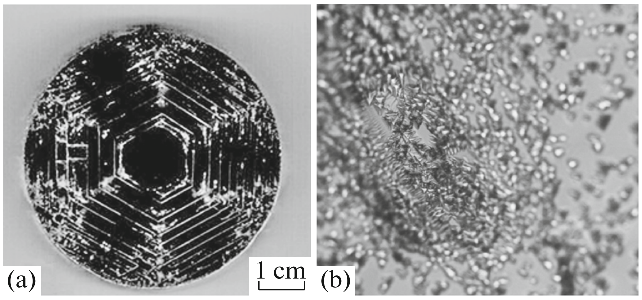

Fig. 2. Microstructure of ingots with a silicon content of (a) 2.5 and (b) 3.0 at %, ×450 magnification.

As the content of silicon is raised to 3.0 at %, there appear incoherent heterogeneous inclusions and the single-crystallinity of the ingot is violated (Fig. 2b).

Polished samples for optical transmission measurements were fabricated from homogeneous single crystals with a silicon content of 0.2 to 0.8 at %.

The results obtained in analyzing the optical characteristics of the experimental samples at the silicon concentrations under study at room temperature and under heating to 60°C are presented in Fig. 3 and Table 1.

Figure 3 shows the transmission spectra of an antimony-doped Ge–Si crystal with a silicon content of 0.6 at % and a resistivity of 3 Ω cm.

It was found that the optical transmittance of the experimental crystal is 46.20% at a wave number of 943 cm^{-1}, which corresponds to a wavelength of 10.6 μm (Fig. 3). To this value of T corresponds an absorption coefficient of 0.013 cm^{-1}. As the temperature is raised from room temperature to 60°C, the transmittance decreases to 43.55% (Fig. 3), and, accordingly, the absorption coefficient increases to 0.057 cm^{-1}. The value of α at 60°C is 0.008 cm^{-1} smaller than the absorption coefficient of a crystal with a resistivity of 3 Ω cm, which contains no silicon additive.

For the samples with a resistivity of 2 Ω cm at a silicon content of 0.6 at %, the absorption coefficient at

Table 1. Optical characteristics of Ge–Si single crystals at a wavelength of 10.6 μm

Si content, at %	Resistivity, Ω cm	25°C		60°C	
		T, %	α, cm^{-1}	T, %	α, cm^{-1}
0.0	3.0	46.10	0.015	43.10	0.065
0.2	3.0	46.10	0.015	43.35	0.060
0.3	3.0	46.20	0.013	43.50	0.058
0.8	2.0	45.60	0.024	43.80	0.053
0.6	2.0	45.40	0.027	43.70	0.054
0.6	3.0	46.20	0.013	43.55	0.057

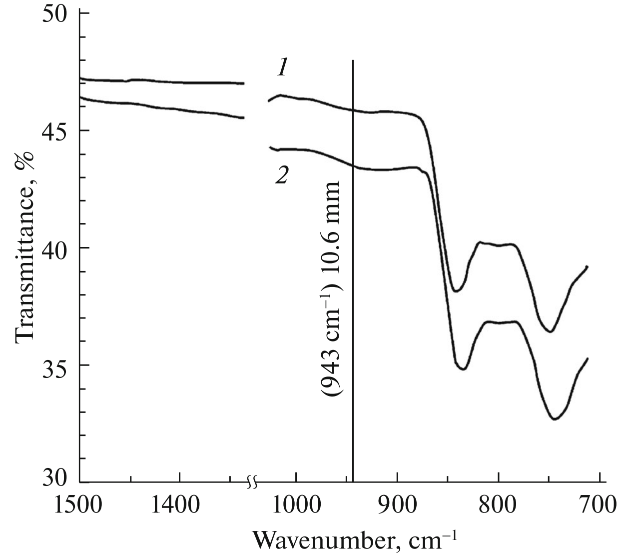

Fig. 3. IR transmission spectra of an antimony doped Ge–Si crystal with a silicon content of 0.6 at % and a resistivity of 3 Ω cm at wave numbers in the range from 1500 to 700 cm^{-1} at (*1*) 25 and (*2*) 60°C.

high temperatures decreases to an even greater extent to 0.054 cm^{-1} (see Table 1). At the same time, as the resistivity decreases from 3 to 2 Ω cm, the optical transmittance of the crystal at room temperature decreases from 46.20 to 45.4%, which corresponds to the data reported in [1, 6, 8, 9] and probably results from an increase in the impurity absorption, caused by the increasing concentration of antimony. The minimum measured absorption coefficient corresponds to the upper limit of the range of silicon concentrations under study. For the sample with a resistivity of 2 Ω cm and 0.8 at % Si, α is 0.053 cm^{-1}.

4. CONCLUSIONS

As the temperature is raised from room temperature to 60°C, the absorption coefficient at 10.6 μm of antimony-doped germanium single crystals with a resistivity of 3 Ω cm increases from 0.015 to 0.065 cm^{-1}. It was confirmed experimentally that the introduction of silicon improves the temperature stability of the optical characteristics of the crystals. As the content of silicon is raised to 0.6%, the optical absorption coefficient at 60°C decreases from 0.065 to 0.057 cm^{-1}.

ACKNOWLEDGMENTS

The study was financially supported by the Russian Foundation for Basic Research, Government of Krasnoyarskii krai, and Krasnoyarskii krai foundation for the support of scientific and scientific-technological activities under project no. 16-43-240719.

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Translated by M. Tagirdzhanov