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Special Properties of Phonon Absorption of Germanium at the Edge of Transparency Range.

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ABSTRACT

There were studied optical properties of pure and alloyed single crystals of germanium within the spectral range of 950-550 cm^{-1}. Influence of alloying admixtures and of oxygen concentration in germanium on location and form of phonon absorption peaks was demonstrated.
Keywords: phonon absorption, Germanium.

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INTRODUCTION

Single-crystal germanium is widely used in science and technology, at that most kinds of practical application require only those single crystals which have low foreign material content. Use of germanium as ionizing-radiation detectors, highly sensitive low-background IR detectors specifies the level of electroactive admixtures concentration in the material between 10^9 - 10^{10} cm^{-3}. Germanium for application in electronics, optics and acoustooptics is being intentionally alloyed, the crystals with the alloying electroactive admixture concentration of 10^{13} cm^{-3} and over are used for the mentioned applications [1, 2]. The elements of the III and the V groups of the Periodic System (low energy levels in the forbidden gap) as well as metals generating high impurity levels are used as electroactive admixtures. Moreover germanium always contains background electroneutral impurities such as oxygen, carbon, nitrogen and other admixtures from the materials of tooling, atmosphere and components of installation which enter hotmelt and further a crystal at time of growing single crystals. The concentration of such impurities is rather high and can reach, for example for oxygen 10^{17} cm^{-3} and higher. The level of oxygen contained in germanium has considerable influence on the following factors: it does not have direct effect on electric conductivity of a semiconductor but determines formation of dislocations, microdefects, termodonors and affects nonequilibrium charge carriers lifetime [3, 4]. Germanium absorption bands in the wavelength range of 12-17 µm are conditioned by interaction of light with phonons [5-6], the bands location and intensity are greatly dependent on the oxygen concentration value.

This work explored peculiarities of dependency of the transmission spectrum within the frequency range from 950 to 550 cm^{-1} for germanium crystals alloyed by cobalt, gallium, antimony, bismuth, aluminum and nickel; dislocation-free germanium alloyed by antimony was under examination. The work also studied dependency of the transmission spectrum on the germanium oxygen concentration.

EXPERIMENTAL PROCEDURE

The work describes the results of investigation of influence of impurities and isotopic composition on the transmission spectrum of single-crystal germanium in IR-region in the frequency range corresponding to the beginning of intensive radiation absorption by crystal latitude, i.e. 950-550 cm^{-1}. The investigations were performed by means of IR FT spectrometer Bruker VERTEX 70, spectral resolution capability made 0.5 cm^{-1}, and photometric accuracy made 0.1 %.

Single crystals alloyed by cobalt, gallium, antimony, bismuth, aluminum and nickel were subject to examination. Samples for the investigation were produced from single crystals grown from holtmelt by Czochralski method, zone-refined polycrystal germanium was used as a starting material. The concentration of electroactive impurities in the grown single crystals was determined on the basis of the specific resistance measurement at the polished end surfaces of the samples by the four-point probe method. Homogeneity of impurities distribution through the cross-section and along the height of the samples was within 5-10%. Average density of dislocations in crystals made $(0.5\text{-}1.2)\cdot 10^4$ cm^{-2}; besides, optical measurements were carried out for dislocation-free germanium (with antimony admixture).

The samples for investigation of the effect of the oxygen concentration on the phonon absorption spectrum were made from non-alloyed single crystals grown from hotmelt by Czochralski method under nitrogen atmosphere under the layer of flux B_2O_3 containing germanic oxide GeO_2 [4, 8]. The concentration of optically active oxygen was determined by intensity of oxygen absorption peak [4].
The investigation samples where shaped like polished parallel-sided plates with crystal-lattice orientation <111> and <100> with the diameter of 30-45 mm and the width of 10 mm.

Influence of impurities on optical transmission of germanium

Due to relatively high transmission within the range of 2.5 – 14.0 µm germanium is widely used in IR optics; it is mainly applied for the atmospheric transparence window of 8.0 – 14.0 µm however the phonon absorption bands present in this region considerably limit its practical use. Germanium is also used in semiconductor engineering for production of highly-sensitive detectors, photodetectors and other semiconductor devices and materials.

Ge alloying by the elements from the III-V groups of the Periodic System results in appearance of "small" energy levels approximating the boundaries of the zones with the energies of about 0.01 eV in the forbidden gap. Other impurities in germanium may be located both in proximity of the zones boundaries and deeply inside the forbidden gap thus creating "deep" energy levels. In this case the effect of deep energy centers on the semiconductor material properties is much more diversified as compared to small ones; presence of such levels have significant influence on charge carriers concentration and mobility, on conductivity and photoconductivity. Properties of alloyed germanium and admixtures used in this work [9-10] are given in Table 1.

Spectral dependencies of the investigated germanium single crystals are shown on Figure 1. According to the theoretical concepts of light absorption by crystal latitude of monoatomic semiconductors like germanium or silicone a multiphonon absorption of light connected both with optical (longitudinal (LO) and transverse (TO)) and with acoustic (by analogy - TO and LO) modes [6] is being observed, the spectrum contains lattice absorption peaks corresponding to the frequencies ν – 841, 749, 645 cm^{-1}.

The absolute transmission value matching germanium with the target admixture is first of all determined by a conduction type and the admixture concentration. The maximum transmission is demonstrated by single crystals alloyed by an admixture with an electronic conduction type which is consistent with the well-known concepts [11]. Run of the transmission curves representing incident frequency is almost concurrent for germanium alloyed by antimony and bismuth as well as for dislocation-free germanium (with antimony admixture). As it seen from the Figure the location of the absorption peaks is not influenced neither by the type or the concentration of an alloying admixture nor by the absolute spectral transmission value.

Table 1: Specifications of samples and properties of used admixtures

Admixture	Specific resistance, Ohm·cm	Conduction type	Admixture property Ionization energy, eV [9, 10]
Sb	5,5; 22, dislocation-free germanium (DFGe)	n	0.0096
Bi	7.0	n	0.01
Ga	15.5	p	0.01
Al	5.0	p	0.0102
Ni	24.5	combined	0.23 (acceptor level, from the valence band ceiling); 0.3 (acceptor level, from the conduction band bottom)
Co	30.0	p	0.09 (donor level, from the valence band bottom); 0.25 (acceptor level, from the valence band ceiling); 0.3 (acceptor level, from the conduction band bottom)

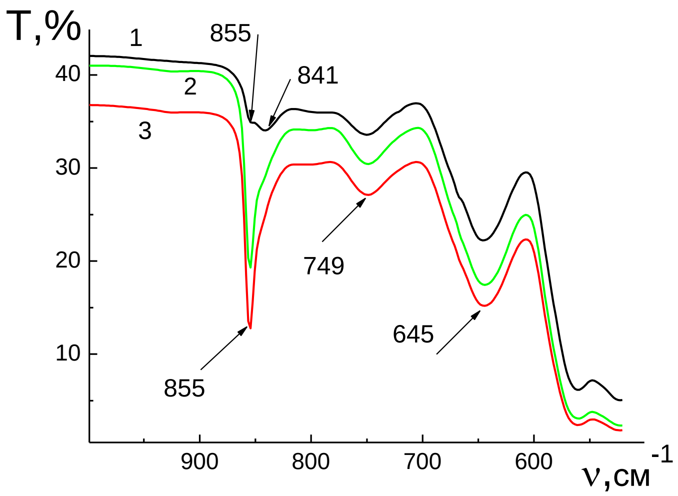

Figure 1: Alloyed germanium spectra (the maximum values of phonon absorption bands with indication of the corresponding wave numbers are shown with arrows)

Starting materials for growing germanium crystals (zone-refined polycrystal germanium) are produced by chloride technology which does not allow to ensure oxygen content in germanium less then (1-2)·10^{16} cm^{-3} [13]. Therefore oxygen is a residual impurity and its concentration in single crystals depends on the method of growing inclusive of the process atmosphere, furnace and tooling materials. As a rule, atoms of oxygen dissolved in germanium occupy interstitial positions and are an optically active admixture. Notwithstanding high dissolubility of oxygen in solid germanium (up to ~ 2.2·10^{18} cm^{-3} at phase transition temperature) the admixture does not result in increase of free charge carriers concentration and is electrically neutral.

Investigation of oxygen behavior in germanium provides for analysis of the processes of oscillation of the atoms of quasi-molecule Ge-O-Ge [3, 14, 15]. Quantum-mechanical calculations of oxygen oscillations [14] demonstrate presence of an absorption band within the range of frequencies of 843-849 cm^{-1}. Experimental studies evidence presence of principal oxygen absorption bands at 856 and 1264 cm^{-1} [15]; the band of 856 cm^{-1} is the most intensive and is associated with asymmetric oscillations of the triatomic molecule GeO_2 [3, 15]. In the work [16] antisymmetric oscillations in germanium single crystals were referred to the frequency of 865 cm^{-1}. The study of optical properties of dislocation-free germanium performed by the authors [17] stated that the absorption band of 841 cm^{-1} is conditioned by presence of oxygen in germanium. The authors of the work [18] found that oxygen absorption had an effect at the frequency of 843 cm^{-1} when the oxygen concentration in crystals made less then 10^{16} cm^{-3}, and then developed a hypothesis that depending on the oxygen content the "oxygen" absorption band could be within the range of 841-861 cm^{-1} [4].

The results of investigation of spectral transmission of germanium (Fig. 1) with various types and nature of admixtures demonstrate presence of the "oxygen" absorption band at the frequency of 841 cm^{-1}. All of the single crystals were grown in vacuum (~ (0.5-1)·10^{-4} mm of mercury) with use of graphite tooling which ensured the oxygen concentration less then 10^{15} cm^{-3}. Electrophysical properties of admixtures (Table 1) and their concentration have no effect on location of the maximum of the absorption band.

Table 2: Germanium single-crystals with known oxygen content

No.	Specific electrical resistivity, Ohm·cm	Conduction type	Oxygen content, cm^{-3}
1	43	p	5.0·10^{15}
1	42	p	5.0·10^{16}
3	30	p	1.0·10^{17}

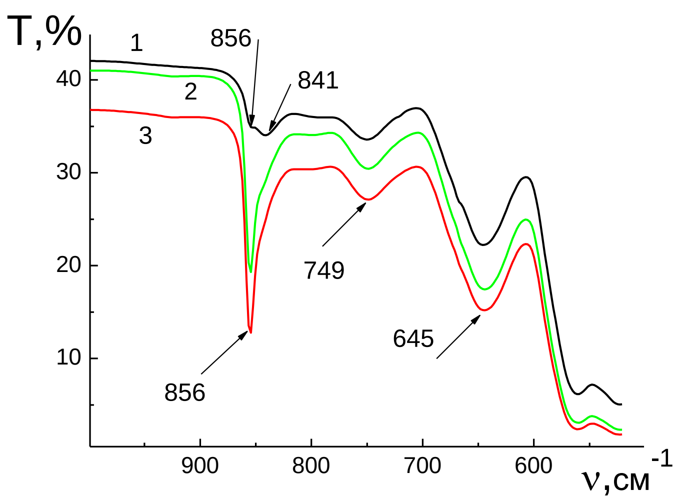

Figure 2: Spectra of oxygen containing single crystals of germanium (the maximum values of phonon absorption bands with indication of the corresponding wave numbers are shown with arrows)

Characteristics of the investigated single crystals of germanium with high content of oxygen and their spectral dependencies are given in Table 2 and on Figure 2 correspondingly. An intensive absorption peak amplitude of which grows with the oxygen concentration increase is clearly marked at the frequency of 856

cm^{-1}. The spectrum of Sample 1 which has higher oxygen concentration as compared to the samples grown in vacuum shows two peaks: at the frequency of 841 $см^{-1}$ typical for germanium with low oxygen concentration and at the frequency of 856 cm^{-1} – start of formation of the second peak typical for germanium with low oxygen concentration.

CONCLUSION

The content of optically active oxygen in germanium single crystals determines the location of the maximum of the corresponding lattice absorption band. For the low oxygen concentration typical for single crystals grown under vacuum (less then 10^{15} cm^{-3}) the absorption band corresponds to the frequency of 841 cm^{-1}. In case of germanium single crystals with the high oxygen content (10^{16}-10^{17} cm^{-3}) we can observe an intensive absorption band having the maximum at 856 cm^{-1}. Simultaneous presence of 2 absorption peaks in single crystals with the intermediate oxygen concentration was found out, the peaks maximum values correspond to the frequencies of 841 cm^{-1} and 856 cm^{-1}.

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