

# Steady distribution structure of point defects near crystal-melt interface under pulling stop of CZ Si crystal



T. Abe<sup>a,\*</sup>, T. Takahashi<sup>a</sup>, K. Shirai<sup>b</sup>

<sup>a</sup> Shin-Etsu Handotai, Isobe R & D Center, 2-13-1 Isobe, Annaka, Gunma 379-0196, Japan

<sup>b</sup> ISIR, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan

## ARTICLE INFO

Communicated by T.F. Kuech

### Keywords:

Vacancies  
Interstitials  
Thermal gradient  
Voids  
Dislocation loops  
Growth from melt

## ABSTRACT

In order to reveal a steady distribution structure of point defects of no growing Si on the solid-liquid interface, the crystals were grown at a high pulling rate, which Vs becomes predominant, and the pulling was suddenly stopped. After restoring the variations of the crystal by the pulling-stop, the crystals were then left in prolonged contact with the melt. Finally, the crystals were detached and rapidly cooled to freeze point defects and then a distribution of the point defects of the as-grown crystals was observed. As a result, a dislocation loop (DL) region, which is formed by the aggregation of interstitials (Is), was formed over the solid-liquid interface and was surrounded with a Vs-and-Is-free recombination region (Rc-region), although the entire crystals had been Vs rich in the beginning. It was also revealed that the crystal on the solid-liquid interface after the prolonged contact with the melt can partially have a Rc-region to be directly in contact with the melt, unlike a defect distribution of a solid-liquid interface that has been growing. This experimental result contradicts a hypothesis of Voronkov's diffusion model, which always assumes the equilibrium concentrations of Vs and Is as the boundary condition for distribution of point defects on the growth interface. The results were discussed from a qualitative point of view of temperature distribution and thermal stress by the pulling-stop.

## 1. Introduction

Almost all researches on point defects in Si crystals up to the present have been conducted on the basis of Voronkov model [1], which assumes that two intrinsic point defects – vacancies (Vs) and interstitials (Is) – are generated at the growth interface with the numerical densities of the point defects in the thermal equilibrium as a boundary condition and then diffuse according to a temperature distribution in which the temperature of any crystal portion to be moved upward by pulling always decreases. It is also assumed that the Vs are dominant defects at the growth interface. In this model, the difference distribution between the numerical densities of the point defects,  $C_I - C_V$  whose signs determines the region of the dominant defect in a crystal is determined by a diffusion equation considering each diffusion coefficient, temperature dependence of each numerical density in the thermal equilibrium, recombination and pulling rate or growth rate, where  $C_I$  and  $C_V$  are numerical densities of Is and Vs respectively, that is, the number per unit volume of each point defect. The boundary of the growth condition where the signs change is also given by  $(G/V)_{Cr} = \xi_0 (=const.)$ , where  $G$  is the temperature gradient of a crystal at growth interface and  $V$  is the growth rate.

However, we recently indicated from the fundamental physical conditions that the sign of the difference distribution  $C_I - C_V$  never changes under Voronkov model [2]. This result means that the interpretations on the distributions of point defects up to this time have no physical meanings and new concepts are necessary for the interpretation on the distribution of the point defects. In particular, the formation mechanism of interstitials is one of the most important problems, because it is known from many experimental results that Vs are introduced from the only growing crystal portion at solid-liquid interface [4,5], but there are no experimental evidences for Is to have been introduced from a growing crystal portion at solid-liquid interface.

Our previous experiments, in which growing crystals were detached from a melt after growths by various growth rates until 0.1 mm/min, showed that DL regions were observed above the growth interface, that is, in the crystal, while only Vs region was in contact with the growth interface [3–5]. These experiments also reported that voids, which are secondary defects of Vs, were generated at a relatively low-temperature region, while DL regions were generated at a high temperature of 1300 °C or more in a shorter time than do the voids. This indicates the reason why a region corresponding to the Is region has been not experimentally observed at the growth interface. In the boundary between the DL region

\* Corresponding author.

E-mail address: [takao.abe@seh.jp](mailto:takao.abe@seh.jp) (T. Abe).

**Table 1**

Crystals classified by their experimental categories, stopping periods and additional heater powers to melt and so forth. Additional constant electric power was given to all the crystals except the crystals A, B and C for period from pulling-stop to finish.

Crystal	A	B	C	D	E	F	G	H	I
Detached process	Sp growth process			Melting process of Sp grown portion			Retaining process of constant diameter		
Stopping period (min)	0	10	20	40	50	80	80	120	240
Sp growth period (min)	0	10	20	20	20	30	20	20	20
Melting period of Sp grown portion (min)	0	0	0	20	30	–	30	30	40
Retaining period of Diameter (min)	0	0	0	0	0	0	30	60	180
Additional power (kW h)	0	0	0	5	5	4	6	4	3

and the Vs region, a recombination (Rc) region like belt-shape always existed until pulling rate of 0.1 mm/min. In particular, in the initial condition of Vs rich, the DL region was always surrounded by the Rc region like belt-shape. Okui et al. obtained the similar results from the detaching experiment of crystals grown by growth rates from 0.3 to 0.4 mm/min [6], though the initial condition was only Is rich.

A purpose of our experiment is to reveal a steady distribution structure of point defects in a crystal portion near the solid-liquid interface under no growing. A system where a crystal is grown by pulling cannot be regarded as a steady state in the strict sense because the size of the crystal varies over time. The steady state in the strict sense can be achieved by a system where the pulling is stopped so that the crystal does not vary in size. This system also gives a suggestion whether it can be assumed that a defect distribution of the solid-liquid interface is in thermal equilibrium. When the pulling is stopped, the maximum temperature gradient and maximum thermal stress are achieved as will be described in the discussion. Hence, this allows us to observe an extreme distribution of the point defects in a steady state to be determined by a pulling apparatus.

## 2. Experimental method

Nine crystals (conductivity type: p-type, resistivity: 10–20  $\Omega$  cm, oxygen concentration: about 20 ppm) having a diameter of about 104 mm, a length from the shoulder portion of about 210 mm, and a weight of about 5 kg were pulled, using two quartz crucibles filled with 50 kg of Si melt, that is, several crystals were pulled by each crucible. In this experimental system, growths at pulling rates of 1.0 mm/min or more, 0.5 mm/min or less, and middle range there between are respectively referred to as high-rate growth, low-rate growth, and middle-rate growth, according to types of defects to be observed. In other words, a growth rate at which only Vs regions are observed corresponds to the high-rate growth; a growth rate at which only DL regions are observed corresponds to the low-rate growth; and the middle-rate growth yields a mixed region that includes DL at the periphery and Vs at the center [4]. In the present experiment, all nine

crystals were pulled at 1.4 mm/min; this rate is higher than the pulling rate of 1.0 mm/min, which makes the entire region Vs-predominant. In the meantime, taking a point 10 mm below the shoulder portion of each crystal as a reference position, positions 0 mm, 100 mm, and 200 mm away from the reference position were respectively marked with first, second, and third markings (to be referred below as Marks 1, 2, and 3, respectively) by a method of reducing oxide precipitates using to decreasing of seed rotation to record the shape of the growth interface in the crystal as it is [4,5]. The pulling was stopped simultaneously with third marking, that is, Mark 3 is the position of the pulling-stop, while a seed rotation (28 rpm) and a crucible rotation (14 rpm) in an opposite direction were continued. After pulling-stop, the crystals were held for 0, 10, 20, 40, 50, 80, 80, 120, and 240 min until those were detached and then rapidly cooled to retain the distributions of defects in the crystals. These crystals are called A, B, C, D, E, F, G, H, and I in order of increasing period of pulling stop.

In generally, a crystal stopped suddenly pulling can continue to grow spontaneously along meniscus and melt surface, and simultaneously into the melt as the crystal tail shown in Fig. 2(b) and (c). The growth along meniscus and melt surface enlarges the crystal diameter and the growth into the melt changes the shape of solid-liquid interface. This growth is referred as spontaneous growth (Sp growth) below.

In order to restore the diameter before the pulling stop by melting of the Sp grown portion, for all the crystals except the crystals A, B and C, an additional constant electric power was continuously given to the heater of the pulling apparatus until the test of each crystal finish, as soon as the pulling was stopped. In spite of the addition of the electric power, each crystal made the Sp growth for about 20 min, because the time constant of the pulling apparatus is very long. The interval from the pulling-stop to the finish of enlarging diameter is called Sp growth process. Each crystal except the crystals A, B and C then began melting of the Sp grown portion, that is, shrinking of the enlarged diameter and finally restored nearly the diameter with the crystal length at pulling stop by about 50 min after the pulling-stop, which is called melting process of Sp grown portion (Table 1, Fig. 1). This diameter and this length restored before the pulling stop were retained until the crystal was detached, which is called as retaining process of diameter (Table 1, Fig. 1).

The crystals were classified into three groups according to the process for each crystal to be detached, that is, Sp growth process, melting process of Sp grown portion and retaining process of diameter. Table 1 shows the classification of the crystals by the conditions described above. Fig. 1 shows the time variation on the diameter of each crystal until detaching or 80 min after pulling-stop.

The crystal A was detached from the melt at the moment of pulling stop. The crystals B and C were detached from melt after the Sp growth for 10 min and 20 min, respectively. The other crystals given the additional power stopped the Sp growth after about 20 min from the pulling-stop and began shrinking those diameters, except for the crystal F. The crystals D and E were detached in the middle of the melting process at 20 and 30 min after the finish of the Sp growth process, respectively. Although the crystal F was hardly molten during the melting process, that is detached at 50 min after the finish of the Sp growth process. The crystal G was detached at 30 min after the finish of the melting process, i.e. had

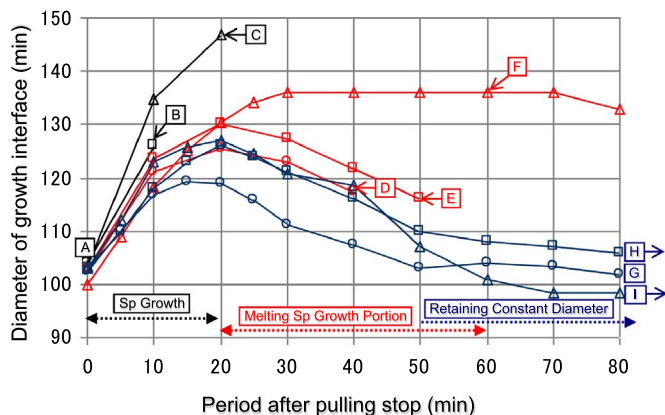
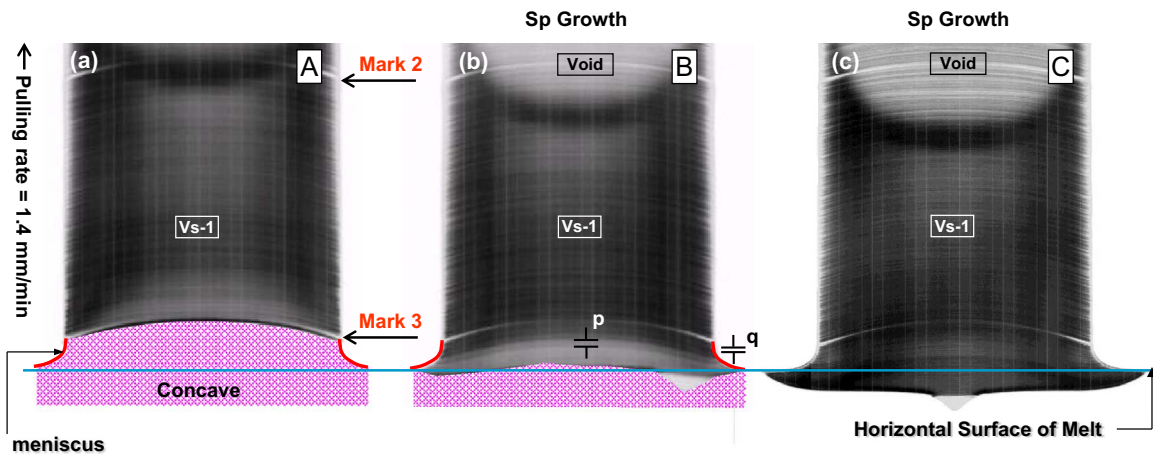


Fig. 1. Diameter changes of crystals versus stopping periods after pulling stop.



**Fig. 2.** X-ray topographs after IOP+AOP annealing of crystals A, B and C, respectively. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

the retaining process of diameter for 30 min.

Although the crystals F and G had the same pulling stop period of 80 min, the additional power could not shrink the diameter of the crystal F. Those crystals differed in the additional electric power to melt the Sp grown crystal portion and the order of the growth for which the quantity of the melt is different, because the amount of melt for the crystal growth differed in each crystal and so heating condition also differed in each crystal. It seemed that the additional power was too low to melt the Sp grown crystal portion. The crystal F was thus detached from the melt with a large crystal diameter. The crystals H and I were detached at 60 and 180 min after the finish of the melting process, respectively.

The diameter of each crystal was indirectly measured every 10 min at an interval up to detaching or 80 min after pulling-stop, through an observation window of a pulling apparatus. This diameter just before the detaching or at 80 min after pulling stop was well consistent with the value measured directly after the pulling tests.

The crystals were then sliced into wafers about 1 mm thick along a (100) plane parallel to the growth direction. These wafers were etched to remove strain caused by slicing and then polished. All of the wafers were subjected to IOP+AOP annealing (in an Ar gas, at 800 °C for 3 h+1000 °C for 16 h) to observe the distribution of defects over the entire wafer by X-ray topography. The X-ray topography allows us to identify the Vs region by black; the DL region by gray; and the belt-shaped Rc region located in the boundary there between by white contrast [3,4]. The degree of the black contrast, which represents the Vs region, is proportional to the amount of oxide precipitates generated by Vs during the above annealing. To quantify the amount of oxide precipitates by infrared absorption spectrometry, variation in the interstitial oxygen concentration before and after the IOP+AOP annealing was measured by using as a reference the interstitial oxygen concentration of as-grown wafers that were sliced out adjacently to the above specimen wafers. From this variation in the interstitial oxygen concentration, variation in the Vs concentration was measured [4]. Thus, the infrared absorption spectrometry supports that the black contrast region in X-ray topography represents the Vs region. Furthermore, an in-plane distribution of minority carrier lifetime was measured on the as-grown wafers by WLT method. It is known that an extremely low lifetime region coincides with the DL region shown by gray in X-ray topography [3,4]. This method thus supports that the gray region in X-ray topography represents the DL region. The X-ray topographs were measured with XRT micro made by Rigaku Co., Ltd., and the WLT maps were measured with WLT-2000 made by SEMILAB Co., Ltd.

### 3. Experimental results

According to the process to be detached, the crystals were classified into three groups, that is, Sp growth process, melting process of Sp grown portion and retaining process of diameter. The purpose to have

prepared the nine crystals classified to three groups is to observe time development from an initial up to a steady distribution of point defects in a crystal near solid-liquid interface.

#### 3.1. Sp growth process (crystals A, B and C)

Fig. 2 shows X-ray topographs of the respective wafers that were sliced from the three crystals A, B, and C in their growth direction after the IOP+AOP annealing. Though the portion of Mark 1 in this figure is cut, these topographs were horizontally aligned with the crystal side of Mark 3, which was made just before pulling-stop as described in the experimental method. Thus, Mark 3 also shows the shape of the growth interface just before pulling-stop. The horizontal surface of melt by the blue line and meniscus by red line, which were determined by the shape of Sp grown portion, were drawn in Fig. 2. The crystals of this group were covered by the black contrast by the Vs region except for the white contrast of the upper part that shows the void region to be formed by aggregation of vacancies. We should note that the dominant defects in the crystals are vacancies at the initial condition under the pulling rate 1.4 mm/min.

As can be seen from Fig. 2(a), the crystal A was detached from the melt immediately after making Mark 3 and then rapidly cooled. Its growth interface shape was concave, like Mark 2 at 100 mm above. The crystal B of Fig. 2(b) was detached after 10 min from the pulling-stop. Consequently, the Sp growth occurred along a meniscus, enlarging the crystal diameter over the melt surface up to 124 mm. Comparing striation intervals at the position p and the position q in Fig. 2(b), the interval at the central position p was larger than that of the position q. This indicates that the growth rate at the central portion was higher than that at the peripheral portion. The average growth rate at the central position p after pulling-stop was 1.3 mm/min. The crystal C of Fig. 2(c) made the Sp growth for 20 min after pulling-stop. It is found from Fig. 1 that after pulling-stop the crystal C had enlarged in a horizontal direction and the enlarging rate was large compared with the crystal B. Its average downward growth rate at the central portion of the growth interface was 1.4 mm/min, slightly higher than the crystal B. These results indicate that the growth interface shape was changed from concave of Mark 2 and 3 to convex, through the high-rate Sp growth, after 10 min from the pulling-stop.

Referring to the void regions shown by the white contrasts on the upper parts of the crystals, this region expanded toward the growth interface with the passage of time after pulling-stop, i.e., in the transition from the crystals A–C.

#### 3.2. Melting process of Sp grown portion (crystals D, E and F)

Fig. 3 shows X-ray topographs of the respective wafers that were sliced from the three crystals D–F in their growth direction after the IOP+AOP annealing. The topographs were horizontally aligned with

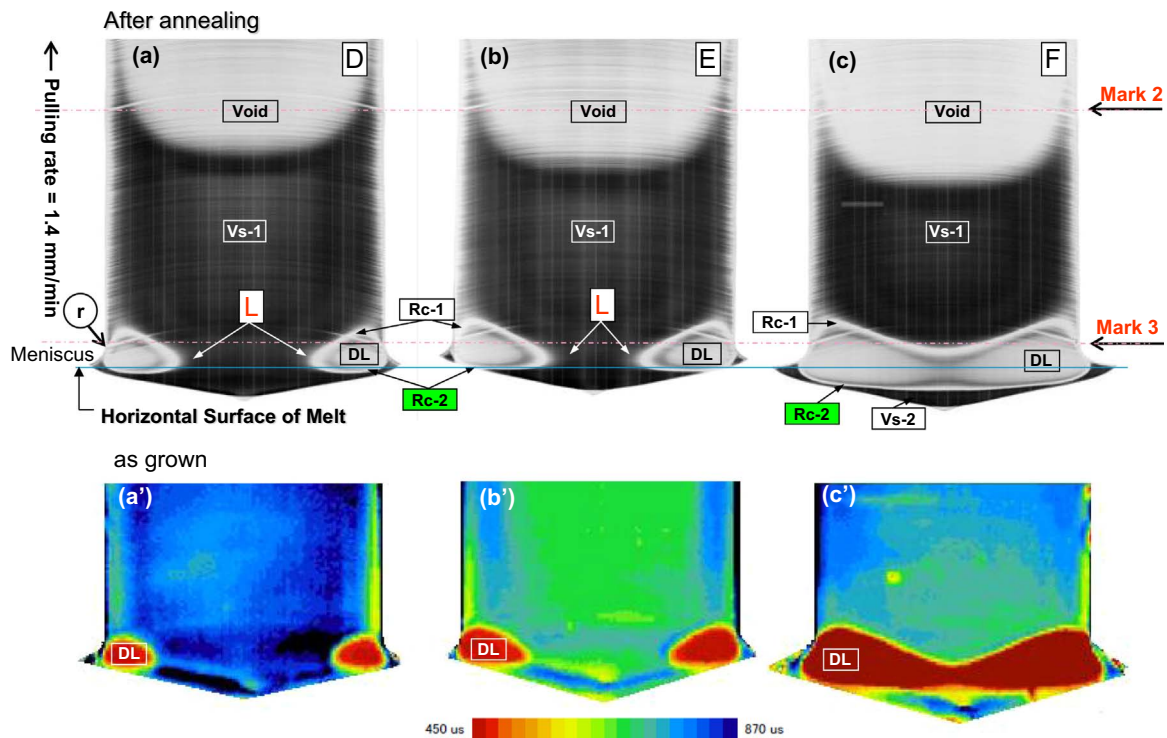


Fig. 3. (a)–(c) X-ray topographs after IOP+AOP annealing of crystals D, E and F; (a')–(c') WLT maps of as-grown wafers of crystals D, E and F, respectively.

the crystal side of Mark 3. The horizontal surface of melt by the blue line was also drawn in Fig. 3.

The crystals D, E, and F shown in Fig. 3(a)–(c), which were detached after 40 min, 50 min, and 80 min from the pulling-stop respectively, were detached in the middle of melting the Sp grown portion by the additional power, as can be seen in Fig. 1. However, the Sp grown portion of the crystal F could not be molten due to a lack of the setting power though the additional power was continuously given to the heater.

In the Sp grown portion in Fig. 3 we can see the formation process of DL region that did not exist in the Sp growth process. Thus, it is found that the DL region was formed after the finish of Sp growth, that is, the stop of the diameter extending. The crystal D of Fig. 3(a) had DL regions formed by aggregation of Is on the right and left above the solid-liquid interface, and belt-shaped Rc regions, shown by the white contrasts, surrounding the DL regions. The crystal E of Fig. 3(b) had DL regions and Rc regions, whose structure was similar to the crystal D. It is found from the diameter in Fig. 1 and the distance between Mark 3 and the bottom of the crystal in Fig. 3 that in the crystal E, however, the crystal interface was further melted upward, and the torus-shaped Rc regions were enlarged, compared with the crystal D. Consequently, this recombination, Rc-2 regions reached the solid-liquid interface. In the crystal F of Fig. 3(c), right and left DL regions and Rc regions, found in the crystals D and E, were joined.

The variation of the structure of the DL region and Rc region in the three crystals D, E, and F is apparently attributable to the time variation of the Sp grown portion. As shown by arrows L, the tips of the right and left Rc-2 regions expanded toward the center of the crystal over time. In addition, the upper void region also expanded toward the solid-liquid interface over time. The contrast of this void region had more whiteness than those at upper parts of Fig. 2(b) and (c). This indicates that isolated Vs and microscopic voids were aggregated into large void with the passage of time.

### 3.3. Retaining process of diameter after melting Sp grown portion (crystals G, H, and I)

Fig. 4(a)–(c) shows states of the distribution of the defects in the case that: the additional electric power was given to the heater to melt the

diameter-enlarged portion formed by the Sp growth after the pulling-stop and to restore the diameter and the length before the pulling-stop; the position of the solid-liquid interface at the peripheral portion of the crystal was thereby substantially restored to the pulling-stop position; and the constant interface was then left in prolonged contact with the melt. The retaining period of the crystal G after the restoration to the pulling-stop position was about 30 min; the crystal H, about 60min; and the crystal I, about 180min, from the respective starts of retaining the diameter shown in Fig. 1. All the solid-liquid interfaces for this process were slightly convex only at the central portion; As the part between Mark 3 and the solid liquid interface is a residue of the Sp grown portion, a residue of the un-melted Sp grown portion, which forms a lower part of the joined DL region and a Vs-2 region and a Rc-2 region between the both regions, was present at this central portion; the lower part of the joined DL region was continuously connected to the upper part of the joined DL region that had been grown prior to the pulling-stop. The expansion of the DL region had the following two features: (1) the thickness of the DL region was increased in vertical direction over time; (2) the shape of the upper DL boundary adjoining Rc-1 was changed from concave of the crystal G to substantially flat of the crystal I over time.

In the crystal I, slip dislocation crowd (called as SDC below) was generated between the Vs-1 region and the Void region, though the generated time is not clear. The WLT map of Fig. 4(c') showed that a region to be similar to the so-called R-OSF distribution [7] exists around a low-temperature region above the SDC in a distribution. From similarity to R-OSF distribution this was considered the generation nuclei of OSF [8–10].

## 4. Discussion

### 4.1. Temperature and stress distributions by pulling-stop and Sp growth

Sirai and Abe showed that steady temperature gradient near growth interface is in reverse proportional to pulling rate [11]. The result is explained as follows: let's consider a portion in a crystal of pulling rate  $V$  through an interval  $(z, z + \Delta z)$ , where  $z$  is the distance measured upward



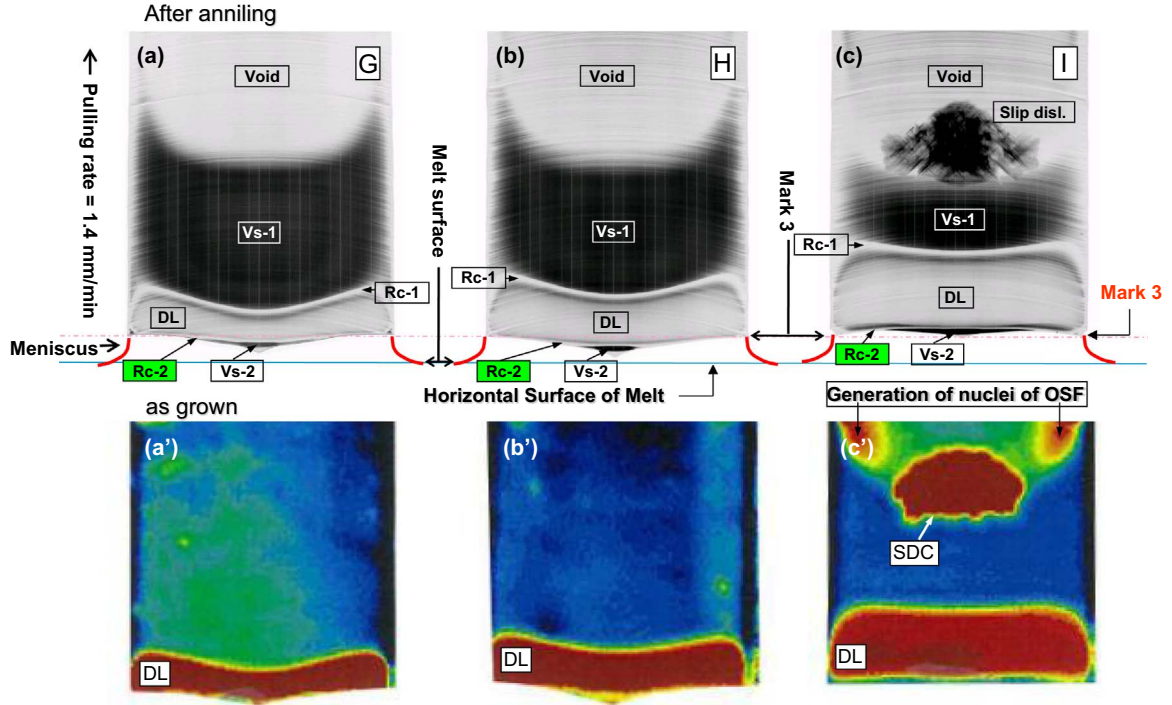


Fig. 4. (a)–(c) X-ray topographs after IOP+AOP annealing of crystals G, H and I; (a')–(c') WLT maps of as-grown wafers of crystals G, H and I, respectively.

from growth interface. The time interval  $\Delta t$  that the portion passes  $\Delta z$  is given by  $\Delta t = \Delta z/V$ .  $\Delta t$  is also the time interval that the portion is cooled at the interval  $(z, z + \Delta z)$ . In this case,  $\Delta t$  is called as cooling time. If the heat flux from the crystal surface does not change, the more the pulling rate decreases, slower, the more the cooling time increase, and as a result, the more the temperature of the portion at the interval  $(z, z + \Delta z)$  decreases. The condition on the heat flux is true because the temperature on the inner surface of a pulling apparatus is kept by only cooled water with constant temperature. When pulling of a crystal is stopped, the temperature of the portion becomes lower than that described above, because a new portion grown at growth interface, which has the melting temperature, does not pass the interval  $(z, z + \Delta z)$  and the heat sources as latent heat for crystallization do not also exist. The pulling-stop also means that no crystal portion with the high temperature, which was crystallized at the growth interface, is carry to the interval  $(z, z + \Delta z)$ , i.e. the same portion at the interval  $(z, z + \Delta z)$  is continuously cooled. Thus, when the crystal is stopped pulling, the temperature gradient near the solid-liquid interface approaches the maximum value to be determined by the pulling apparatus according as the time increases.

It is well known that thermal stress is induced by non-uniform distribution of temperature in a crystal. In isotropic elastic body, the equation of equilibrium takes the form under the non-uniform distribution of temperature and the force of gravity

$$\left(K + \frac{4}{3}\mu\right)\nabla(\nabla \cdot \mathbf{u}) - \mu \nabla \times \nabla \times \mathbf{u} = K\alpha \nabla T - \rho \mathbf{g},$$

where  $\nabla$  is the vector differential operator,  $\mathbf{u}$  the displacement vector from the uniform reference state at the melting temperature,  $K$  the bulk modulus,  $\mu$  the shear modulus,  $\alpha$  the thermal expansion coefficient of the body, the  $T$  the temperature,  $\rho$  the density,  $\mathbf{g}$  the gravitational acceleration. Therefore, when the temperature gradient has the maximum value, the thermal stress has the maximum through the strain in a crystal. It should be emphasized, however, that the diffusion of the point defects never occur in the limit of the elastic body and need the generation of plastic deformation as diffusion creep [2].

When crystal pulling is suddenly stopped and the additional electric power is given to the heater, the time variations of the crystal interface

can be explained by balance of the heat flow near the solid-liquid interface. The heat balance at an interface is given by Stefan formula. In the constant pulling rate before pulling-stop, Stefan formula satisfies  $-(\mathbf{q}_c - \mathbf{q}_l) \cdot \mathbf{n}_c = -QV \cdot \mathbf{n}_c > 0$ , where  $\mathbf{q}_c$  and  $\mathbf{q}_l$  are the heat fluxes of the crystal and the melt at the growth interface, respectively, and  $\mathbf{n}_c$  the outward normal of the crystal at the growth interface,  $Q > 0$  the latent heat per unit volume for crystallization. The sign of each heat flux is positive for the heat flow toward each material.

After the pulling stop the heat flux, i.e. the temperature gradient in the crystal approaches a certain value to be determined by the pulling apparatus with the lapse of time, if the following two effects are ignored:

- 1) the decreasing of radiation from the melt surface by enlarging of a crystal diameter and the going down of the interface position due to the Sp growth.
- 2) the going up of the interface position by melting of the Sp grown portion

These effects are called as the growing effect and the melting effect for the Sp growth. On the other hand, the heat flux in the melt near the interface approaches a certain value to be determined by an additional power with the lapse of time.

The occurrence of the Sp growth can be explained as follows. The heat balance at the solid-liquid interface after the pulling stop cannot satisfy  $(\mathbf{q}_c - \mathbf{q}_l) \cdot \mathbf{n}_c = 0$  at once, and so the Sp growth occurs at the solid-liquid interface as satisfied  $-(\mathbf{q}_c - \mathbf{q}_l) \cdot \mathbf{n}_c = RQ > 0$ , where  $R$  is the growth rate for Sp growth. The temperature gradient in the crystal near the solid-liquid interface increases with the lapse of time after pulling-stop as described above, so  $|\mathbf{q}_c \cdot \mathbf{n}_c|$  also increases. To stop the Sp growth ( $R = 0$ ) and to melt the Sp grown portion ( $RQ < 0$ ) and then to restore the diameter and the crystal length before pulling-stop ( $R = 0$ ), it is necessary that the heat flux from the melt to the crystal should be increased by a suitable additional electric power as satisfied  $(\mathbf{q}_c - \mathbf{q}_l) \cdot \mathbf{n}_c = 0$  at the retaining process of a constant diameter. However, this operation was very difficult and the only skilled operator could do it.

Now, let us consider the relation among the heat fluxes during each process after the pulling stop. It is found from the discussion described above that both the heat fluxes  $|\mathbf{q}_c^{Sp} \cdot \mathbf{n}_c|$  and  $|\mathbf{q}_l^{Sp} \cdot \mathbf{n}_c|$  ( $|\mathbf{q}_c^{Sp} \cdot \mathbf{n}_c| > |\mathbf{q}_l^{Sp} \cdot \mathbf{n}_c|$ ) at

the growth interface during the Sp growth are large compared with the heat fluxes  $|\mathbf{q}_c^0 \cdot \mathbf{n}_c|$  and  $|\mathbf{q}_l^0 \cdot \mathbf{n}_c|$  ( $|\mathbf{q}_c^0 \cdot \mathbf{n}_c| > |\mathbf{q}_l^0 \cdot \mathbf{n}_c|$ ) before the pulling stop, respectively; moreover, both the heat fluxes  $|\mathbf{q}_c^{Melt} \cdot \mathbf{n}_c|$  and  $|\mathbf{q}_l^{Melt} \cdot \mathbf{n}_c|$  ( $|\mathbf{q}_c^{Melt} \cdot \mathbf{n}_c| < |\mathbf{q}_l^{Melt} \cdot \mathbf{n}_c|$ ) during the melting process of the Sp grown portion are large compared with fluxes  $|\mathbf{q}_c^{Sp} \cdot \mathbf{n}_c|$  and  $|\mathbf{q}_l^{Sp} \cdot \mathbf{n}_c|$  respectively, because the additional power brings to  $|\mathbf{q}_c^{Melt} \cdot \mathbf{n}_c| > |\mathbf{q}_l^{Sp} \cdot \mathbf{n}_c|$  and the difference  $|\mathbf{q}_c^{Melt} \cdot \mathbf{n}_c| - |\mathbf{q}_l^{Sp} \cdot \mathbf{n}_c|$  is partly absorbed as the latent heat of the melting, and so  $|\mathbf{q}_c^{Melt} \cdot \mathbf{n}_c| > |\mathbf{q}_c^{Sp} \cdot \mathbf{n}_c|$  must be satisfied.

Finally, both the heat fluxes  $|\mathbf{q}_c^{Ret} \cdot \mathbf{n}_c|$  and  $|\mathbf{q}_l^{Ret} \cdot \mathbf{n}_c|$  under the retaining process of a constant diameter satisfy the relation  $(\mathbf{q}_c^{Ret} - \mathbf{q}_l^{Ret}) \cdot \mathbf{n}_c = 0$ . Comparing the crystal F with the crystals D and E, the crystal F suffered only the growing effect for a long time, on the other hand, the crystals D and E suffered shortly only the growing effect, but for the crystal F the height of the DL region measured from the horizontal surface of the melt is nearly equal to those of the crystals D and E, in spite of the large variation of the horizontal regions of the crystals D, E and F. Comparing the crystal G with the crystal F, the crystal G suffered both of the growing and the melting effect for the Sp growth, but the height of the DL region measured from the solid-liquid interface considered the meniscus is nearly equal to that of the crystal F described above, in spite of the large variation of heights for the crystals G, H and I.

We find from the facts described above that the growing and melting effects for the Sp growth on the distribution of the point defects are small. Thus the relations  $|\mathbf{q}_c^{Ret} \cdot \mathbf{n}_c| > |\mathbf{q}_c^{Melt} \cdot \mathbf{n}_c|$  and  $|\mathbf{q}_l^{Ret} \cdot \mathbf{n}_c| > |\mathbf{q}_l^{Melt} \cdot \mathbf{n}_c|$  should be satisfied. It is found from these considerations that the thermal stress in the crystal also increases with the lapse of time and approaches a certain value to be determined by the final temperature gradient at the steady state.

The growth interface by the Sp growth expands along a meniscus with the increase in a crystal diameter, and the crystal is simultaneously grown beneath the melt surface. The Sp growth generates latent heat and it is impossible for the solid-liquid interface beneath the melt surface to flow the heat from the side of the crystal to the melt because the temperature of the melt is increasing along all the directions in the melt. The heat is conducted only through the inner of the crystal, especially the center. Consequently the growth interface shape changes from concave to convex toward the melt.

At about 20 min after the pulling stop the heat flux satisfies  $-(\mathbf{q}_c - \mathbf{q}_l) \cdot \mathbf{n}_c = 0$ . However, as the Sp growth rate measured from Fig. 3(c) is still high, i.e. the thermal stress is still small for the generation of the Is, and so the entire Sp grown portion becomes Vs region.

With regard to the crystal F, the Sp grown portion was hardly melted although the Sp growth was stopped after about 30 min from the pulling-stop (Fig. 1). On other hand, the Sp growths of the crystals G, H and I were stopped after about 20 min from the pulling-stop, and the melting of the Sp grown portions was completed within 40 min after the stopping of the Sp growth. The difference between the crystal F and crystals G, H and I was caused by that between the only conditions of the additional power and the pulling order.

In the melting process, Is are continuously generated at the Sp grown portion mainly and the already-grown portion partly. The DL regions that were separately generated on right and left at first are enlarged over time and finally joined into one region (Fig. 3). This DL region is characterized by being surrounded with a belt-shaped Rc-region. However, if an initial condition of pulling rate is low, that is, Is rich, a belt-shaped Rc-region appears at the only boundary between the DL region and the Vs region at the solid-liquid interface [6]. This is the reason why there are no Vs recombined with the Is. Thus we find the belt-shaped Rc-region is formed by the recombination between the Vs and Is. This belt-shaped Rc-region is not uniform and varies in thickness with site.

The change of the distribution of the point defects near the solid-liquid of the crystals G, H, and I under the melting process of the Sp grown portion and the diameter retaining process after the melting process is considered as follows: the Sp grown portions of the crystals G, H, and I were melted more than those of the crystals D and E by the additional

power; and then the crystals was retained for a long time with a constant diameter. However, the DL regions of the crystals G and H are similar to that of the crystal F, which was hardly melted; the central portion at the upper boundary of the DL region is convex downward. Also, these DL regions have almost the same vertical thickness. The distribution of the DL for the crystal F was formed at the interval between 30 min and 80 min after the pulling-stop, that is, by 50 min after the finish of the Sp growth at longest (Fig. 1), because the DL region was not formed during the Sp growth (Fig. 2). The distributions of the DL for the crystals D and E were formed by 20 min and 30 min after the finish of the Sp growth, respectively. However, the Sp grown portion of the crystal G was completely molten by 30 min after the finish of the Sp growth and so the position of the cylindrical surface at the solid-liquid interface was restored before the pulling-stop (Fig. 1). Therefore, the variation of the DL region from the crystals D and E to the crystal G was carried out by about 30 min, that is, the joined DL region of the crystal G was formed by about 50 min after the Sp growth was stopped. This time is consistent with the fact that the crystal F had a joined DL region formed in about 50 min after the Sp growth was stopped, though the crystal F was hardly molten.

The crystal H passed about 60 min, the crystal I passed about 180 min under the retaining process of diameter which is no growing after completion of melting the Sp growth portion. Moreover, these time intervals are very longer than that of formation DL region, i.e. about 20 min. Thus, we can conclude that the distribution of the point defects near the solid-liquid interface of the crystals G, H and I was in steady state.

The solid-liquid interfaces of the crystals G, H, and I after the retaining process of diameter had partly an area where the Rc-2 region is in direct contact with the melt, unlike the growth interface that have been growing.

In summary, the following two phenomena occur:

- 1) The Is are generated above the solid-liquid interface and formed into a DL region even during melting the crystal and during long-term pulling-stop.
- 2) The obtained solid-liquid interface has partly an area where the Rc-2 region, which hardly contains point defects Vs and Is, is in direct contact with the melt.

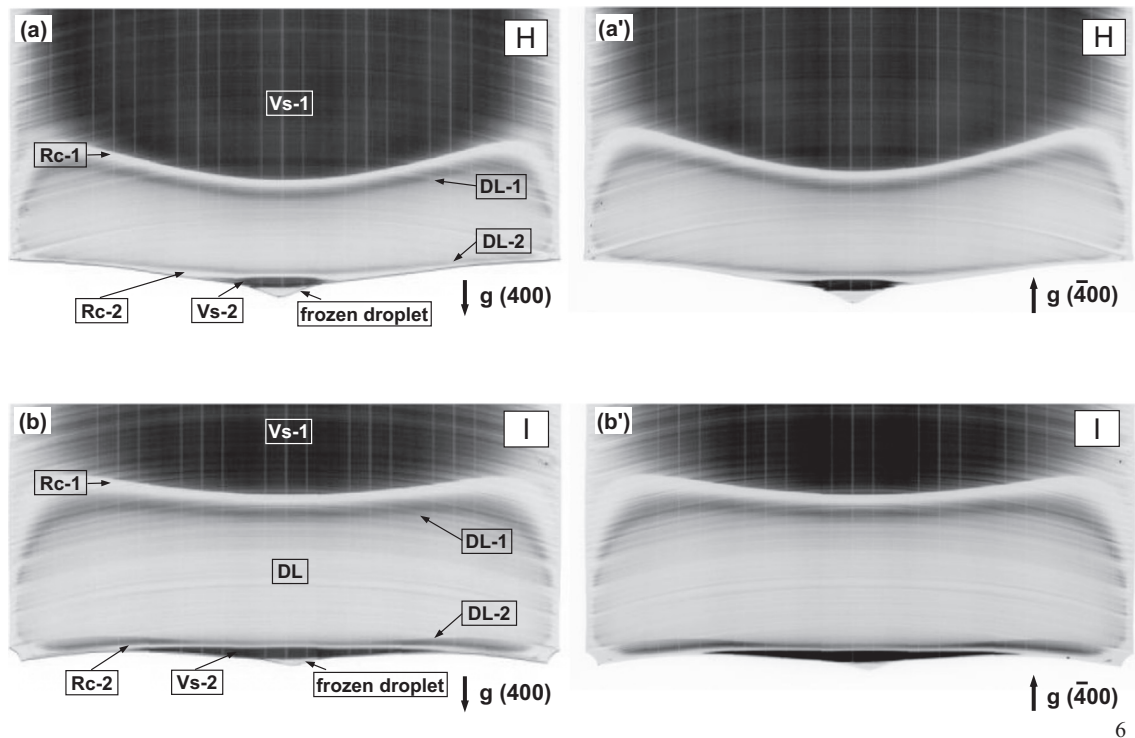
These two phenomena will be discussed below.

#### 4.2. Interstitial generation during melting and pulling-stop

Fig. 5(a) and (b) are enlarged views showing the DL regions above the solid-liquid interfaces of Fig. 4(b) and (c), respectively. These figures indicate that, in the present experiment, i.e., in case of pulling-stop, the DL region generated near the growth interface expands upward; as well as in case of continuing the growth, such as low-rate growth [4] or growth at a gradually decreasing growth rate [5], where the DL region was considered to be formed by accumulating DL regions generated near the growth interface during the growth, according to an IGA mechanism [4,5]. Given this thought, the upper DL region adjoining the Rc-1 and the lower DL region adjoining the Rc-2 are distinguished into DL-1 and DL-2, respectively. The expansion of the DL region is likely to be caused by the DL-1 region that progresses upward. Fig. 5(a) and (b) show a state where the DL region is just being formed by the progress of DL-1. This phenomenon appears to occur as follows:

Pulling-stop causes a maximum thermal stress through a maximum temperature gradient near the solid-liquid interface at the upper part of the crystal as described above, thereby causing. When the thermal stress exceeds the elastic limit at a region, interstitials are generated to relax the thermal stress at the region and then diffuse into a region. As a result, by the generation and the recombination of interstitials, the DL-1 region apart from the solid-liquid interface expands upward over time, in order of the crystals G, H, and I, while the upper shape of the DL region is changed from convex of the crystal G to flat of the crystal I.

Although Is have been considered to be generated at a high



**Fig. 5.** (a) and (b) Enlarged topographs of Fig. 4(b) and (c) for which (400) plane perpendicular to growth direction is used; (a') and (b') enlarged topographs of Fig. 4(b) and (c) for which (−400) plane is used.

temperature of 1300 °C or more, the present experimental result demonstrate that Is can be generated at a lower temperature of 1200 °C or thereabout.

To relax the thermal stress, Is are generated. One may consider the possibility of diffusing Is generated in the DL-2 region into the upper DL-1 region, which is a low-temperature region. However, such a long-distance diffusion is impossible since the Is are formed into a secondary defect, i.e., DL, as soon as they are generated.

#### 4.3. Rc-2 region in direct contact with melt

In the previous section, we described the reason why the DL-1 region is formed. More specifically referring to inner and outer structures of the DL regions in the X-ray topographs of the crystals D, E, F shown in Fig. 3(a)–(c), each DL region has a gray middle portion edged with dark gray. Outside the DL region is present a Rc-region, which hardly contains Vs and Is: the solid-liquid interface side is referred to as Rc-2, and the upper side is referred to as Rc-1. These Rc regions are a region obtained by only recombination of Vs and Is, because the Rc-1 does not appear at the low growth rate where the initial condition is Is rich except the growth interface [6]. The Rc regions, which hardly contain defects, are shown by the white contrasts in the X-ray topographs since they have no lattice strain, which induces oxide precipitates after the annealing. The vertical width of the Rc-regions is broader at Rc-1 and narrower at Rc-2. This difference is attributable to the variation in the Is generation rate in the DL regions [5]. In the DL region near the solid-liquid interface, which has a large temperature gradient and thus a large thermal stress, Is are considerably generated. These Is are recombined with Vs that exist at a constant concentration without appearing and disappearing and has a finite small quantity without supply by the growth. Thus the recombining region advances to the solid-liquid interface, and so the width of the Rc-2 region is reduced.

A part of the Rc-2 region in the crystal E of Fig. 3(b) is in direct contact with the melt, not via the Vs region. Essentially, the DL region is not directly in contact with the melt, that is, the Rc-2 region exists there between, for the thermal stress is substantially zero at the side face of the

crystal and at the solid-liquid interface. We consider the reason why the Rc-2 region exists with a finite width at the side face and the solid-liquid interface is that Is are fixed as secondary defects in the DL region after generation and difficultly diffuse into the Rc-2 region.

Fig. 5(a) and (b) are enlarged views of Fig. 4(b) and (c), respectively. The solid-liquid interface side of the Rc-2 region is edged with the black contrast. In the X-ray topographs of Fig. 5(a') and (b'), on the other hand, the solid-liquid interface side of the Rc-2 region is not edged with a clear black contrast. This difference is attributable to the difference in reflection vector  $\mathbf{g}$ . Fig. 5(a) and (b) are X-ray topographs in which ray was entered from the solid-liquid interface side and emitted toward the interface side, i.e., the reflection vector  $\mathbf{g}$  is directed in a growth direction. By contrast, the reflection vector  $\mathbf{g}$  in Fig. 5(a') and (b') is in a direction opposite to the growth direction. Since the side of the sample of the solid-liquid interface has a thickness of about 0.8 mm, the reflection intensity in X-ray diffraction topography depends on the reflection vector  $\mathbf{g}$  [12]. This indicates that the Rc-2 region has so perfect crystallinity, more than those of the Vs region and the DL region, that the method combining IOP+AOP annealing and X-ray topography is difficult to discriminate the boundary between the crystal and a space where no crystal exists. The region in direct contact with the melt consists of two parts, one is the Rc-2 region with perfect crystallinity and the other is the un-melted Vs region at the central portion of the Sp grown portion. The crystals G, H, and I, which were stopped from growing for a long time and were in a steady state, do not have solid-liquid interface that is only Vs region assumed by Voronkov model [1]. On the contrary, the solid-liquid interface has partly the region that hardly contains point defects.

In particular, we did not discuss the distributions like generation nuclei of the R-OSF and the SDC in Fig. 4, these are the subjects in the future.

## 5. Conclusion

We obtained the following results through the previous experiments {3,4,5}; Vs are introduced into a crystal at a concentration from growth interface regardless of the growth rate as long as the crystal is grown. The Vs are retained as voids in the crystal unless they are recombined

with Is. In the meantime, Is are generated above the growth interface to relax a thermal stress that is increased with a decrease in pulling rate, and rapidly agglomerated to form a DL region. At a finite growth rate, the Vs region exists right above the growth interface, and a belt-shaped recombination region always surrounds the entire DL region when the DL region exists in the Vs region.

However, in the present experimental condition where the pulling was stopped, i.e., the growth rate is zero, a maximum temperature gradient is achieved in the system, and a steady distribution of points defect near the solid-liquid interface exhibits the following two features:

- 1) The DL region is always surrounded by a belt-shaped Rc-region under the initial condition to be Vs rich;
- 2) The crystal can have a defect distribution in which the Rc-region is partly in direct contact with the melt.

This conclusion apparently contradicts Voronkov's diffusion model.

## References

- [1] V.V. Voronkov, *J. Cryst. Growth* 59 (1982) 625.
- [2] T. Takahashi, T. Abe, K. Shirai, *J. Cryst. Growth* 449 (2016) 166.
- [3] T. Abe, T. Takahashi, *J. Cryst. Growth* 334 (2011) 16.
- [4] T. Abe, T. Takahashi, K. Shirai, X.W. Zhang, *J. Cryst. Growth* 434 (2015) 128.
- [5] T. Abe, T. Takahashi, K. Shirai, *J. Cryst. Growth* 436 (2015) 26.
- [6] M. Okui, T. Tanaka, T. Kanda, T. Ono, Oyobuturi (Appl. Phys.) 66 (1997) 703 (in Japanese).
- [7] M. Hasebe, Y. Takeoka, S. Shinomiya, S. Naitou, in: K. Sumino (Ed.), *Defect Control in Semiconductors*, North Holland, 1990, p. 157.
- [8] K. Sueoka, A. Akatsuka, K. Nishihara, T. Yamamoto, S. Kobayashi, *Mater. Sci. Forum* 196–201 (1995) 1737.
- [9] S. Sadamitsu, M. Okui, K. Sueoka, K. Marsden, T. Shigematsu, *Jpn. J. Appl. Phys.* 34 (1995) 1597.
- [10] K. Harada, H. Furuya, M. Kida, *Jpn. J. Appl. Phys.* 36 (1997) 3366.
- [11] K. Shirai, T. Abe, *J. Cryst. Growth* 351 (2012) 141.
- [12] A. Authier, *Dynamical Theory of X-Ray Diffraction*, Oxford University Press, Oxford, 2001.