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

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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 disscussed 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

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 protion			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 grwon 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 Ω cm, oxygen concentration: about 20 ppma) 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

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

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 m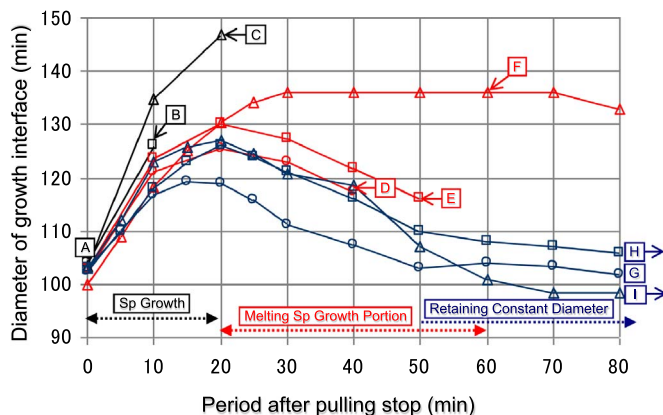in after the finish of the melting process, i.e. had