Conference Paper

Effect of Annealing on The Behavior of Oxygen Dissolved in Germanium and Optical Properties of Single Crystals

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Abstract

The annealing effect in the temperature range from 350 to 450 °C on the behavior of interstitial oxygen O_i dissolved in germanium and on optical properties of single crystals has been investigated by Fourier transformed infrared spectrometry. It was found that oxygen band maximum of 843 cm^{-1} shifted toward the 856 cm^{-1} with oxygen concentration increasing after annealing at the oxygen partial pressure ranged from 1 to 10^3 Pa. The annealing at lower P_{O_2} values led to the decrease of 843 cm^{-1} band intensity due to the formation of thermal donors (TD) on the basis of dissolved oxygen atoms O_i. It was established that TD formation and the decrease of unbound oxygen concentration affected optical properties of the crystals.

Keywords: germanium, single crystals, oxygen, IR-spectroscopy, optical properties, annealing, thermal donors

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1. Introduction

Germanium single crystals have extensive application in nanoelectronics, detector engineering, and IR optics. In photovoltaics germanium is used as a substrate material for solar cells GaInP/GaInAs/Ge type with the conversion efficiency up to ~ 39 % [1–5]. It requires low impurity dislocation-free Ge-crystals since dislocations and uncontrolled impurities can cause a mismatch between the lattice parameters of germanium and $A^{III}B^{V}$ compounds, impeding the growth of high-quality epitaxial layers on germanium [1, 3–4].

High carrier mobility in dislocation-free Ge promotes its application in the radiation-hardened power MOSFET transistors and other fast digital electronics of the space class [6]. Dislocations and foreign impurities limit the use of germanium in infrared optics, since they change the optical properties of germanium [5]. Recent studies have proved the oxygen to be one of the main impurities affecting structural perfection, electrical and optical properties of germanium single crystals, and operational characteristics of Ge-based electronics [7–17].

Oxygen atoms dissolved in germanium are located at interstitial positions O_i. This defect in the simplest model may be regarded as a nonlinear symmetric quasi-molecule Ge–O–Ge, with vibration modes ν_1, ν_2, and ν_3. It is the general practice to determine oxygen concentration in the crystals by the absorption peak at 856 cm^{-1} in the infrared spectra, which is identified with asymmetrical vibration mode ν_3 [7–9]. In the recent research [10–12] the oxygen peak at 856 cm^{-1} has been reported to have a "shoulder" at $\bar{\nu}$, that equals 843 cm^{-1}, which is also identified with O_i vibrations.

Oxygen is known to exist in atomic and bond states, e.g. in the form of precipitates GeO_x, formed either during crystal growth or due to decomposition of supersaturated solid solution of oxygen in the process of post-growth annealing and cooling. The oxygen content in precipitates can achieve 20 % of its total concentration. It is established that the annealing of Germanium at the temperatures from 350 to 450 °C leads to the formation of the precipitates with electric activity, named thermal donors (TD). The majority of modern TD models are based on the idea that these centers are complexes with an electrically active core and different bounded numbers of oxygen atoms [4, 13–16].

It should be noted that oxygen concentration in the crystals investigated in the studies [7–16] is typically ~10^{17} cm^3 or higher. Thus, germanium was oxygen enriched.

In this regard, the study aims to investigate germanium single crystals with lower oxygen concentration in the order of 10^{16} cm^{-3}, the annealing impact in the temperature range from 350 to 450 °C on the behavior of the oxygen, the form of its existence in germanium and the optical properties of single crystals depending on the oxygen partial pressure ranging from 10^{-3} to 10^3 Pa.

2. Methods

The studies were made on Sb-doped Ge single crystals with a donor concentration between $1.1{\cdot}10^{15}$and $7.0{\cdot}10^{14}$ cm^{-3}, corresponding to a specific electric resistivity in the range of 2 to 4 Ohm·cm. The material with dislocation content about ~10^4 cm^{-2} has absorption coefficient α of 0.15-0.20 cm^{-1} at the wavelength of 10.6 μm [4, 5].

Ge crystals were grown by the Czochralski method using a graphite crucible in argon atmosphere. Polished plane-parallel plates with the thickness of metricconverterProductID1 cm1 cm were prepared to study optical properties with Fourier transformed infrared spectrometry. The infrared measurements were performed in the 600-4000 cm^{-1} spectral range with SPECTRUM BXII spectrometer. The optical density measurement error was no more than ± 0,001.

The oxygen concentration $[O_i]$ was calculated from the measured amplitude of the absorption band at 843 cm^{-1} using the formula:

$$[O_i] = 1.05 \cdot 10^{17} \left(\frac{2.3D}{d}\right), \quad (1)$$

where *D* – is the optical density relative to the baseline; *d* – is the sample thickness; $1.05{\cdot}10^{17}$ cm^2 – is the calibration factor [4].

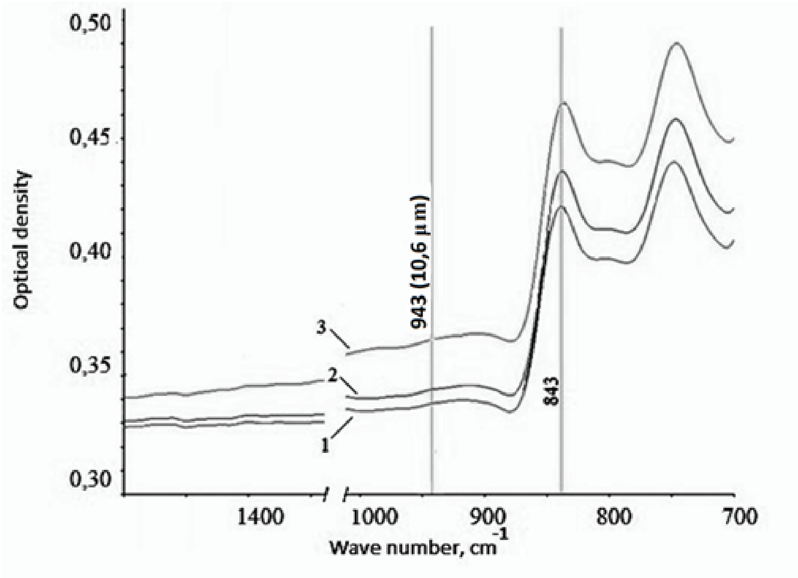

Figure 1: IR spectra of Sb-doped Ge single crystals with specific resistance of 3 Ωm×cm (1 – 23 °C; 2 – 40 °C; 3 – 60 °C).

The influence of isothermal annealing in gas with P_{O_2} ranging from 10^3 to 10^3 Pa on the optical properties of single crystals was determined by the optical density value and absorption coefficient α at a wavelength of 10.6 μm. For IR measurement with the temperature rising up to 60 °C the heat device ensuring a stable sample thermostating with accuracy ± 0.1 °C was used.

3. Results

Fig. 1 shows IR absorption spectra of Sb-doped Ge single crystals with specific electrical resistance of 3 Ohm·cm at room temperature and heated up to higher temperatures in the range of wave numbers from 600 to 1500 cm^{-1}.

Only one absorption peak 843 cm^{-1} was observed at the range of wave numbers from 800 cm^{-1} to 900 cm^{-1} (Fig. 2). We identify the peak as the "oxygen" band [10, 17]. The oxygen concentration in the germanium crystals under study was determined by the value of optical density in this band maximum as ~ $1.10 \cdot 10^{16}$ cm^3.

The oxygen band position in Ge IR spectrum is disputable. We can suggest considering the findings of the experiments in the studies [10-12, 17] that the absorption band position corresponding to the vibrational mode of O_i atoms can be 843 or 856 cm^{-1}, depending on their content in the crystal.

This hypothesis was confirmed by the results of the influence of diffusion annealing on optical properties of Ge crystals. The annealing was conducted in gas, containing residual oxygen with the partial pressure range from 1 to 10^3 Pa and in the temperature interval from 350 to 450 °C with an intermediate registration of infrared spectra data. Fig. 3 shows Ge IR spectra after annealing at $P_{O_2} \approx 10^3$Pa at temperature 400 °C. It was found that absorption intensity at wavelength 843 cm^{-1} increased after the four-hour period annealing with the oxygen concentration increase from ~$1.10 \cdot 10^{16}$ to ~$1.30 \cdot 10^{16}$

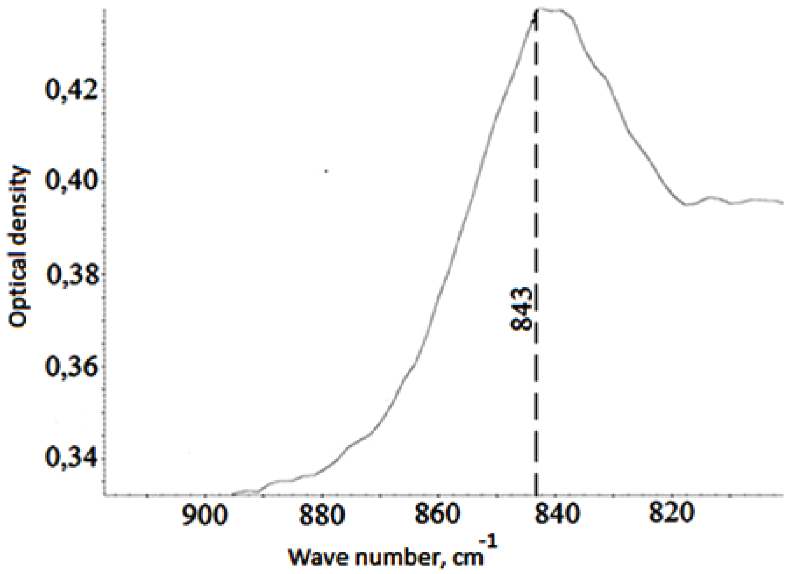

Figure 2: Oxygen band in the germanium IR spectrum.

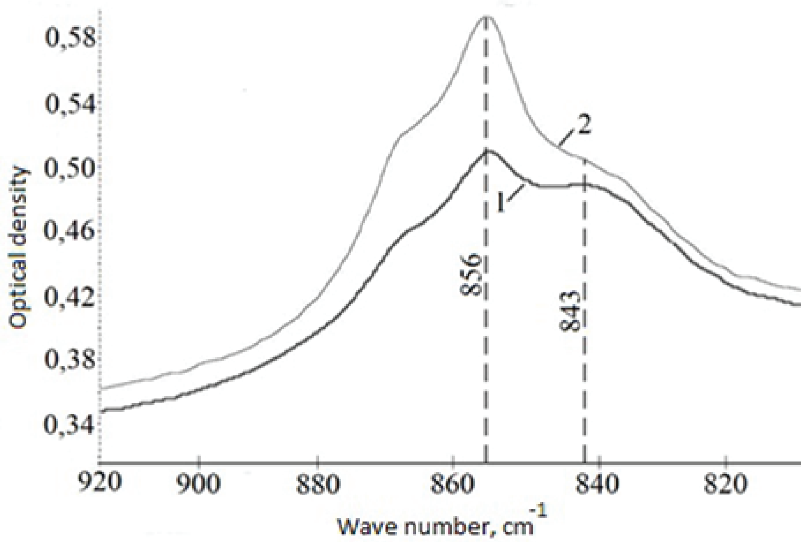

Figure 3: Ge IR spectra transformation in the wave number range 800-900 cm^{-1} induced by annealing at 400 °C at $P_{O_2} \approx 10^3$Pa (1-6 hrs; 2-8 hrs).

cm^{-3}. The six-hour or eight-hour period annealing leads to even greater increase of oxygen concentration in the crystal. It results in a new band at wavelength 856 cm^{-1} that corresponds to O$_i$ vibrations.

Therefore, annealing at 400 °C and partial pressure range from 1 to 10^3 Pa is responsible for the increase of oxygen concentration in Ge and a new absorption band appearancewith the increasing intensity at the wavelength856 cm^{-1}in addition to band 843 cm^{-1}.

The experiment has proved that annealing at a lower oxygen partial pressure of P_{O_2}< 1 Pa leads to the reduction of band intensity 843 cm^{-1} that corresponds to the

П/П	Electrical resistance, Ωm·cm	Before annealing				After annealing at 400°C and P_{O_2}≈10^{-3}Pa during 90 hrs	
		Optical Density	Absorption coefficient, cm^{-1}	Optical Density	Absorption coefficient, cm^{-1}	Optical Density	Absorption coefficient, cm^{-1}
		Temperature 20 °C		Temperature 60 °C		Temperature 60 °C	
1	2	0,339	0,020	0,364	0,062	0,359	0,054
2	2,5	0,339	0,020	0,366	0,066	0,364	0,062
3	3	0,337	0,017	0,365	0,065	0,360	0,056
4	3,5	0,336	0,015	0,370	0,073	0,361	0,057
5	4	0,334	0,010	0,366	0,067	0,362	0,059

Table 1: Effect of annealing on optical properties of Ge single crystals.

content decrease of O_i. The 90- hour period annealing at $P_{O_2} \approx 10^{-3}$ Pa and temperature 400 °C in Krypton (6N) leads to the oxygen band 843 cm^{-1}intensity reduction on 5 %.

The phenomenon observed in a similar way in papers [11, 16] can be explained by the formation of thermal donors (TD) based on dissolved oxygen in the germanium crystal lattice during annealing. Thus, the part of dispersed oxygen is bound in TD structure due to annealing. It was found that the germanium annealing at low oxygen partial pressure $\sim 10^{-3}$ Pa resulted in the change of optical characteristics of crystals, such as optical density and absorption coefficient.

The data in Fig. 1 show that the optical density of the sample with electrical resistance of 3 Ωm·cm at the room temperature and wavelength 10.6 μm is 0.337. When the temperature increases up to 60°C, the optical density increases to 0.365. *D* change matches the absorption coefficient increase from 0.017 to 0.065 cm^{-1}. This temperature destabilization of germanium optical properties impedes its application in IR optics at overheating to 45 °C.

Table 1 shows the optical properties of the samples annealed at temperature 400 °C and $P_{O_2} \approx 10^{-3}$ Pa during 90 hour-period. It was found that optical density of these samples at 60 °C decreases from 0.365 to 0.360 after annealing at low oxygen partial pressure and the absorption coefficient decreases from 0.066 to 0.056 cm^{-1}. On average the absorption coefficient of Ge single crystals at 60 °C decreases by 13 % for the samples with electrical resistance in the range from 2 to 4 Ωm·cm as the result of annealing. The annealing influence on the optical properties of crystals at the room temperature was insignificant.

The experimental data show that the annealing of Ge single crystals at 400 °C and $P_{O_2} \approx 10^{-3}$ Pa provides the temperature stability of their optical properties. It is assumed that the temperature stability improvement of the optical properties is due to oxygen concentration decrease and TD formation.

4. Conclusion

The annealing at the oxygen partial pressure ranging from 10^{-3} to 10^{3} Pa in the temperature range from 350 to 450 °C leads to the change of concentration and existence form of oxygen dissolved in Ge crystals with oxygen content of $\sim 10^{16}$ cm^{-3}. The oxygen concentration is increased after annealing at partial oxygen pressure from 1 to 10^{3} Pa. The oxygen band maximum shifts from 843 to 856 cm^{-1} when its concentration increases.

Annealing of Ge crystals at $P_{O_2} \approx 10^{-3}$ Pa leads to the oxygen band 843 cm^{-1} intensity reduction due to TD formation. The decrease of unbound oxygen and TD formation are accompanied by the improvement of the temperature stability of the crystal optical properties.

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References

[1] F. Dimroth and S. Kurtz, High-efficiency multijunction solar cells, *MRS Bulletin*, **32**, no. 3, 230–235, (2007).

[2] D. Rakwal and E. Bamberg, Slicing, cleaning and kerf analysis of germanium wafers machined by wire electrical discharge machining, *Journal of Materials Processing Technology*, **209**, no. 8, 3740–3751, (2009).

[3] S. Hegedus and A. Luque, Achievements and Challenges of Solar Electricity from Photovoltaics, *Handbook of Photovoltaic Science and Engineering*, 1–38, (2011).

[4] C. Claeys and E. Simoen, Germanium-Based Technologies, *Germanium-Based Technologies*, (2007).

[5] B. Depuydt, A. Theuwis, and I. Romandic, Germanium: From the first application of Czochralski crystal growth to large diameter dislocation-free wafers, *Materials Science in Semiconductor Processing*, **9**, no. 4-5, 437–443, (2006).

[6] A. Chroneos and R. V. Vovk, Oxygen diffusion in germanium: interconnecting point defect parameters with bulk properties, *Journal of Materials Science: Materials in Electronics*, **26**, no. 10, 7378–7380, (2015).

[7] T. Taishi, H. Ise, Y. Murao, T. Osawa, M. Suezawa, Y. Tokumoto, Y. Ohno, K. Hoshikawa, and I. Yonenaga, Czochralski-growth of germanium crystals containing high concentrations of oxygen impurities, *Journal of Crystal Growth*, **312**, no. 19, 2783–2787, (2010).

[8] B. Pajot, Clauws P: High resolution local mode spectroscopy of oxygen in germanium, **2**, 911–914

[9] P. Clauws, Oxygen related defects in germanium, *Mater Sci Eng B Solid State Mater Adv Technol*, **36**, no. 1, 213–220, (1996).

[10] I. A. Kaplunov, V. E. Rogalin, and M. Y. Gavalyan, The influence of impurity and isotopic composition of single-crystal germanium on optical transmission in the range of 520–1000 cm−1, *Optics and Spectroscopy (English translation of Optika i Spektroskopiya)*, **118**, no. 2, 240–246, (2015).

[11] B. Pajot, *Clerjaud B: Optical absorption of impurities and defects in semiconducting crystals electronic absorption of deep centres and vibrational spectra*, Springer, Berlin, 2013.

[12] K. Inoue, T. Taishi, Y. Tokumoto, Y. Murao, K. Kutsukake, Y. Ohno, M. Suezawa, and I. Yonenaga, Interstitial oxygen behavior for thermal double donor formation in germanium: Infrared absorption studies, *Journal of Applied Physics*, **113**, no. 7, Article ID 073501, (2013).

[13] L. I. Khirunenko, Y. V. Pomozov, M. Sosnin, V. P. Markevich, L. I. Murin, V. V. Litvinov, A. Carvalho, R. Jones, J. Coutinho, S. Öberg, and P. R. Briddon, Complexes of self-interstitials with oxygen atoms in germanium, *Materials Science in Semiconductor Processing*, **11**, no. 5, 344–347, (2008).

[14] O. Cryse and J. Vanhellomont, *Clawus P: Determination of oxide precipitated phase and morphology in silicon and germanium using infra-red absorption spectroscopy. Mater Sci Semicond Process*, **9**, 9 (1, 246-251, 2006.

[15] H. H. P. T. Bekman, T. Gregorkiewicz, I. F. A. Hidayat, C. A. J. Ammerlaan, and P. Clauws, Metastable thermal donor states in germanium: Identification by electron paramagnetic resonance, *Physical Review B*, **42**, no. 16, 9802–9809, (1990).

[16] K. Inoue, T. Taishi, Y. Tokumoto, and Y. Murao, Kutsukake K: Formation of Thermal Double Donors in Ge, **1**

[17] AF. Shimanskii and OI. Podkopaev, *Baranov VN: Oxygen impurity in germanium single crystals determination by infrared spectrometry. Adv Mat Res*, **1101**, 115-119, 1101, 2015.