SPECTROSCOPY OF CONDENSED STATES

Optical Properties of Single-Crystal Germanium in the THz Range

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Abstract—The transmission of intrinsic, antimony-doped, and gallium-doped Ge single crystals in the THz spectral range have been experimentally investigated. It is shown that the attenuation coefficient of intrinsic germanium in the range of $160-220 \,\mu\text{m}$ is at a level of $\sim 0.5 \,\text{cm}^{-1}$, a value comparable with that for silicon. The free-carrier absorption cross sections of silicon and germanium are significantly different, which may be caused by the difference in the mechanisms of carrier—phonon interaction in these materials.

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INTRODUCTION

It is generally accepted to refer to the long-wavelength part of electromagnetic spectrum (~3 mm- $30 \,\mu\text{m}, 3-300 \,\text{cm}^{-1}$) as "terahertz (THz) radiation" [1]. THz waves, unlike shorter wavelength radiation, can penetrate organic materials: skin, plastics, clothes, or paper. Low-energy photons do not cause any damage characteristic of ionizing radiations (e.g., X rays). For this reason, the possibility of replacing medical X-ray devices with devices based on THz sources is being actively investigated. Since THz radiation does not penetrate metals, it can be used for finished product quality control. It is also of great interest to use THz radiation in such applications as safety monitoring; packing control; characterization of semiconductors; analysis of chemical composition; biochemical studies; remote detection of explosive, poisoning, and narcotic substances; etc.

The THz spectral range has been investigated for about a century [1]. It is rather problematic to choose appropriate optical materials for this range. Generally, relatively inexpensive organic materials are used for low-intensity sources [2]. Their application in lasers is limited. Until recently, the THz range has barely been mastered in laser technology, although the possibility of designing a THz laser was demonstrated for the first time in 1970 [3]. Nevertheless, studies aimed at pumping THz media by a high-power CO₂ laser are being actively performed [4]. In this context, an urgent problem is to search for THz-transparent materials. Germanium is promising for such applications, because it is transparent both in the THz range and at the CO₂ laser wavelength [5]. It is applied in the IR technique [6, 7] as a material for optical parts of devices and instruments for various purposes. Examples are protective windows, lenses, and acoustooptic elements, which are applied in ground-, sea-, and air-based optical devices and in spacecraft design. Germanium is also used as a material for high-efficiency solar cells and detectors in ionizing radiation sensors.

Germanium and silicon have been investigated quite thoroughly due to their very wide use in electronics and IR optics. However, the application of germanium is limited to a great extent by the scarcity of this material in nature. Generally, designers try to use Ge in cases in which its advantage over silicon is doubtless. These are primarily IR optics applications (atmospheric window of $8-14 \mu m$), since the silicon absorption is high in the IR range. In the THz range, silicon was initially on such solid grounds that the potential of germanium has barely been considered, although Ge properties in the THz range were investigated previously [8, 9]. Germanium is of interest as a THz material for active elements of acoustooptic devices [10, 11]. High reflection losses can be compensated for by creating periodic relief structures (with a high degree of regularity and a period smaller than the radiation wavelength) on the surface [12]. In addition, germanium can be used in multispectral imaging devices operating in the IR/THz range and in THz lasers pumped by a CO_2 laser. In this paper, we report the results of a detailed study of the optical transmission of pure and doped (with impurities of different conductivity types) germanium in the THz spectral range.



Fig. 1. Optical transmission of (1) 1-mm-thick undoped Ge single crystals, (2) 10-mm-thick undoped Ge single crystals, and (3-6) 10-mm-thick antimony-doped Ge single crystals with resistivities of (3) 46, (4) 20, (5) 5, and (6) 2.7 Ω cm (spectra 3-6 were obtained using 10-mm-thick samples).

EXPERIMENTAL TECHNIQUE

Experiments were performed with Bruker Vertex 70 and Bruker IFS 66v/s Fourier spectrometers in the spectral range of $1.3-670 \ \mu m$ and with a Tera K8 Menlo Systems spectrometer in the range of $100-1500 \ \mu m$.

Germanium was grown from melt by the Czochralski method in the $\langle 111 \rangle$ crystallographic direction. We investigated single crystals grown from undoped melt and single crystals doped with antimony and gallium. The influence of conductivity on transmission was studied using doped crystals. As was shown in [11], surface treatment affects the THz transmission; therefore, the experimental samples (39 mm in diameter and 10 mm thick) were polished with tolerances N < 1and $\Delta N < 0.5$. The actual transmittance values were determined with a photometric accuracy of 0.1%.

Attenuation coefficient α was calculated with allowance for multiple reflections from the well-known formula [13, 14]

$$T = \frac{\left(1-R\right)^2 e^{\alpha h}}{e^{2\alpha h} - R^2},$$

where T and R are, respectively, the transmittance and reflectance and h is the sample thickness.

The dependence of germanium refractive index *n* on wavelength λ in the spectral range under consideration was obtained using the best approximation polynomial (λ in μ m):

$$n(\lambda) = 4 + 0.001106337 - 0.00314503/\lambda$$

+ 0.492812/\lambda² - 0.601906/\lambda³ + 0.982897/\lambda⁴.



Fig. 2. Optical transmission of 10-mm-thick galliumdoped Ge single crystals with resistivities of (1) 16 and (2) 4.2 Ω cm.

EXPERIMENTAL RESULTS

The spectral dependences for single crystals with different resistivities doped with antimony and gallium are presented in Figs. 1 and 2.

Figure 3 shows the attenuation coefficient spectra for the most characteristic germanium samples in the wavelength range of $60-1500 \mu m$. One can clearly see that the loss decreases with an increase in the wavelength, reaching a value of ~ 0.5 cm^{-1} (in the range of $160-220 \mu m$) in intrinsic germanium, and then monotonically increases. Note that the loss increases with a decrease in the crystal resistivity.

In the IR spectral range *n*-Ge crystals have a higher transmittance, which is explained by the lower absorption cross section of electrons in comparison with that of holes [6, 15–17]. In the vicinity of 10 μ m, the absorption is minimum for the *n*-type material with a



Fig. 3. Attenuation coefficients of (1) undoped Ge single crystals and (2-5) antimony-doped Ge single crystals with resistivities of (2) 46, (3) 20, (4) 5, and (5) 2.7 Ω cm.

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resistivity of $5-10 \Omega$ cm rather than for intrinsic crystals [6, 15].

As this experiment showed, the absorption of doped crystals significantly increases in the THz range, where maximum transmission is observed for undoped germanium (Fig. 3) with a resistivity of 47 Ω cm. An increase in the concentration of impurities (both electron and hole) leads to an increase in the absorption.

A comparison of the optical transmission of silicon and germanium [18] in the wavelength range above 25 um shows that the transmission of silicon is high (about 55%) in comparison with germanium. Primarily, this is due to the difference in the Fresnel reflectances (the refractive indices of Ge and Si in the IR region are, respectively, ~ 4.0 and ~ 3.42). Maximum values were observed for silicon crystals grown by floating zone melting, with a resistivity of several $k\Omega$ cm. One can suggest that the absorption in the spectral range under consideration occurs mainly on free carriers (both intrinsic and impurity), the concentrations of which in pure silicon and germanium significantly differ (47 Ω cm, E = 0.67 eV, and $n = 2.5 \times 10^{13}$ cm⁻³ for intrinsic Ge and 2 k Ω cm, E = 1.12 eV, and $n = 5 \times$ 10^{10} cm^{-3} for intrinsic Si).

Proceeding from these considerations, the THz absorption in germanium should be much higher than in silicon. However, a comparison of our results for germanium (Fig. 3b, $\lambda \sim 160-220 \mu m$) with the data on silicon reported in [19] shows that the attenuation coefficient is approximately the same for these materials: ~0.5 cm⁻¹. At the same time (Figs. 1, 2), the transmission spectra indicate that the range of 160-220 μm corresponds to the upper limit of multiphonon absorption region, and one would expect lower absorption at longer wavelengths. Nevertheless, one can observe a rise in loss in this region, which is caused by another mechanism: free-carrier absorption, which is known to be enhanced with an increase in wavelength.

In the near- and mid-IR ranges, Ge single crystals of different conductivity types exhibit a significant distinction in absorption. According to different sources, the ratio of the electron and hole absorption cross sections at a wavelength of 10.6 μ m is ~16–100. For this reason, minimum absorption in the vicinity of 10 µm is observed for crystals doped with a donor impurity rather than for intrinsic crystals. However, the electron and hole absorption cross sections in the THz region are almost equal, as can clearly be seen in Fig. 1. There is hardly any influence of resistivity on the transmission of our antimony-doped samples in the range of $25-50 \,\mu\text{m}$, whereas this influence is pronounced in the range of 120-220 µm. Nevertheless, the THz absorption in gallium-doped Ge samples is somewhat higher than in antimony-doped ones. At similar impurity concentrations, $(2.5-3.0) \times 10^{14} \text{ cm}^{-1}$ (this concentration range corresponds to crystals with

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resistivities of 5 (antimony) and 16 Ω cm (gallium)), the transmittance of gallium-doped crystals is ~2.5% lower, whereas the attenuation coefficient is higher by a factor of 1.45 (for a wavelength of 120 μ m).

CONCLUSIONS

The results of this study indicate that the free-carrier absorption cross sections for silicon and germanium significantly differ, which may be due to the difference in the mechanisms of carrier—phonon interaction.

In contrast to the IR range, where minimum absorption (~0.02 cm⁻¹ at $\lambda = 10.6 \,\mu$ m) is exhibited by *n*-type crystals with a resistivity of 5–10 Ω cm, minimum THz loss (~0.5 cm⁻¹) is observed in intrinsic crystals.

In the range of $160-220 \,\mu\text{m}$, the attenuation coefficient of germanium is ~0.5 cm⁻¹, a value comparable with that for silicon. The Fresnel reflection loss can be compensated for to a great extent by forming periodic relief structures (with a high degree of regularity and a period smaller than the radiation wavelength) on the surface. Therefore, optical elements made of intrinsic single-crystal germanium can be used in the THz region—specifically, in the range of 120–300 μm .

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