

# Czochralski-growth of germanium crystals containing high concentrations of oxygen impurities

Toshinori Taishi<sup>a,†,\*</sup>, Hideaki Ise<sup>a</sup>, Yu Murao<sup>a</sup>, Takayuki Osawa<sup>a</sup>, Masashi Suezawa<sup>a</sup>, Yuki Tokumoto<sup>a</sup>, Yutaka Ohno<sup>a</sup>, Keigo Hoshikawa<sup>b</sup>, Ichiro Yonenaga<sup>a</sup>

<sup>a</sup> Institute for Materials Research, Tohoku University, Sendai 980-8577, JAPAN

<sup>b</sup> Faculty of Engineering, Shinshu University, Nagano 380-8553, JAPAN

Oxygen-containing germanium (Ge) single crystals with low density of grown-in dislocations were grown by the Czochralski (CZ) technique from Ge melt, both with and without a covering by boron oxide (B<sub>2</sub>O<sub>3</sub>) liquid. Interstitially-dissolved oxygen concentrations in the crystals were determined by the absorption peak at 855cm<sup>-1</sup> in the infrared absorption spectra at room temperature. It was found that the oxygen concentration in a Ge crystal grown from melt partially or fully covered with B<sub>2</sub>O<sub>3</sub> liquid was about 10<sup>16</sup> cm<sup>-3</sup> and was almost the same as that in a Ge crystal grown without B<sub>2</sub>O<sub>3</sub>. The oxygen concentration in a Ge crystal was enhanced to be greater than 10<sup>17</sup> cm<sup>-3</sup> by growing a crystal from a melt fully covered with B<sub>2</sub>O<sub>3</sub>, with the addition of germanium oxide powder, the maximum oxygen concentration achieved being 5.5 × 10<sup>17</sup> cm<sup>-3</sup>. The effective segregation coefficients of oxygen in the present Ge crystal growth were roughly estimated to be between 1.0 and 1.4.

PACS CODE: 81.10.Fq; 61.72.Ff; 61.72.uf

Keywords: A1. Doping, A1. Oxygen impurity, A2. Single crystal growth, A2. Czochralski method, B2. Semiconducting germanium

\*Corresponding author

†Present address: Institute of Carbon Science and Technology, Shinshu University, Nagano 380-8553, Japan

Tel.: +81-26-269-5574, Fax.: +81-26-269-5388

E-mail address: taishi@shinshu-u.ac.jp (T. Taishi)

## 1. Introduction

Germanium (Ge) has been studied for possible application in the next generation of high-speed ULSI devices as well as in lens and window materials for infrared optics. Its use as a substrate for GaAs solar cells has also been investigated as it provides a higher conversion efficiency than Si [1]. In particular, it is expected that Ge can be used as a material for the bottom cell of III-V-based triple-junction solar cells, and one of the leading results of conversion efficiency has been reported, at around 41.4 % under focused sunlight [2]. For such use, dislocations in the substrate would have a negative influence as severe carrier killers in the bottom cell and the upper layer constructed by III-V-based epitaxial growth. Thus, Ge crystals free from dislocations, or with an extremely low density of grown-in dislocations, are desirable as a substrate for that purpose. However, it is commercially well recognized that the growth of dislocation-free Ge crystals is very difficult.

Recently, we proposed a new Czochralski (CZ) method for growing Ge crystals with an extremely low dislocation density using boron oxide ( $B_2O_3$ ) and a silica crucible [3]. The Ge melt was partially covered with liquid  $B_2O_3$ , but only in the outer region of the melt surface. The formation of germanium-oxide ( $GeO_2$ )-related particles, which act as a dislocation source on the growing Ge crystal surface, was effectively suppressed by the  $B_2O_3$ -covered melt, and a particle-free “melt-window” was realized in the central portion of the melt in the silica crucible. From such a Ge melt we succeeded in growing dislocation-free Ge single crystals. The mixing of B atoms from  $B_2O_3$  into the Ge crystal was lower than the detection limit of SIMS analysis of  $2 \times 10^{15} \text{ cm}^{-3}$ .

The thermo-mechanical stability of crystals is important for avoiding dislocation generation during the device fabrication process. At present, CZ-silicon (Si) crystals containing oxygen atoms in a concentration of  $\sim 10^{18} \text{ cm}^{-3}$  are used exclusively in industry on account of their high mechanical strength in comparison with float-zone Si crystals [4]. Basically, oxygen impurities interstitially dissolved in Si crystals are clarified to preferentially segregate on and immobilize dislocations, leading to high mechanical stability of the crystal [5].

A similar effect of oxygen on Ge is expected to offer a similar advantage for the wide application of Ge crystals [6,7]. Ge crystals are generally grown by the CZ method using a graphite

crucible in a vacuum, since oxygen atoms form stable oxides on the melt surface. Thus, the knowledge of the effect of oxygen in Ge growth is very limited. The maximum solid solubility of oxygen atoms in Ge has been estimated to be  $2 \times 10^{18} \text{ cm}^{-3}$  [8] in several growth experiments under argon and oxygen ambient, where the highest concentration of oxygen atoms achieved in a Ge crystal was reported to be  $6 \times 10^{17} \text{ cm}^{-3}$ . The oxygen concentration in Ge crystals grown under nitrogen and oxygen ambient became saturated at  $7 \times 10^{17} \text{ cm}^{-3}$  [9]. The segregation coefficient of oxygen into Ge has not yet been determined.

In the present paper, the growth of an oxygen-containing CZ-Ge crystal using  $\text{B}_2\text{O}_3$  and a silica crucible is reported. The interstitially-dissolved oxygen concentration in CZ-Ge crystals grown from Ge melt, both with and without a covering by  $\text{B}_2\text{O}_3$  liquid, was determined by the absorption band at  $855 \text{ cm}^{-1}$  of the infrared absorption spectra resulting from the antisymmetric ( $\nu_3$ ) stretching mode of Ge-O-Ge quasi-molecules at room temperature (RT). Preliminary results for the segregation coefficient of oxygen in Ge are also reported.

## 2. Experimental procedure

Ge ingots of 150 g with a purity of better than 4N ( $50 \Omega \text{ cm}$ , n-type) were charged in a silica crucible 50 mm in diameter. For most cases, a chunk of  $\text{B}_2\text{O}_3$ , either 5 g or 20 g in mass, with a residual moisture content of 100–200 ppm, was set on the Ge ingot. For some cases,  $\text{GeO}_2$  powder (0.04 or 0.42 at% in melt) with a purity of 5N was also added.  $\langle 111 \rangle$  oriented Ge crystals, 1 inch in diameter, were grown by the CZ method at a pulling rate of 10 mm/h under an Ar gas flow of 1 liter/min at 1 atm. Detailed growth conditions were described previously [3]. For comparison, a Ge crystal was grown from a Ge melt under the same growth conditions but without any  $\text{B}_2\text{O}_3$  liquid.

The grown Ge crystals were cut into wafers or blocks. The carrier concentration in Ge specimens was determined by Hall-effect measurement using the van der Pauw method at RT. The dislocation density in wafers cut from the top portion of the crystal was evaluated by observing etch pits at five different positions (center,  $r/2$ :  $r$  is radius of wafers) using optical microscopy after preferential etching using Billig etchant [10] at  $85^\circ\text{C}$  for 3 min. Detailed conditions were described previously [3].

Ge blocks with a thickness of 3 or 9 mm were prepared for evaluating the interstitial oxygen

concentration. After the specimens had been lapped and chemically etched, the infrared absorption of each block was measured at RT using a Fourier-transform spectrometer (JASCO FT-IR 610). A high-purity polycrystalline Ge ingot with the same thickness was used as a reference. The spectral resolution was  $1\text{ cm}^{-1}$ . From the absorption band at  $855\text{cm}^{-1}$  due to the antisymmetric ( $\nu_3$ ) stretching mode, the interstitially dissolved oxygen concentration was determined using the calibration coefficient of  $1.05 \times 10^{17}\text{ cm}^{-2}$ , which has been recently proposed [7]. Total oxygen concentration in some specimens was chemically evaluated by secondary ion mass spectroscopy (SIMS) using Cameca IMS-4f.

### 3. Results

#### 3.1 Electrical properties and dislocation density in grown crystals

Six Ge crystals were grown by the CZ method from Ge melt which was covered fully, partially or not at all, by  $\text{B}_2\text{O}_3$  liquid. Typical crystals are shown in Fig. 1. Table 1 summarizes the growth conditions and characteristics of the grown crystals.

Crystal (N-054) was undoped grown, using a silica crucible without  $\text{B}_2\text{O}_3$ . Although Dash necking was performed to eliminate dislocations generated by thermal shock, the dislocation density was  $4 \times 10^3\text{ cm}^{-2}$ . A number of particles floating on the melt were observed and probably became attached to the crystal during the growth, resulting in the crystal dislocated. The crystal was n-type and the carrier concentration was  $1.6 \times 10^{14}\text{ cm}^{-3}$ .

In the cases when a 5 g chunk of  $\text{B}_2\text{O}_3$  was added to the Ge ingot, the Ge melt was partially covered by  $\text{B}_2\text{O}_3$  liquid over the outer region while a particle-free Ge melt was obtained in the central region. Ge crystal (N-046) was grown from such a particle-free Ge melt. Thin Dash necking was also carried out, and then a dislocation-free Ge crystal was successfully obtained. The crystal was n-type and the carrier concentration was  $2.0 \times 10^{14}\text{ cm}^{-3}$ , slightly higher than that of crystal N-054. The result of a SIMS analysis also showed that the B concentration was below the detection limit of  $2 \times 10^{15}\text{ cm}^{-3}$ .

When a  $\text{B}_2\text{O}_3$  chunk of 20g was added, the Ge melt was fully covered with  $\text{B}_2\text{O}_3$  liquid. The Ge melt could be observed below the transparent  $\text{B}_2\text{O}_3$  layer during the growth. Crystal (N-061) was grown from such melt. Initially the seed was lowered through the  $\text{B}_2\text{O}_3$  liquid until

it dipped into the Ge melt. Then, during the crystal growth, the crystal was drawn up through the  $B_2O_3$  layer. The dislocation density was  $1.0 \times 10^3 \text{ cm}^{-2}$ , lower than that in crystal N-054. The crystal was n-type and the carrier concentration was  $3.3 \times 10^{15} \text{ cm}^{-3}$ .

Crystal (N-059) was grown from a Ge melt partially covered with  $B_2O_3$ , with the intentional addition of  $GeO_2$  powder of 0.04 at%. The added  $GeO_2$  powder dissolved into the melt when the Ge starting materials were fully melted, and in this way a particle-free Ge melt was realized, as in the case of crystal N-046. The dislocation density was  $5.3 \times 10^2 \text{ cm}^{-2}$ , lower than that in crystal N-061. The crystal was n-type and the carrier concentration was  $3.3 \times 10^{15} \text{ cm}^{-3}$ .

Crystal (N-055), grown from a Ge melt fully covered with  $B_2O_3$ , with the addition of  $GeO_2$  at 0.04 at%, was a single crystal although the thin Dash necking had not been performed. It was found that when the Ge starting materials were fully melted, the Ge melt was cloudy and it changed to be fully transparent during the crystal growth. The dislocation density was  $1.3 \times 10^3 \text{ cm}^{-2}$ . The crystal was n-type and the carrier concentration was  $3.3 \times 10^{15} \text{ cm}^{-3}$ .

Crystal (N-058) was grown from Ge melt fully covered with  $B_2O_3$ , with the addition of  $GeO_2$  at 0.42 at%. The crystal was a “bicrystal” accompanying one grain boundary inside the crystal. The Ge melt as observed through the  $B_2O_3$  layer was cloudy at all times during the crystal growth. The crystal was n-type, and the carrier concentration was  $2.0 \times 10^{16} \text{ cm}^{-3}$ . The dislocation density was  $3 \times 10^3 \text{ cm}^{-2}$ .

### 3.2 Oxygen concentration in grown crystals evaluated by infrared absorption spectra

Fig. 2 shows infrared absorption spectra of grown crystals in the range  $700\text{--}1300 \text{ cm}^{-1}$ . Ge blocks were prepared from the top part of each crystal (solidified fraction,  $g < 0.2$ ). The thickness was 9 mm except in the case of crystal N-058, for which it was 3 mm. Absorption peaks were observed at  $855 \text{ cm}^{-1}$  in each crystal, but the height of the peaks were quite different, depending on the growth method. Using a calibration coefficient of  $1.05 \times 10^{17} \text{ cm}^{-2}$  [7], interstitial oxygen concentrations in crystals were determined to be from  $8.5 \times 10^{15}$  to  $5.5 \times 10^{17} \text{ cm}^{-3}$ . In addition, very small absorption peaks at  $1264 \text{ cm}^{-1}$ , related to the combination of asymmetric  $\nu_3$  and symmetric  $\nu_1$  stretching modes of the Ge-O-Ge quasi-molecules, were observed in crystals N-055 and N-058. No peaks were observed at the range of  $880\text{--}900 \text{ cm}^{-1}$ , indicating that there were no Ge-O-related

defects [11] or the concentration is lower than the detection limits in all the Ge crystals. In addition, absorption peaks were not observed at  $1106\text{ cm}^{-1}$ , related to the  $\nu_3$  stretching mode of Si-O-Si quasi-molecules or at  $1225\text{ cm}^{-1}$ , related to  $\text{SiO}_2$  precipitates, in any the infrared spectra, indicating that Si-O-related defects should be lower than the detection limits in all the Ge crystals.

For crystals N-055 and N-058, total oxygen concentrations, including interstitial atoms, evaluated by SIMS analysis were  $1.8 \times 10^{17}$  and  $6.5 \times 10^{17}\text{ cm}^{-3}$ , respectively.

The interstitial oxygen concentrations in crystals N-059, N-055 and N-058 were measured at positions with various solidified fractions. Fig. 3 shows the relationship between the oxygen concentration in the crystal and the solidified fraction. The oxygen concentration decreased from the top part to the bottom for crystals N-059 and N-055, while the values measured for crystal N-058 were almost constant. Assuming that all oxygen atoms in Ge crystals are interstitially dissolved, the effective segregation coefficients of oxygen in each Ge crystal were estimated by using Pfann's equation [12] as eq. (1):

$$C_S(g) = kC_0(1-g)^{k-1} = C_S(0)(1-g)^{k-1}, \quad (1)$$

where  $C_S(g)$  is the oxygen concentration in the crystal with a solidified fraction of  $g$ ,  $k$  is the effective segregation coefficient, and  $C_0$  is the initial oxygen concentration in the Ge melt before starting the crystal growth. Although  $C_0$  was not determined precisely, the experimental results could be fitted by selecting  $k$  and  $C_S(0)$  suitably. The experimental results were well fitted by the dotted lines shown in Fig. 4, and the effective segregation coefficients were estimated to be  $k = 1.2$ ,  $1.4$  and  $1.0$  for crystals N-059, N-055 and N-058, respectively. The confidence limits for the segregation coefficient by fitting is approximately 3%.

## 4. Discussion

### 4.1 Incorporation of oxygen atoms into Ge crystals

The oxygen atoms in crystal N-054 came mainly from thin oxide films covering the Ge starting materials and residual oxygen in the furnace. They slightly dissolved into the Ge melt and oxygen atoms segregated into the crystal during the growth. Such an oxygen concentration level is

very low. Since the wetting ability between the Ge melt and silica glass is not good and the weight of the crucible did not change from before to after the growth, no reaction between the Ge melt and silica glass would have occurred. Therefore, the dissolution of oxygen atoms from the silica crucible can be assumed to be very small and can be neglected.

The oxygen concentrations in crystals N-046 and N-061 were not so greater than that in crystal N-054. This indicates that  $B_2O_3$  liquid does not contribute to the observed dramatic enhancement of the oxygen concentration. That is, we can assume that there was no dissolution of oxygen atoms either from  $B_2O_3$  or from the silica crucible into the Ge melt. These conclusions are supported by two results: First, the B concentration in crystal N-046 was below the detection limit of SIMS. Second, no absorption peaks related to the  $\nu_3$  stretching mode of Si-O-Si quasi-molecules were observed at  $1106\text{ cm}^{-1}$  in the infrared spectra, as shown in Fig. 2.

In the case of crystals N-059 and N-055, for which  $GeO_2$  powder was added at 0.04 at%, the oxygen concentration was slightly enhanced from that in crystals N-054, N-046 and N-061 for crystal N-059, while it was dramatically enhanced to be greater than  $10^{17}\text{ cm}^{-3}$  for crystal N-055. Moreover, the concentration in crystal N-058 was further enhanced to be  $5.5 \times 10^{17}\text{ cm}^{-3}$  by the further addition of  $GeO_2$  powder. A common condition of crystals N-055 and N-058 was that the Ge melts were fully covered by  $B_2O_3$  liquid. These results indicate the following two mechanisms. (i) The increase in oxygen concentration was caused by the decomposition of  $GeO_2$  into Ge and 2O under the existence of  $B_2O_3$  liquid. This may be supported by the fact that Gibbs standard free energy of  $B_2O_3$  is smaller than that of  $GeO_2$  at the melting point of Ge [13]. (ii) Oxygen atoms resulting from decomposition in the Ge melt evaporate from the Ge melt window, resulting in only a slight enhancement in the oxygen concentration for crystal N-059. However, when the Ge melt is fully covered by  $B_2O_3$  liquid, evaporation is strongly suppressed, resulting in a high oxygen concentration for crystals N-055 and N-058. Therefore, we conclude that fully covering the Ge melt by  $B_2O_3$  liquid and the addition of  $GeO_2$  are both keys for the enhancement of the oxygen concentration in Ge crystals.

The carrier concentration in Ge crystals increased with increasing oxygen concentration, maintaining n-type conductivity. For instance, It was  $3.3 \times 10^{15}\text{ cm}^{-3}$  for crystal N-055 with the oxygen concentration of  $2.2 \times 10^{17}\text{ cm}^{-3}$ . This result was good agreement with that reported by

Clauws [14]. These indicate that oxygen impurities dissolved in as-grown Ge crystals act as thermal donors. In fact, the carrier concentration reduced to  $5.4 \times 10^{13} \text{ cm}^{-3}$  for crystal N-055 after annealing at  $550 \text{ }^\circ\text{C}$  for 1h with subsequent fast cooling. Then, the peak height at  $855 \text{ cm}^{-1}$  in infrared spectra became higher about 12 % after the annealing, implying that oxygen atoms interstitially dissolved of about 12 % form thermal donors and the other atoms still keep electrically inactive state. More precise ratio will be reported elsewhere. Anyway, such thermal donors can be annihilated by suitable annealing for practical use.

Although there is a discrepancy about 20% between the total concentration analyzed by SIMS and corresponding interstitial oxygen concentration measured by FT-IR. Considering error ranges of both measurements and homogeneity of oxygen concentration in the specimen, we consider that that almost all oxygen atoms are not in a form of oxygen precipitates but are interstitially dissolved in the Ge crystals. Such idea is consistent with results of infrared spectra, no peaks appeared related to Ge-O-related defects at  $880 - 900 \text{ cm}^{-1}$  and Si-O-related defects at  $1106$  and  $1225 \text{ cm}^{-1}$ .

The oxygen concentrations in crystals N-055 and N-058 are of the same order as that in Ge crystal grown in an oxygen-containing ambient [8, 9]. To our knowledge, the growth of Ge crystals in such an ambient leads to the formation of a number of  $\text{GeO}_2$ -related particles in the Ge melt, resulting in a highly dislocated crystal. As an alternative, we propose the present CZ technique using  $\text{B}_2\text{O}_3$ ,  $\text{GeO}_2$  and a silica crucible in order to grow a Ge crystal with no dislocations or at least a low density of dislocations, while controlling the oxygen concentration to be at a level of  $10^{16} - 10^{17} \text{ cm}^{-3}$ , and forming a crystal free from contamination of Si impurities. The growth processes are simple and are similar to the conventional CZ method.

In the present study, although oxygen-containing Ge crystals could be grown, however dislocation could not be completely suppressed when Ge melt was fully covered by  $\text{B}_2\text{O}_3$  and  $\text{GeO}_2$  powder was intentionally added. One of the reasons is probably due to residual  $\text{GeO}_2$  impurities which are not completely decomposed under  $\text{B}_2\text{O}_3$  liquid. In such cases, dislocation-free Ge crystals would be grown by changing growth conditions such as time or temperature maintained before the crystal growth, i. e., if  $\text{GeO}_2$  impurities are completely decomposed in Ge melt the dislocation-free growth probably becomes possible. Such approaches are now in progress.



## 4.2 Segregation coefficient and solid solubility of oxygen in Ge

Estimated values of the segregation coefficient of oxygen in Ge were apparent and lie between 1.0 and 1.4. These may include the effects not only of segregation but also of other oxygen transportation processes such as evaporation from the Ge melt and B<sub>2</sub>O<sub>3</sub> liquid, reaction of oxygen atoms during the crystal growth and so forth. But, for crystal N-055, the evaporation of oxygen from the Ge melt would be suppressed by B<sub>2</sub>O<sub>3</sub> liquid covered fully with the melt, implying that the obtained segregation coefficient of 1.2 is close to the real value without any effect of the evaporation. At least, this value is useful in the present growth method.

The oxygen concentration in crystal N-058 was independent of solidified fraction and was approximately  $5.5 \times 10^{17} \text{ cm}^{-3}$ . Corresponding total oxygen concentration evaluated by SIMS analysis was  $6.5 \times 10^{17} \text{ cm}^{-3}$ . This value has two possible interpretations. First, it may be the solid solubility of O in Ge solid. Second, it may be affected by the solid solubility of oxygen in Ge liquid at temperatures close to the melting point. Regarding the former possibility, a maximum value of solid solubility of  $2 \times 10^{18} \text{ cm}^{-3}$  has been reported [8]. However, this was estimated by several experimental results in which the highest oxygen concentration, measured by vacuum fusion gas analysis, was  $6 \times 10^{17} \text{ cm}^{-3}$ , close to the value found in the present research. It has also been reported that the oxygen concentration in a Ge crystal grown under a mixed nitrogen and oxygen ambient was saturated at  $7 \times 10^{17} \text{ cm}^{-3}$  [9], which value was calculated theoretically from the infrared absorption coefficient. In this case the calibration coefficient may be derived to be  $1.25 \times 10^{17} \text{ cm}^{-2}$ . If the other calibration coefficient, used in the present study, of  $1.05 \times 10^{17} \text{ cm}^{-2}$  [7] is applied, the oxygen concentration is also very close to our maximum value. In such a case many particles or precipitates would be observed in the crystals due to the saturation of oxygen atoms in the Ge crystal, but no visible defects were observed in crystal N-058 by optical microscopy after the preferential etching. Thus, in the case of the second possible interpretation, considering that the constant oxygen concentration in crystal N-058 was probably affected by the solid solubility of oxygen in Ge liquid, the following scenario may be assumed. The Ge melt was saturated with oxygen atoms. Un-decomposed GeO<sub>2</sub> powder may be remaining in the Ge melt, which could lead to a cloudy Ge melt, as observed during the growth. During the crystal growth, oxygen atoms

resulting from decomposition in the Ge melt segregated into the crystal and are newly and continuously supplied by decomposition of the remaining GeO<sub>2</sub> powder, resulting in an almost constant oxygen concentration in the crystal irrespective of the solidified fraction. That is, the apparent segregation coefficient becomes close to 1. In such a case, the real effective segregation coefficient of oxygen in Ge is thought to be  $k > 1$ . This is consistent with the estimation of  $k = 1.2$  and 1.4 for crystals N-059 and N-055, respectively. The precise segregation coefficient of oxygen in Ge and the solid solubility of oxygen in both Ge solid and Ge liquid will be reported elsewhere.

## 5. Conclusion

Oxygen containing Ge crystals 1 inch in diameter and 50 mm in length with low dislocation density were successfully grown from Ge melt covered with B<sub>2</sub>O<sub>3</sub> liquid with the addition of GeO<sub>2</sub> powder in a silica crucible. Interstitial oxygen concentrations in such crystals were determined by the absorption band at 855 cm<sup>-1</sup> in infrared absorption spectra. The oxygen concentration in a Ge crystal grown from melt partially covered with B<sub>2</sub>O<sub>3</sub> liquid was about 10<sup>16</sup> cm<sup>-3</sup> and was almost the same as that in a Ge crystal grown without B<sub>2</sub>O<sub>3</sub>. Consequently, B<sub>2</sub>O<sub>3</sub> itself is not a dominant source of oxygen concentration. The oxygen concentration in a Ge crystal was enhanced to be greater than 10<sup>17</sup> cm<sup>-3</sup> by growing the crystal from a melt fully covered by B<sub>2</sub>O<sub>3</sub> and with the addition of germanium oxide powder. Therefore, we conclude that fully covering the Ge melt by B<sub>2</sub>O<sub>3</sub> liquid and the addition of GeO<sub>2</sub> are both keys for the enhancement of the oxygen concentration in Ge crystals. The maximum oxygen concentration in Ge was  $5.5 \times 10^{17}$  cm<sup>-3</sup>. The effective segregation coefficient of oxygen in the present Ge crystal growth was roughly estimated to be between 1.0 and 1.4.

## Acknowledgement

This work was supported in part by a Grant-in-Aid for Science Research (20760003) from the Ministry of Education, Science, Sports and Culture.

## References

- [1] J. Vanhellemont, E. Simoen, J. Electrochem. Soc. **154** (2007) H572.
- [2] W. Guter, J. Schone, S. P. Philipps, M. Steiner, G. Siefer, A. Wekkeli, E. Welser, E. Oliva, A. W. Bett, F. Dimoroth, Appl. Phys. Lett. **94** (2009) 223504.
- [3] T. Taishi, Y. Ohno, I. Yonenaga, J. Cryst. Growth **311** (2009) 4615.
- [4] M. Imai, K. Sumino, Phil. Mag. A **47** (1983) 599.
- [5] I. Yonenaga, K. Sumino, J. Appl. Phys. **80** (1996) 734.
- [6] O. De Gryse, P. Vanmeerbeek, J. Vanhellemont, P. Clauws, Physica B **376-377** (2006) 113.
- [7] V. V. Litnov, B. G. Svensson, L. I. Murin, J. L. Lindström, V. P. Markevich, A. R. Peaker, J. Appl. Phys. **100** (2006) 033525.
- [8] W. Kaiser, C.D. Thurmond, J. Appl. Phys. **32** (1961) 115.
- [9] J. Bloem, C. Haas, P. Penning, J. Phys. Chem. Solids **12** (1959) 22.
- [10] E. Billig, Proc. Roy. Soc. A **235** (1956) 37.
- [11] O. De Gryse, P. Vanmeerbeek, J. Vanhellemont, P. Clauws, Physica B **376-377** (2006) 113.
- [12] W. G. Pfann, J. Metals **4** (1952) 747.
- [13] I. Barin, Thermochemical Data of Pure Substances, Part I and Part II, VCH, Weinheim, 1989.
- [14] P. Clauws, Mat. Sci. Eng. **B36** (1996) 213.

## Figure captions

Fig. 1. Photographs of Ge crystals grown (a) by the conventional method (N-054), (b) from  $B_2O_3$ -partly-covered Ge melt (N-046), (c) from  $B_2O_3$ -fully-covered Ge melt (N-061) and (d) from  $B_2O_3$ -fully-covered Ge melt with 0.42 at%  $GeO_2$  powder addition (N-058).

Fig. 2. Infrared absorption spectra of Ge crystals measured at RT. Arrows indicate oxygen-related peak positions. See text.

Fig. 3. Variation of interstitial oxygen concentrations in Ge crystals N-059, N-55 and N-058 against the solidification ratio.

Table 1 Growth conditions and characteristics of Ge crystals grown from B<sub>2</sub>O<sub>3</sub>-covered Ge melts

Crystal No.	B <sub>2</sub> O <sub>3</sub> covering	GeO <sub>2</sub> addition (at%)	Carrier conc. (cm <sup>-3</sup> )	Oxygen conc. (cm <sup>-3</sup> )	Dislocation density (cm <sup>-2</sup> )
(1) N-054	---	---	n: $1.6 \times 10^{14}$	$8.5 \times 10^{15}$	$4.0 \times 10^3$
(2) N-046	partial	---	n: $2.0 \times 10^{14}$	$1.6 \times 10^{16}$	0
(3) N-061	full	---	n: $3.3 \times 10^{15}$	$1.7 \times 10^{16}$	$1.0 \times 10^3$
(4) N-059	partial	0.04	n: $3.3 \times 10^{15}$	$2.3 \times 10^{16}$	$5.3 \times 10^2$
(5) N-055	full	0.04	n: $3.0 \times 10^{14}$	$2.2 \times 10^{17}$	$1.3 \times 10^3$
(6) N-058	full	0.42	n: $2.0 \times 10^{16}$	$5.5 \times 10^{17}$	$3.0 \times 10^3$



(a)



(b)



(c)



(d)

Fig.1

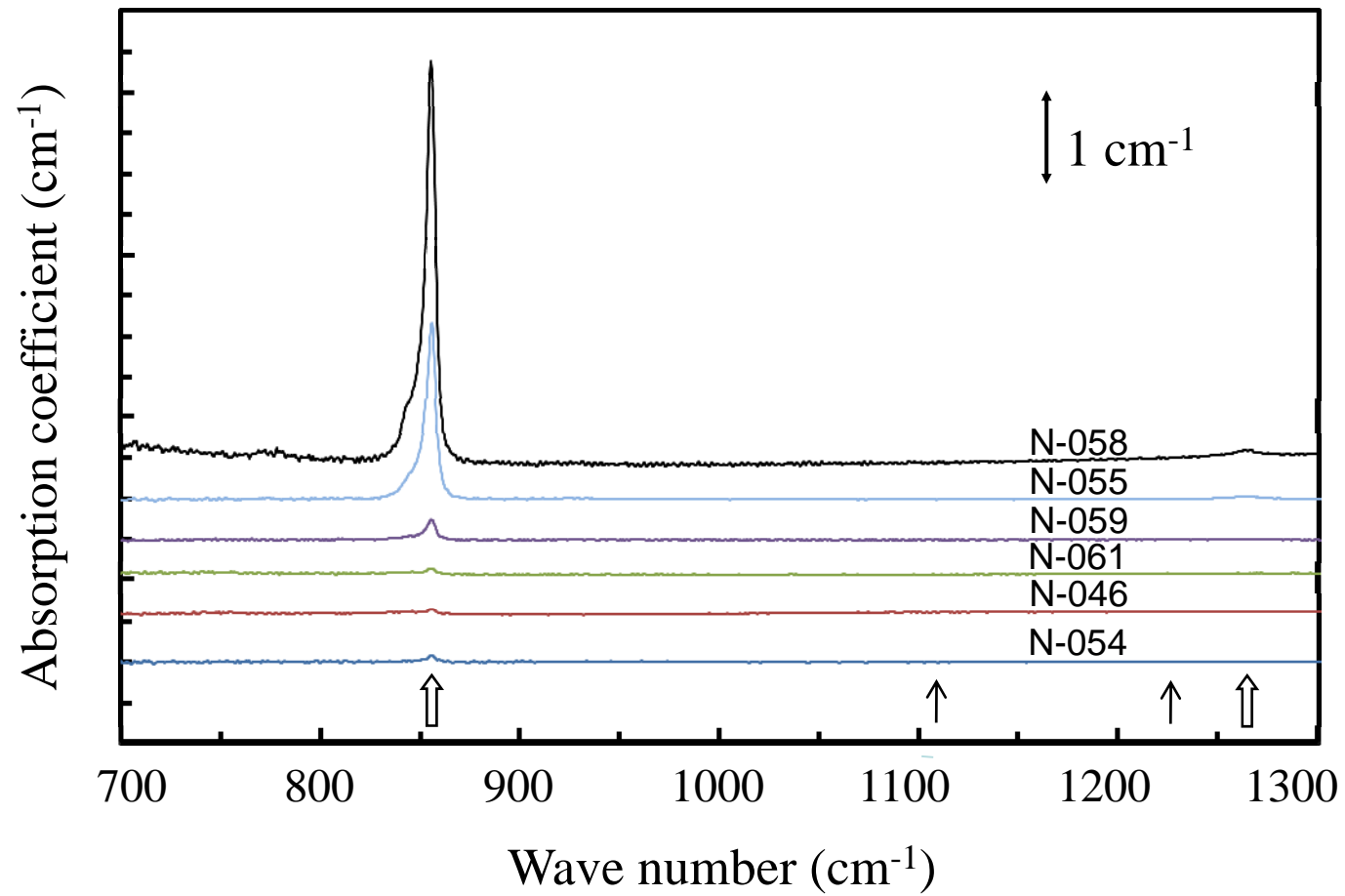


Fig.2

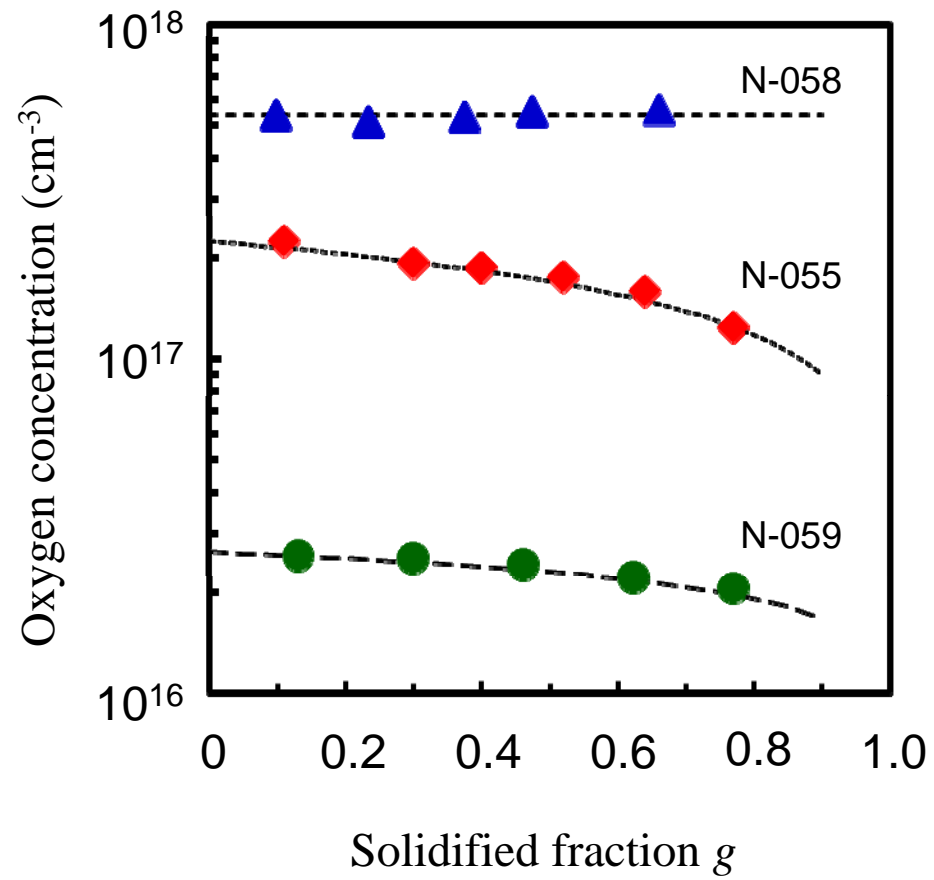


Fig.3