Behaviour of oxygen-related thermal donors in Ge crystals
Czochralski-grown from the melt covered fully by B$_2$O$_3$

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Abstract. Oxygen-related thermal donors (OTDs) in oxygen-enriched Czochralski Ge crystals grown from a melt fully covered by B$_2$O$_3$ liquid were investigated by infrared spectroscopy. Interstitially dissolved oxygen concentrations [$O_i$] and thermal donor concentrations $N_{TD}$ in Ge specimens annealed at 350˚C for 64h and at 550˚C for 1h, followed by subsequent fast cooling to room temperature, were measured in comparison with those in as-grown Ge. By annealing at 350˚C, an absorption peak developed at 780 cm$^{-1}$ and the peak height at 855 cm$^{-1}$, related to [$O_i$], decreased. The absorption coefficient at 780 cm$^{-1}$ showed the same correlation to the difference between the total concentration of oxygen atoms and the dissolved oxygen concentration in the annealed specimens. It was found that the number of oxygen atoms forming the OTD increases with increasing annealing time at 350˚C.

1. Introduction

Recently, Ge has been revisited for its unique properties in the semiconductor industry [1]. Owing to its lattice matching to GaAs, Ge has been used as a substrate or a bottom cell of III-V-based triple-junction solar cells for space use. Indeed, a very high conversion efficiency of 41.1 % has been reported in a system with focused sunlight [2]. In addition, the application of Ge to high-speed MOSFET devices is expected due to faster carrier mobility in Ge than in Si [1]. In these circumstances, Ge crystals with higher quality will be demanded for production of such devices with higher performance.

In the case of Si, crystals are generally grown by the Czochralski (CZ) method using a silica crucible. During the growth, oxygen atoms dissolve from the silica crucible into the Si melt and incorporate inevitably into the grown crystal. Such interstitially dissolved oxygen atoms ($O_i$) contribute some benefits such as suppression of dislocation generation, leading to high strength stability [3]. Also, interstitially dissolved oxygen atoms $O_i$ form oxygen-related thermal donors (OTDs or act as nuclei for precipitates. Therefore, it is well recognized that for practical applications the oxygen concentration in Si crystals has to be strictly controlled. Recently, magnetic fields have been used for controlling melt convection during the crystal growth. Basic behavior of OTDs and
oxygen precipitates in Si crystals have been widely studied [4-6], and suitable growth and post-anneal conditions have already been established for application in industry.

Oxygen can be expected to offer a similar advantage in Ge as in Si for the wide applications of Ge crystals [7,8]. Ge crystals are generally grown by the CZ method using a graphite crucible in a vacuum or inert gas (N₂ or Ar) ambient [9]. That is, the oxygen concentration in conventional Ge crystals is very low. Germanium-oxide-related particles coming from residual oxygen in the growth furnace are easily formed on the melt surface, and then they attach to the growing Ge crystal surface. At these locations, dislocations generate into the crystal. Dislocations seriously influence device performance. Oxygen-enriched Ge crystals have been grown under oxygen-containing ambient [7,8,10,11]. Indeed, maximum concentration of interstitially dissolved oxygen is reported using a later reported method to be 7 × 10¹⁷ cm⁻³ in Ge grown in ambient [10], although the dislocation density is high. Behavior of oxygen in such Ge crystals was intensively studied using infrared spectroscopy. Oxygen atoms occupy interstitial sites in the Ge lattice similar to Si, and the concentration [Oᵢ] of interstitially dissolved oxygen can be determined from the peak height of an absorption at 855 cm⁻¹ in the spectrum. The absorption relates to the asymmetric (ν₃) stretching mode of Ge-O-Ge quasi-molecules.

OTDs in such Ge crystals have also been investigated. First, a structure with four atoms of oxygen was proposed for OTD [10] and experimentally confirmed by a subsequent study [12]. According to the latter study, OTDs were saturated at donor concentrations of 9 × 10¹⁶ cm⁻³ by prolonged annealing at 350°C. Recently, double donor structures have been accepted for OTDs in Ge crystals with a relevant model [13]. Clauws et al. [14,15] reported behavior of OTDs by annealing in detail and showed three absorption bands at 600, 740 and 780 cm⁻¹ in infrared spectra.

Recently, we grew Ge crystals with various concentrations of interstitially dissolved oxygen atoms up to 5.5 × 10¹⁷ cm⁻³ using B₂O₃ and a silica crucible [16]. Full coverage of the Ge melt by B₂O₃ liquid and also addition of GeO₂ powder are keys to enhance oxygen concentration in Ge crystals. In the crystals, B concentration was lower than the detection limit of SIMS analysis, and contamination of Si atoms and formation of GeO₂-related precipitates could not be detected from infrared spectra [17]. Behavior of OTDs and other oxygen-related defects in such crystals using B₂O₃ and silica crucible have not yet been well understood.

This paper reports some preliminary results of OTDs formed by post-annealing in an oxygen-enriched Ge crystal grown using B₂O₃ liquid. Formation and annihilation of OTDs were evaluated by Fourier-transform infrared spectroscopy (FTIR) and by the Hall effect. The interstitial oxygen concentrations and oxygen-related thermal donor concentration were compared in as-grown and post-annealed Ge specimens.

2. Experimental procedures

A Ge crystal was grown from a melt fully covered by B₂O₃ liquid without any doping of electrically active impurities. The interstitial oxygen concentration of the as-grown crystal was 5.5 × 10¹⁷ cm⁻³. Detailed crystal growth conditions were as described previously [16,18]. The oxygen concentration in this crystal was also analyzed chemically by secondary ion mass spectroscopy (SIMS) to be 6.5 × 10¹⁷ cm⁻³. The accuracy of the measurement was ±5%.

In order to determine interstitially dissolved oxygen concentrations, Ge blocks of 3 mm thickness were cut from the grown crystal. The blocks were then mechanically lapped, followed by chemical polishing. Infrared absorption spectroscopy was conducted at room temperature (RT) using a Fourier-transform spectrometer (JASCO FT-IR 610). The spectral resolution was 1 cm⁻¹. From the absorption peak height at 855 cm⁻¹, oxygen concentration [Oᵢ] was determined using the calibration coefficient of 1.05 × 10¹⁷ cm⁻² [8]. To evaluate carrier concentrations, specimens 5×5×1.5 mm in size were also prepared. The carrier concentration in the Ge specimens was determined by Hall-effect measurements using the Van der Pauw method at RT. As-grown specimens were annealed in a vacuum ampoule as follows: One was at 350°C for 64 h to increase the quantity of OTDs [15], the other at 550°C for 1 h in
order to annihilate OTDs [8]. In both cases, subsequent fast cooling to RT was carried out after annealing.

Table 1. Anneal condition and characteristics related to oxygen of Ge specimens grown from melt fully covered by B$_2$O$_3$.

| Anneal condition |Interstitial oxygen concentration [O$_i$] [cm$^{-3}$]|Carrier concentration $N_{TD}$ [cm$^{-3}$]|Absorption coefficient at 780 cm$^{-1}$ $\alpha_{780}$ [cm$^{-1}$]|
|------------------|------------------------------------------|---------------------------------|---------------------|
| (a) as-grown     | $5.5 \times 10^{17}$                   | $2.0 \times 10^{16}$          | 0.04                |
| (b) 350°C × 64h  | $2.5 \times 10^{17}$                   | $5.4 \times 10^{16}$          | 0.19                |
| (c) 550°C × 1h   | $6.2 \times 10^{17}$                   | $1.4 \times 10^{14}$          | ≈ 0                 |

3. Results and discussion

With regard to three Ge specimens of (a) as-grown, (b) annealed at 350°C for 64 h and (c) annealed at 550°C for 1 h, interstitial oxygen concentration [O$_i$], absorption coefficients around 780 cm$^{-1}$ ($\alpha_{780}$) obtained from infrared spectra and thermal donor concentrations ($N_{TD}$) determined from Hall-effect measurement are summarized in Table 1.

Infrared absorption spectra of three Ge specimens in the range 750–900 cm$^{-1}$ are shown in Figure 1. Absorption peaks related to O$_i$ were observed at 855 cm$^{-1}$ in all the specimens, though the peak height was quite different, dependent on the post-annealing conditions. [O$_i$] in specimens (a), (b) and (c) was determined to be $5.5 \times 10^{17}$, $2.5 \times 10^{17}$ and $6.2 \times 10^{17}$ cm$^{-3}$, respectively. It was found that [O$_i$] in the as-grown state was reduced by $3 \times 10^{17}$ cm$^{-3}$ after annealing at 350°C for 64 h. On the other hand, an enhancement of [O$_i$] by $0.8 \times 10^{17}$ cm$^{-3}$ was seen after annealing at 550°C for 1 h. An absorption peak was observed around 780 cm$^{-1}$ due to OTDs, especially clear in specimen (b). The absorption coefficient ($\alpha_{780}$) at 780 cm$^{-1}$ of specimens (a), (b) and (c) was 0.04, 0.19 and ≈ 0 cm$^{-1}$, respectively.

Figure 1. Infrared absorption spectra of three Ge specimens, (a) as-grown, (b) post-annealed at 350°C for 64 h and (c) post-annealed at 550°C, for 1 h in the range 750–900 cm$^{-1}$ measured at RT. The vertical line in the figure shows an absorption intensity of 1 cm$^{-1}$. 
In the Hall-effect measurement, all the three specimens were found to be \( n \)-type. \( N_{TD} \) in specimens (a), (b) and (c) were \( 2.0 \times 10^{16} \), \( 5.4 \times 10^{16} \) and \( 1.4 \times 10^{14} \) cm\(^{-3} \), respectively. Specimen (b) was additionally annealed at 550 °C for 1 h. The specimen showed a reduction of \( N_{TD} \) to \( 1.5 \times 10^{14} \) cm\(^{-3} \) which is in good agreement with the magnitude of \( N_{TD} \) in specimen (a). This means that OTDs in the as-grown specimen were all dissolved by annealing at 550 °C for 1h. In that case, \([O_i]\) in Ge specimens was \( 6.2 \times 10^{17} \) cm\(^{-3} \) free from OTDs.

The oxygen concentration in all the specimens was determined to be \( 6.5 \times 10^{17} \) cm\(^{-3} \) by SIMS analysis. The difference between the values determined by infrared spectra and SIMS analysis was within the accuracy of the measurement, therefore we assumed that the former value of \( 6.2 \times 10^{17} \) cm\(^{-3} \) was the total oxygen concentration \([O_{total}]\). Reduction of the interstitial oxygen concentration \( \Delta[O_i] \) by annealing at 350°C from the as-grown specimen was calculated to be \([O_{total}] - [O_i]\). Figure 2 shows the relationship between \( \Delta[O_i] \) or \( N_{TD} \) and \( \alpha_{780} \). Solid circles represent \( \Delta[O_i] \). \( \Delta[O_i] \) seems to show a linear increase with an increase of the intensity of \( \alpha_{780} \). It is reported that the intensity of absorption at 780 cm\(^{-1} \) may relate to the concentration of oxygen atoms specifically at the ends of the TD structure, not of all oxygen atoms in the TD [19]. Probably some concentration proportions among the growing OTDs in annealed specimen remains constant, leading to the observed linear relationship. On the other hand, \( N_{TD} \) also increased with increasing \( \alpha_{780} \) with saturation at \( 5.4 \times 10^{16} \) cm\(^{-3} \). This implies that the structure of OTDs formed by annealing at 350°C is not the same as that responsible for the absorption peak at 780 cm\(^{-1} \). Clauws et al. [15] reported that another absorption band at 600 cm\(^{-1} \) developed earlier than that at 780 cm\(^{-1} \) during early stage of annealing at 350°C. Therefore, the structure of OTDs related to the absorption band at 780 and 600 cm\(^{-1} \) may be different, and the number of oxygen atoms contributing to the formation of OTDs related to the 780 cm\(^{-1} \) band may be more than that for 600 cm\(^{-1} \).

Such speculation may be supported by Figure 3, which shows a dependence of the ratio of \( \Delta[O_i] \) and \( N_{TD} \) on the annealing time at 350°C. Data reported by Clauws et al. [15] are also shown as squares.

**Figure 2.** Relationships between interstitial oxygen concentration reduced by annealing, \( \Delta[O_i] \) (\( [O_{total}] - [O_i] \)) (circles) and donor concentration, \( N_{TD} \) (triangles) as a function of absorption coefficient at 780 cm\(^{-1} \), \( \alpha_{780} \).

**Figure 3.** Dependence of the ratio of \( \Delta[O_i] \) and \( N_{TD} \) on the annealing time at 350°C. Data reported by Clauws et al. [15] are also shown as squares.
symbol close to the left-side axis represents a result for the as-grown specimen, the annealing time at 350°C can be estimated to be 2 h or less considering cooling rate (500°C/h) after the crystal growth. Values of $\Delta [O_i]/N_{TD}$ are 5 and 7.5 for annealing times of < 2 h (as-grown) and 64 h, respectively. Results reported by Clauws et al. [15] are also superimposed in Figure 3 as square symbols. Their results of $\Delta [O_i]/N_{TD}$ logarithmically increase with increasing annealing time, a similar tendency is seen in the present results. According to Clauws et al. [15], the value finally approaches eight after prolonged annealing and it is in agreement with Fuller’s model which identified them as GeO$_4$ assuming single donors [12].

In our preliminary results, we see that the observed behaviour of OTD formation and annihilation in Ge crystals grown from a melt fully covered by B$_2$O$_3$ is similar to those in Ge grown under oxygen-containing ambient. Effects of very long or short time annealing on the formation and annihilation of OTDs and detailed structures of OTDs in Ge crystals are now being investigated. Oxygen-enriched Ge crystals grown using B$_2$O$_3$ described above have the advantage that it is possible to reduce dislocation density. Therefore, new knowledge related to the formation of OTDs and oxygen precipitates in such Ge crystals would be useful in the future.

4. Conclusion

The behaviour of OTDs in oxygen-enriched CZ-Ge crystals grown from a melt fully covered by B$_2$O$_3$ liquid was investigated by infrared spectroscopy. A Ge crystal with [O$_i$] of $5.5 \times 10^{17}$ cm$^{-3}$ in the as-grown state was prepared. The specimens were post-annealed at 350°C for 64h or at 550°C for 1 h, both with subsequent fast cooling to room temperature. [O$_i$] and $N_{TD}$ in the Ge specimens as-grown or annealed were compared. In the case of a specimen annealed at 350°C, an absorption peak grew at 780 cm$^{-1}$, while a peak at 855 cm$^{-1}$ became small. The absorption intensity $\alpha_{780}$ shows a linear correlation to $[O_i]$ in the annealed specimen. On the other hand, $N_{TD}$ increased with the intensity of $\alpha_{780}$, showing similar tendency with the previously reported results. This implies that the structure of OTDs formed by annealing at 350°C is not same which relates to the absorption peak at 780 cm$^{-1}$. It was found that oxygen atoms contributing to the formation of OTDs increased with increasing annealing time at 350°C. Such behavior of OTDs is similar to that of Ge crystals grown in oxygen-containing ambient.

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References

[1] Vanhellemont J, Simoen E 2007 J. Electrochem. Soc. 154 H572
[2] Guter W, Schone J, Philipps S P, Steiner M, Siefer G, Wekkeli A, Welser E, Oliva E, Bett A W, Dimoroth F 2009 Appl. Phys. Lett. 94 223504.
[3] Yonenaga I, Sumino K 1996 J. Appl. Phys. 80 734.
[4] Fuller G, Ditzenberger J, Hannay N, Buehler E 1954 Phys. Rev. 96 833.
[5] Kaiser W 1957 Phys. Rev. 105 1751.
[6] Kanamori A, Kanamori M 1979 J. Appl. Phys. 50 8095.
[7] De Gryse O, Vanmeerbeek P, Vanhellemont J, Clauws P 2006 Mater. Sci. Semicond. Process. 9 246.
[8] Litvinov V V, Svensson B G, Murin L I, Lindström J L, Markevich V P, Peaker A R 2006 J. Appl. Phys. 100 033525.
[9] Depuydt B, Jonghe M, Baets W 2007 Germanium-Based Technologies ed C Claeys and E Simoen (Oxford: Elsevier) p 17.
[10] Bloem J, Haas C, Penning P 1959 J. Phys. Chem. Solids 12 22.
[11] Kaiser W, Thurmond C 1961 J. Appl. Phys. 32 115.
[12] Fuller C, Kaiser W, Thurmond C 1961 J. Phys. Chem. Solids 17 301.
[13] Jones R, Coutinho J, Öberg S, Briddon P 2001 Physica B 308-310 8.
[14] Clauws P 1996 Mat. Sci. Eng. B36 213.
[15] Clauws P, Vanmeerbeek P 1999 Physica B 273-274 557.
[16] Taishi T, Ise H, Murao Y, Ohsawa T, Suezawa M, Tokumoto Y, Ohno Y, Hoshikawa K, Yonenaga I 2010 J. Cryst. Growth 312 2783.
[17] Taishi T, Ise H, Murao Y, Ohsawa T, Tokumoto Y, Ohno Y, Yonenaga I 2011 Microelectro. Eng. in press.
[18] Taishi T, Ohno Y, Yonenaga I 2009 J. Cryst. Growth 311 4615.
[19] Coutinho J, Jones R, Murin L I, Markevich V P, Lindström J L, Öberg S, Briddon P R 2001 Phys. Rev. Lett. 87 235501.