Czochralski growth techniques of germanium crystals grown from a melt covered partially or fully by liquid B_2O_3

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We propose two unique Czochralski (CZ) techniques for growing germanium (Ge) crystals with an extremely low dislocation density and high interstitial oxygen concentration ([Oi]) using boron oxide (B_2O_3) and a silica crucible. When a Ge melt is partially covered with liquid B_2O_3, but only on the outer region of the melt surface, germanium-oxide (GeO_2)-related particles forming naturally in the melt are effectively dissolved by the liquid B_2O_3. The clean central portion of the melt produces dislocation-free undoped or Ga-doped Ge crystals. In addition, Ge crystals with [Oi] up to 6×10^{17} cm^{-3} can be grown from a melt fully covered by liquid B_2O_3 with added GeO_2 powder. The reaction and transportation of oxygen atoms during the growth process using B_2O_3 was investigated, revealing that liquid B_2O_3 acts like a catalyst without heavy contamination of the growing Ge crystal by B and Si atoms.

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1. Introduction

Bulk germanium (Ge) crystals are currently in practical use as lens and window materials for infrared optical systems and as substrates for GaAs solar cells [1]. In particular, Ge can be used as the bottom cells of III-V-based triple-junction tandem solar cells for space use, and conversion efficiency as high as 41.1 % has been reported under focused sunlight [2]. For such uses, Ge must be free from dislocations to avoid their negative influence as severe carrier killers in the bottom cell or the upper III-V epitaxial layers. This means that Ge crystals become more commercially desirable the closer they come to being dislocation-free.

Ge crystals are generally grown by the Czochralski (CZ) method using a graphite crucible in a vacuum or inert gas (N_2 or Ar) atmosphere [3]. Recently, dislocation-free Ge single crystals up to 300 mm in diameter have been grown by Umicore Corporation [1]. In addition, the growth of high quality Ge crystals by the vertical Bridgman (VB) [4] and the vertical gradient freeze (VGF) techniques [5,6] has also been reported. One of the common outcomes of these techniques is that the interstitial oxygen concentration ([Oi]) in the Ge crystals is very low. It is well known that germanium oxide (GeO_2)-related particles coming from residual oxygen in the growth furnace are easily formed on the melt surface. They then attach to the growing Ge crystal surface, finally generating dislocations in the crystal around these locations. Oxygen-enriched Ge crystals can be grown under an oxygen-containing atmosphere using a silica crucible or ampoule [7-10]. Indeed, the maximum concentration of interstitially dissolved oxygen in Ge crystals grown by such a method is reported to be 7×10^{17} cm^{-3} [7], although the quality of the grown crystal is not good, the dislocation density in the crystal is high. Generally, Si atoms (contaminants from the silica

container) have been detected in such grown crystals by infrared spectroscopy [9-11].

In the case of CZ-Si crystal growth, a silica crucible is generally used, and therefore oxygen atoms are enriched in the grown crystals. At present, CZ-Si crystals containing oxygen atoms at a concentration of $\sim 10^{18}$ cm^{-3} are used exclusively in industry on account of their high critical resolved shear stress for dislocation generation [12] and high mechanical strength in comparison with float-zone Si crystals [13]. Basically, oxygen impurities interstitially dissolved in Si crystals have been found to preferentially segregate on and immobilize dislocations, leading to high mechanical stability of the crystal [14]. In the case of Ge, a similar phenomenon produced by oxygen doping was recently reported [15], and application in solar cells and other electric devices using such Ge crystals with high mechanical strength is expected in the near future.

On the other hand, III-V semiconductors such as GaAs, GaP and InP have been grown by the liquid encapsulated Czochralski (LEC) technique [16-18]. Generally, boron oxide (B_2O_3) has been used as a stable and suitable liquid encapsulant. The evaporation of volatile elements such as As and P can be suppressed by a B_2O_3 layer constructed on the compound melt surface. In these cases, free boron atoms are formed by the dissolution of B_2O_3 and some of them incorporate into the grown crystals. However, almost all B atoms that are incorporated replace a Ga or In at a site in their sphalerite structure, and are electrically inactive in the crystals.

In this paper, we report two CZ techniques for growing Ge crystals from a melt covered by liquid B_2O_3. First, a unique CZ technique for growing dislocation-free Ge crystals using B_2O_3 is presented. Second, growth from a melt fully covered by liquid B_2O_3, similar to LEC growth, is introduced. Oxygen-containing Ge crystals with low dislocation densities can be obtained from

such a melt by the intentional addition of GeO_2 powder to the melt. The chemical and electrical properties of the Ge crystal evaluated showed that contamination levels of B and Si atoms in the crystal were very low, and these aspects of the technique are discussed.

2. Growth of Ge crystals from a melt partially covered by liquid B_2O_3

Ge ingots (~150 g) were charged in a silica crucible 50 mm in diameter, and B_2O_3 chunks (5 g or 7.5 g) were placed on the Ge ingots. [111] or [001]-oriented Ge crystals 1 inch in diameter were grown by the CZ method at a pulling rate of 10 mm/h at 1 atm in an Ar atmosphere. Detailed growth conditions were described previously [19]. For comparison, two Ge crystals were grown under the same conditions: one grown normally from a Ge melt but without any liquid B_2O_3, another grown from a melt with added B_2O_3 chunks (5 g) and GeO_2 powder (0.04 at% in melt) with a purity of 5N. Ga-doped Ge crystals with a Ga concentration up to 6×10^{17} cm^{-3} were also grown with and without liquid B_2O_3 under the same conditions.

After melting B_2O_3 chunks at 480˚C and Ge ingots at 938˚C, only the outside region of the Ge melt was covered with the liquid B_2O_3 in a silica crucible [19]. No particles to hinder dislocation-free crystal growth were observed in the melt. Finally, a clean and particle-free Ge melt surface was produced in the central region of the crucible, making it possible to grow from a "clean" Ge melt. Figure 1 (a) illustrates the present crystal growth technique from such a melt.

Figure 1 (b) shows a [001]-oriented undoped Ge crystal grown from a Ge melt partially covered with B_2O_3. It has a diameter of about 1 inch and a length of about 50 mm. No grain boundary is observed in the entire crystal until the tail, and no particles are detected on the surface

of the crystal. Four habit lines can be clearly observed. The crystal growth procedure was almost the same as that in the conventional method except that the Ge melt was partially covered with B_2O_3 liquid. The dislocation density at the top of the crystal shown in Fig. 1 (b) was evaluated by preferential etching using a solution of 1 HF + 1 H_2O_2 + 4 H_2O [20] for [001]-oriented crystals or Billig etchant [21] for [111]-oriented crystals, both for comparison with that of a Ge crystal grown by the conventional CZ method. Figures 2 (a) and (b) show optical micrographs of a Ge crystal grown by the present technique and by the conventional CZ method, respectively. No etch pits are observed in Fig. 2 (a). In contrast, in the conventionally grown Ge crystal, many rectangular etch pits of about 8×10^{3} cm^{-2} were observed (Fig 2 (b)), with dislocation density higher at the periphery than in the central region. The present work shows that the dislocation density in a Ge crystal can be considerably reduced by using the technique of partially-B_2O_3-covered CZ-Ge growth. Etch pits could also not be detected in [111]-oriented undoped and Ga-doped Ge crystals with a Ga concentration up to 6×10^{17} cm^{-3}. These results indicate that the growth of Ge crystals from a partially-B_2O_3-covered melt is also effective for any orientation and for, at least, undoping and Ga doping. The detailed results for Ga doping will be reported elsewhere.

The carrier concentration in the top portion of the as-grown undoped crystal after annealing at 550 $^{\circ}$C with subsequent cooling to RT for annihilation of oxygen-related thermal donors (OTD) [10] was 1×10^{14} cm^{-3}. The crystal kept n-type conduction before and after donor annihilation. The B concentration in the crystals as evaluated by SIMS analysis was lower than the detection limit of 2×10^{15} cm^{-3}. These findings indicate that the contamination of the crystal by B atoms was very low, at least lower than the carrier concentration after donor annihilation.

In order to confirm that particles were not formed, or were caught or dissolved by the liquid B_2O_3, powdered GeO_2 was intentionally added at 0.04 at% to the partially-B_2O_3-covered melt and a crystal was grown from the melt. The added GeO_2 powder completely disappeared when the Ge starting materials were fully melted, and in this way a particle-free Ge melt was produced at the central position. The dislocation density in the crystal grown from this melt was 5×10^2 cm^{-2}, lower than that in an undoped crystal, in spite of the intentional addition of GeO_2 powder. Therefore, it is likely that any GeO_2-related particles that may form in the Ge melt during crystal growth dissolve when liquid B_2O_3 is present.

3. Growth of Ge crystals from a melt fully covered by liquid B_2O_3

Ge ingots (~150 g) were charged in a silica crucible, as for the partially-B_2O_3-covered melt, and B_2O_3 chunks weighing 20 g were placed on the Ge ingots. GeO_2 powder (0~0.42 at% in melt) with a purity of 5N was intentionally added in the crucible with the Ge ingots and B_2O_3 chunk. Five [111]-oriented Ge crystals 1 inch in diameter were grown at a pulling rate of 10 mm/h. Detailed growth conditions were comparable to those for growth from the partially-B_2O_3-covered melt. In these procedures, the intentional formation of a neck portion for the complete elimination of dislocations generated by thermal shock was not carried out.

In all procedures, Ge melts were fully covered by liquid B_2O_3. With the intentional addition of GeO_2 powder, the Ge melt below the B_2O_3 layer was obscured by cloudiness at first, but could be seen below a clear layer of B_2O_3 after stirring the layer by rotating the seed before initiating growth. Ge crystals could be grown through the B_2O_3 layer as shown in Fig. 3(a). A [111]-oriented Ge

crystal shown in Fig. 3(b) was grown from fully-B_2O_3-covered melt with the intentional addition of GeO_2 powder at 0.20 at%. Any attachment or inclusion of GeO_2-related particles or B_2O_3 solid would have occurred on the crystal surface, but the surface was very clean. Three habit lines were identified on the crystal surface, except for the crystal grown with the highest GeO_2 powder addition of 0.42 at% (leading to a twin). Dislocation densities in the top portion of grown crystals evaluated by preferential etching using Billig etchant [21] were less than 3×10^3 cm^{-2}. In the crystal shown in Fig. 3(b), grown with intentional addition of GeO_2 powder at 0.20 at%, the dislocation density was lower than 5×10^2 cm^{-2}.

The carrier concentration in as-grown crystals increased with increasing GeO_2 powder addition in melts, from 7×10^{14} to 2×10^{16} cm^{-3}. The origin of such carriers was based on OTDs [22], and could be annihilated by post-annealing at 550 °C for 1h with subsequent cooling to RT. All crystals were n-type conduction before and after annealing, and the B concentration in all crystals was lower than the detection limit of SIMS analysis of 2×10^{15} cm^{-3}.

The interstitial oxygen concentration [Oi] in Ge as-grown crystals was evaluated by infrared absorption band at 855 cm^{-1} due to the antisymmetric (ν_3) stretching mode at RT using the calibration coefficient of 1.05×10^{17} cm^{-2} [10]. Detailed conditions for the evaluation have been reported previously [23]. Figure 4 shows the relationship between the [Oi] determined in eight crystals and their growth conditions, especially the amount of GeO_2 powder added, and the inset shows typical infrared spectra of Ge crystals around 855 cm^{-1}. In crystals from the melts with no covering or partial covering by liquid B_2O_3, [Oi] was about 10^{16} cm^{-3}. No remarkable enhancement of absorption peak height at 855 cm^{-1} could be detected when GeO_2-powder was added to a

partially-B_2O_3-covered melt. On the other hand, in crystals grown from a fully-B_2O_3-covered melt without the addition of GeO_2 powder, [Oi] was at a similar level as in crystals grown from a partially-B_2O_3-covered melt, but it increased remarkably with increasing amounts of added GeO_2 powder. When the amount of added GeO_2 powder was 0.20 and 0.42 at%, [Oi] in as-grown crystals was 5.5×10^{17} cm^{-3}. The [Oi] was enhanced to 6.2×10^{17} cm^{-3} after annealing for OTD annihilation, and this was the highest value observed in crystals in the present study. However, both high [Oi] and low dislocation density were realized by growth from a fully-B_2O_3-covered melt with GeO_2 powder added at 0.20 at%. The total oxygen concentration in this crystal as analyzed by SIMS was 6.5×10^{17} cm^{-3} and was comparable to the value obtained after OTD annihilation (within about 5%), indicating that other oxygen-related precipitates such as GeO_2 are very few in number and almost all oxygen atoms exist in interstitial sites in the Ge lattice.

As other remarkable features, we note that no absorption peaks were observed at 1106 cm^{-1}, related to the ν_3 stretching mode of Si–O–Si quasi-molecules or at 1225 cm^{-1}, related to SiO_2 precipitates, in any of the infrared spectra [23]. These indicate that Si–O-related defects were lower than the detection limits in all the Ge crystals.

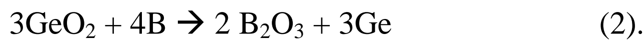
4. Reaction during crystal growth using liquid B_2O_3 and formation of free oxygen atoms

Several experimental results lead us to suppose that the following phenomena took place during CZ-Ge crystal growth using liquid B_2O_3: (i) GeO_2-related particles or powder were dissolved by B_2O_3 liquid. (ii) Interstitial oxygen concentration ([Oi]) was slightly enhanced by some amount of B_2O_3 addition to the melt. (iii) [Oi] was dominantly enhanced up to 5.5×10^{17} cm^{-3} (as-grown state)

when more GeO_2 powder was added. (iv) When the Ge melt was not fully covered by liquid B_2O_3 and GeO_2 powder was added, [Oi] was not enhanced. (v) The level of Ge crystal contamination with B and Si atoms was very low.

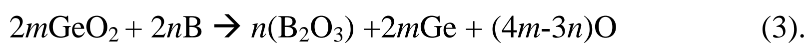
Phenomena (i), (ii) and (iii) could be supported by the Gibbs standard free energy of the relevant oxides during crystal growth at the melting point of Ge [24]. The Gibbs standard free energy of B_2O_3 formation (-6.50 kJ/mol) is lower than those of Ge-related oxides such as GeO (-3.04 kJ/mol) and GeO_2 (-3.41 kJ/mol) at the melting point of Ge. In addition, B_2O_3 is thermodynamically stable, almost as much so as SiO_2 (-6.80 kJ/mol). Assuming that free B atoms are formed from B_2O_3 near the B_2O_3/Ge melt interface, it can be understood that GeO_2 particles are dissociated by the following reactions:

$$B_2O_3 \leftrightarrow 2B + 3O \qquad (1),$$



$$3GeO_2 + 4B \rightarrow 2\,B_2O_3 + 3Ge \qquad (2).$$

Here, free oxygen atoms are not formed by eq. (2), indeed, [Oi] is not enhanced when the melt is fully covered by liquid B_2O_3. However, [Oi] increased as more GeO_2 powder was added. So we suppose that free oxygen atoms are formed during dissolution of some GeO_2 molecules by free B atoms, as in the following equation:



$$2mGeO_2 + 2nB \rightarrow n(B_2O_3) + 2mGe + (4m-3n)O \qquad (3).$$

Finally, some quantity of the formed free oxygen atoms might segregate into a grown crystal. The highest oxygen level of 6.2×10^{17} cm^{-3} (after OTD annihilation) obtained in the present study was comparable with that obtained by crystal growth using a silica crucible in oxygen-containing ambient (7×10^{17} cm^{-3}) [7]. This value may be the highest oxygen concentration in a Ge crystal obtained by the present growth techniques, although the maximum solid solubility of oxygen in Ge has been reported to be 2×10^{18} cm^{-3} [8].

However, in phenomenon (iv), free oxygen atoms formed in the melt were lost from the partially-B_2O_3-covered melt. This indicates that the oxygen atoms evaporated from the melt window in the early stage of crystal growth. In other words, liquid B_2O_3 fully covering a Ge melt acts as a liquid encapsulant for free oxygen atoms formed by dissolution of GeO_2 powder, as evaporation of volatile elements can be suppressed by a B_2O_3 layer in LEC growth. Therefore, full coverage of the Ge melt by B_2O_3 liquid and the addition of GeO_2 are both key requirements for the enhancement of oxygen concentration in Ge crystals.

With regard to the contamination in Ge crystals related to phenomenon (v), chemical and electrical experiments revealed that the contamination level by B atoms in the melt was very low. As one of the reasons, the phase diagram of B and Ge is the monotectic type [25], implying that free B atoms in a Ge melt may be unstable. If B_2O_3 is significantly stable in the melt, the lifetime of free B atoms formed by dissociation of B_2O_3 (eq. (1)) in Ge melt should be very short. This is consistent with the experimental results.

However, the entry of Si atoms into the crystals could not be detected in infrared spectra.

According to the Gibbs standard free energy, SiO_2 is the most stable of the relevant oxides, but it is only slightly more stable than B_2O_3. Thus, while a reaction between SiO_2 and B_2O_3 may occur, it will be very weakly driven near the B_2O_3/silica crucible interface, yielding little product. Also, according to Si-doped LEC-GaAs growth, Si atoms doped in the melt are easily absorbed into the B_2O_3 layer [17]. A similar reaction may occur, and Si atoms dissolved from the silica crucible may easily be absorbed into the B_2O_3 layer in the present CZ-Ge crystal growth. More detailed investigations using other crucibles, such as those made from graphite or pBN, are necessary and are now in progress.

In the present growth techniques, the addition of B_2O_3 and GeO_2 powder leads to the growth of high quality Ge crystals with high mechanical strength. Liquid B_2O_3 acts like a convenient catalyst to prevent heavy contamination of the crystal by B and Si atoms during its growth. Such uncommon and fortuitous, but useful combinations as that of molten Ge and liquid B_2O_3 may also exist for growing other high-quality materials, such as metals, semiconductors, oxides and other functional crystals. The present techniques appear to be important early models of this, and more detailed investigation and analyses are indispensable. Although, the crystal size of Ge crystals shown in the present study is 1 inch in diameter and only an academic level, currently, as a next step, some trials for growing Ge crystals 2 inches in diameter using the present techniques are beginning. Such larger crystals with low dislocation density and high mechanical strength will be applicable for III-V solar cells with high conversion efficiency. Experimental results will be reported elsewhere in the near future.

5. Conclusion

Two unique CZ techniques for growing Ge crystals with an extremely low grown-in dislocation density and high [Oi] using B_2O_3 and a silica crucible are described. There is hesitation to use silica crucibles and B_2O_3 for CZ-Ge crystal growth because of the possibility the crystal will be contaminated with Si and B atoms. However, dislocation-free Ge crystals can be grown from a partially-B_2O_3-covered melt, and oxygen-enriched Ge crystals from a fully-B_2O_3-covered melt, in both cases with very little contamination from Si and B atoms. GeO_2-related particles are dissolved by the liquid B_2O_3 that covers the molten Ge, and [Oi] can be enhanced up to 6×10^{17} cm^{-3} both by the intentional addition of GeO_2 powder and fully covering the melt with liquid B_2O_3. Such uncommon and useful combinations as that of molten Ge and liquid B_2O_3 may also exist for growing other materials. High quality Ge crystals with large diameter grown using such techniques with high mechanical strength due to oxygen doping are expected to be used for solar cells or other electric devices in the near future.

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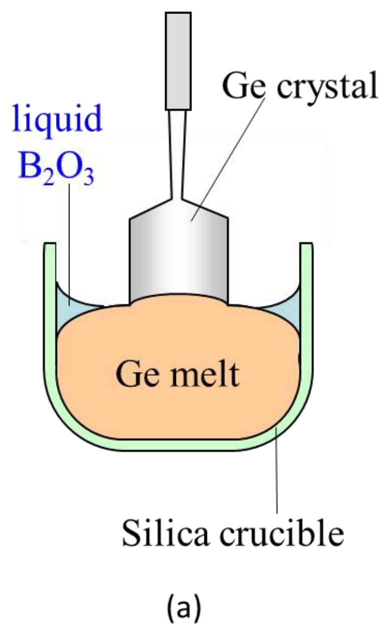
Figure captions

Fig. 1 An illustration of Ge crystal growth from a melt partially covered by B_2O_3 and (b) a photograph of a [001]-oriented undoped Ge crystal grown as shown in (a).

Fig. 2 Optical micrographs of etch pits in [001]-oriented undoped Ge crystals (a) grown from partially-B_2O_3- covered Ge melt and (b) grown by the conventional CZ method.

Fig. 3 An illustration of Ge crystal growth from a melt fully covered by B_2O_3 and (b) a photograph of a [111]-oriented Ge crystal grown as shown in (a). [Oi] in this as-grown crystal was 5.5×10^{17} cm^{-3}, and the etch pit density was less than 5×10^{2} cm^{-2}.

Fig. 4 A relationship between the [Oi] in eight crystals and their growth conditions, especially the amount of GeO_2 powder added. The inset shows typical three infrared spectra of Ge crystals grown from fully-B_2O_3-covered melt with different amount of GeO_2 powder addition around 855 cm^{-1}.



(a)

(b)

Fig. 1

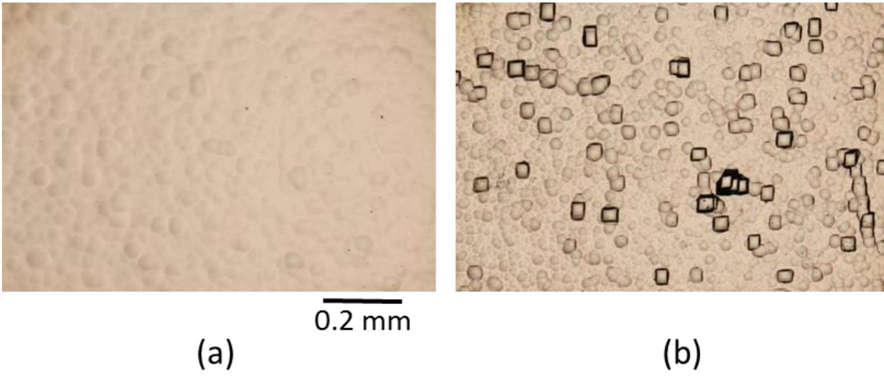
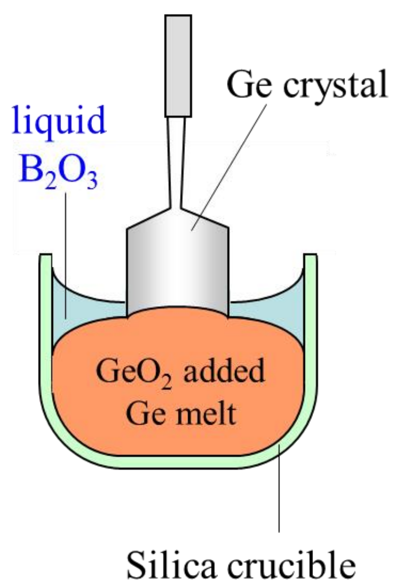


Fig. 2



(a)

(b)

Fig. 3

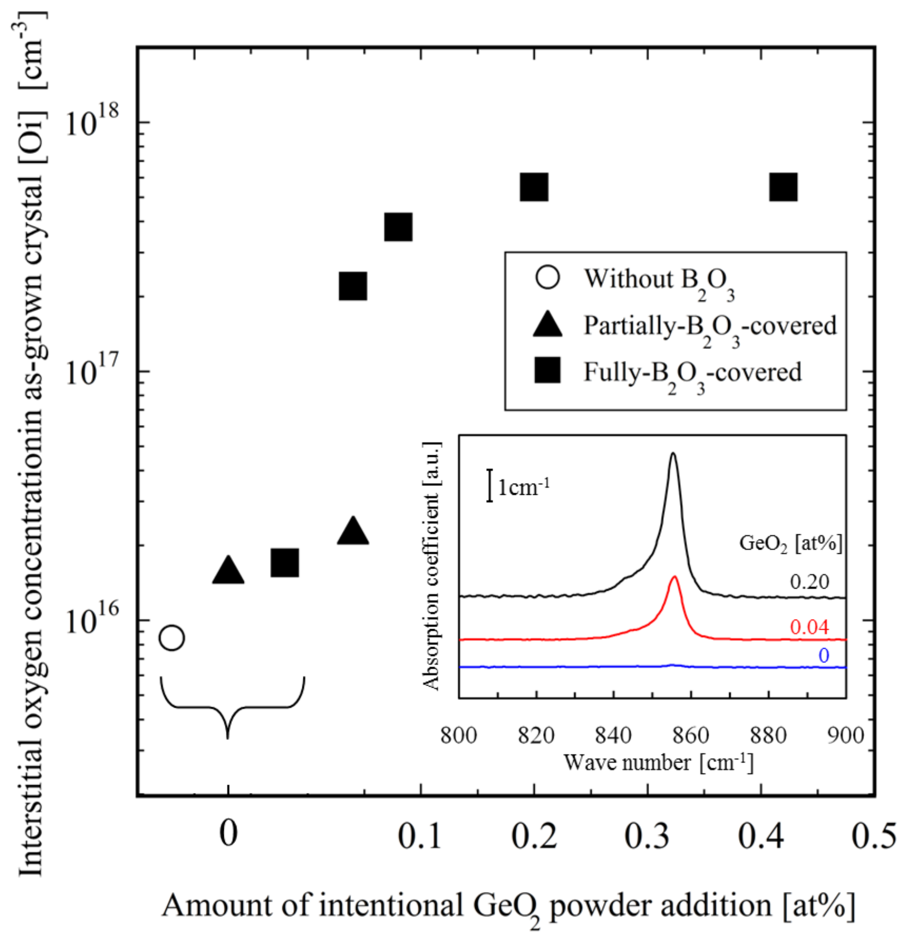


Fig. 4