Effect of oxygen dissolved in germanium on defect formation and optical properties of single crystals

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Abstract: Oxygen impurities and optical properties of Sb-doped germanium single crystals were investigated with Fourier transformed infrared spectrometry. The effect of oxygen on crystal structure was shown. The effects of annealing in the temperature range 623–723 K on the behavior of oxygen dissolved in germanium and on optical properties of single crystals have been investigated. It was found that annealing at lower oxygen partial pressure leads to the formation of thermal donors (TD) on the basis of dissolved oxygen atoms. It was established that TD formation and the decrease of unbound oxygen concentration is accompanied by the increase in temperature stability of the optical properties of crystals.

Germanium single crystals have extensive application in nanoelectronics, detector engineering and IR optics. In photovoltaic 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 AIIIB 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 that affects 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 О i. This defect in the simplest model may be regarded as a nonlinear symmetric quasi-molecule Ge–O–Ge, with vibration modes ν1, ν2 and ν3. 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, 11] the oxygen peak at 856 cm −1 has been reported to have a “shoulder” at ν that equals 843 cm −1, which is also identified with О i vibrations.

It should be noted, that oxygen concentration in crystals being investigated was ~10 17 cm−3 and more [7–11]. Our paper [14], as well as other papers [12, 13] show, that there is no band at 856 cm −1 in infrared spectrum with low oxygen (about 10^16 cm−3 and less). In the interval from 800 to 900 cm −1 the band at 843 (841) cm −1 is observed. This band is interpreted as an “oxygen band” by us and by other authors [12, 13].

Oxygen is known to exist in atomic and bond state, e.g. in the form of precipitates GeOx which are 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 623 to 723 K 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, 15–18].

Oxygen concentration in the crystals being investigated in papers [4, 15–18], as well as in papers [7–11] was ~10 17 cm−3 and more. Thus, Ge was sufficiently oxygenated.

In this regard, the aim of our work is to investigate the behavior of oxygen, dissolved in Ge and its effect on the structure and optical properties of single crystals with lower oxygen content (about 10^16 cm−3).
The studies were made on Sb-doped Ge single crystals with a donor concentration between 1.1 \times 10^{15} and 7.0 \times 10^{14} cm^{-3}, corresponding to a specific electric resistivity in the range of 2 to 4 \Omega \text{cm}. The material with dislocation content about \sim 10^{4} cm^{-2} has absorption coefficient \alpha of 0.15–0.20 cm^{-1} at the wavelength of 10.6 \mu m [4, 5].

Ge crystals were grown by the Czochralski method. The annealing of crystals at \text{P}_{O_2} \approx 10^{-3} \text{Pa} and temperature interval from 623 to 723 K was conducted in Krypton (6N).

Polished plane-parallel plates with the thickness of 1 cm were prepared to study optical properties with Fourier transformed infrared spectrometry. The infrared measurements were performed in the 700–1500 cm^{-1} spectral range with SPECTRUM BXII spectrometer. The optical density measurement error was no more than \pm 0.001.

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

\[
\left[ O_i \right] = 1.05 \times 10^{-7} \left( \frac{2.3D}{d} \right),
\]

where \text{D} – is the optical density relative to the baseline; \text{d} – is the sample thickness; 1.05 \times 10^{-7} cm^{-2} – is the calibration factor [4].

The influence of isothermal annealing on the optical properties of single crystals was determined by the optical density value and absorption coefficient \alpha at a wavelength of 10.6 \mu m. For IR measurement with the temperature rising up to 60°C the heat device ensuring a stable sample thermostating with accuracy \pm 0.1 K was used.

The table 1 lists the changes in standard Gibbs energy for reactions involving germanium and its oxides and the corresponding germanium dioxide pressures logarithm \text{lgP}_{O_2(GeO_2)}

| \text{T}[\text{K}] | 923 | 1073 | 1223 | 1433 |
|-------------------|-----|-----|-----|------|
| \Delta G^\circ \text{[J/mol]} | 2GeO_\text{2} = GeO_2 + Ge | -165250 | -112930 | -61660 | 0 |
| \Delta G^\circ \text{[J/mol]} | GeO_2 = Ge + O_2 | +401350 | +375540 | +345630 | +303540 |
| \text{lgP}_{O_2(GeO_2)} | -22.75 | -18.21 | -14.78 | -11.10 |

The results of calculations were used to determine the regions of existence of germanium and GeO_2 in the temperature range of 923–1433 K (Fig. 1).
In the process of a single crystal growth germanium melt was heated to some degrees above the melting point ($T_{\text{melt}} = 1210 \, \text{K}$), the melt temperature was ~1223 K. Fig. 1 shows that germanium dioxide GeO$_2$ can be in balance with liquid germanium at this temperature (its dissociation pressure $P_{\text{O}_2(\text{GeO}_2)}$ at $T = 1223 \, \text{K}$ is $1.66 \times 10^{-15} \, \text{atm}$ ($1.66 \times 10^{-10} \, \text{Pa}$)). This means that germanium is oxidized when partial pressure of gaseous oxygen is higher than this value, making GeO$_2$ emerge on the surface of the melt. GeO$_2$ microparticles in the melt can be captured by the growing crystal to form heterogeneous inclusions, thus disturbing the homogeneity of the germanium crystal structure and causing dislocation formation. Dislocation formation, affected by oxygen in molten Ge was also mentioned in other papers [7].

If the oxygen partial pressure is lower than $1.66 \times 10^{-15} \, \text{atm}$ ($1.66 \times 10^{-10} \, \text{Pa}$), O$_2$ is completely soluble in germanium. In the process of crystal growth a solid solution is formed from melt, where oxygen is present as interstitial atomic O$_i$, which can also affect the structure and properties of Ge crystals. In view of this, the investigation of dissolved oxygen and its effect on optical properties of single crystals was conducted.

Fig. 2 shows IR absorption spectra of Sb-doped Ge single crystals with specific electrical resistance of 3 $\Omega \cdot \text{cm}$ at room temperature and heated up to higher temperatures in the range of wave numbers from 700 to 1500 cm$^{-1}$.

Judging by the value of optical density in the maximum of a band at 843 cm$^{-1}$ regarding baseline the concentration of atomic oxygen in the investigated Ge crystal was determined. It was ~ $1.10 \times 10^{16} \, \text{cm}^{-3}$.

The effect of annealing in the temperature range from 623 to 723 K with partial pressure of oxygen $P_{\text{O}_2} \approx 10^{-3} \, \text{Pa}$ during the period of 24-90 hours on the behavior of interstitial oxygen and optical absorption of Ge crystals was investigated.

The experiment has proved that annealing leads to the reduction of band intensity 843 cm$^{-1}$ that corresponds to the content decrease of interstitial atomic O$_i$ as a component of quasi-molecules Ge–O–Ge. The 90-hour period annealing at $P_{\text{O}_2} \approx 10^{-3} \, \text{Pa}$ and temperature 673 K in Krypton (6N) leads to the oxygen band 843 cm$^{-1}$ intensity reduction on 5 % (Fig. 3).
The phenomenon observed in a similar way in papers [11, 18] 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 ~ $10^{-3}$ Pa results in the change of optical characteristics of crystals, such as optical density and absorption coefficient.

The data in Fig. 2 show that the optical density of the sample with electrical resistance of 3 $\Omega\text{m}\cdot\text{cm}$ at the room temperature and wavelength 10.6 $\mu\text{m}$ is 0.337. When the temperature increases up to 333 K the optical density increases to 0.365 accordingly. That $D$ 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 318 K.

Table 2 shows the optical properties of the samples annealed at temperature 673 K and $P_{O_2} \approx 10^{-3}$ Pa during 90 hour-period.

| № n/n | Electrical resistance [Ωm·cm] | Optical Density | Absorption coefficient [cm$^{-1}$] | Optical Density | Absorption coefficient [cm$^{-1}$] | Optical Density | Absorption coefficient [cm$^{-1}$] |
|-------|-------------------------------|----------------|-----------------------------------|----------------|-----------------------------------|----------------|-----------------------------------|
|       |                               | Before annealing | After annealing at 673 K and $P_{O_2} \approx 10^{-3}$ Pa during 90 hrs |
|       |                               | Temperature 293 K | Temperature 333 K | Temperature 333 K |
| 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                |

It was found that optical density of these samples at 333 K is decreased from 0.365 to 0.360 after annealing at low oxygen partial pressure and the absorption coefficient is decreased from 0.066 to 0.056 cm$^{-1}$ accordingly. On average the absorption coefficient of Ge single crystals at 333 K decreases by 13% for the samples with electrical resistance in the range from 2 to 4 $\Omega\text{m}\cdot\text{cm}$ 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 673 K 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.

Oxygen in Ge is one of the main impurities, which defines the structural perfection and properties of crystals.

When the partial pressure of oxygen in the process of growing is higher than $1.66\times10^{-15}$ atm ($1.66\times10^{-10}$ Pa) germanium is oxidized with oxide GeO$_2$ on the surface. Microparticles GeO$_2$ can be captured by a growing crystal from melt and it leads to dehomogenization of crystal structure and formation of dislocations.

Dissolved oxygen in its turn affects optical properties of crystals.

Annealing of Ge crystals at $P_{O_2} \approx 10^{-3}$ Pa and temperature 673 K 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] Dimroth F, Kurtz S 2007 MRS bulletin 32 (03) p 230–235
[2] Rakwal D, Bamberg E 2009 Journal Mater Process Technol 209 (8) p 3740-3751
[3] Hegedus S S, Luque A 2003 Handbook of photovoltaic science and engineering (John Wiley & Sons)
[4] Claeys L, Simoen E 2007 Germanium-based technologies: from materials to devices (Elsevier, Oxford)
[5] Depuydt B, Theuwis A, Romandic I 2006 Mater Sci Semicond Process 9 (4) p 437–443
[6] Chroneos A, Vovk R V 2015 Journal of Materials Science: Materials in Electronics 26 (10) p 7378–7380
[7] Taishi T, Ise H, Murao Y, Osawa T et al. 2010 Journal Cryst Growth 312 (19) p 2783–2787
[8] Pajot B, Clauws P 1987 The Proc of the 18th Int Conf on the Phys Of Semicond 2 p 911–914
[9] Clauws P 1996 Mater Sci Eng B Solid State Mater Adv Technol. 36 (1) p 213–220
[10] Pajot B, Clerjaud B 2013 Optical absorption of impurities and defects in semiconducting crystals electronic absorption of deep centres and vibrational spectra (Springer, Berlin)
[11] Inoue K, Taishi T, Tokumoto Y, Murao Y, Kutsukake K 2013 Appl. Phys. 113 (7) p 1–5
[12] Kaplunov I A, Rogalin V E, Gavalyan M Yu 2015 Optic and spectroscopy 118 (2) p 240–246
[13] Seref K, Romandieb I, Theuwisb A 2006 Mater.s Sci. in Semicond. Proc. 9 p 753–758
[14] Shimanskii A F, Podkopaev O I, Baranov V N 2015 Adv Mat Res. 1101 p 115-119
[15] Khirunenko L I, Pomozov Yu V, Sosnin M G et al. 2008 Mater Sci Semicond Process 11 (5) p 344–347
[16] Cryse O, Vanhellomont J, Clauws P 2006 Mater Sci Semicond Process 9 (1) p 246–251
[17] Bekman H H P, Gregorkiewicz T, Hidayat I F A et al. 1990 Phys Rev B 42 (16) p 9802
[18] Inoue K, Taishi T, Tokumoto Y, Murao Y, Kutsukake K, 2014 Proceedings of the 12th Asia Pacific Physics Conference / JPS Conference Proceedings 1 (1)