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Effects of Grown-in Hydrogen on Electrical Properties of Czochralski Silicon Crystals

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We recently showed the presence of residual hydrogen contamination (grown-in H) in commercially available as-grown Czochralski silicon (CZ Si) ingots at 10^{11} cm^{-3} [1,2]. In this paper, we studied the effects of grown-in H on the electrical properties of CZ Si crystals.

We used 4-inch as-grown ingots supplied from three wafer vendors (table 1). The ingots were grown without hydrogen doping. We confirmed the presence of grown-in H in the ingots. Details of this method have been described elsewhere [1,2]. Figure 1 shows the order of our experiments. We performed all annealing in dry-oxygen or nitrogen gas. We prepared 10-mm and 1-mm thick crystals from the ingots. We prepared both samples from same region of the ingot to avoid differences in oxygen and carbon content, and in thermal history. First, we annealed them at 750°C for 5 minutes to eliminate the thermal donors (TDs) formed during crystal growth. The CZ Si ingots are annealed at a low temperature (<500°C) for a long time during crystal growth. To study how the quality of CZ Si crystals is influenced by grown-in H and in situ annealing at a low temperature during crystal growth, we annealed the crystals at 425°C for 6 hours, for simplicity, to simulate low temperature thermal history during crystal growth. We prepared 800 μm thick wafers from 1-mm crystals (wafer A), and from the surface (wafer B) and the middle (wafer C) of a 10-mm thick crystal. We then annealed them at 600°C for 30 minutes to eliminate TDs formed during annealing at 425°C for 6 hours.

We measured distribution of lifetimes of wafers A, B, and C using a non-contact microwave system at room temperature (SEMILAB Lifetime Scanner WT-85) with chemical passivation of surface state. The average lifetimes of the wafers were also obtained by using software. Figure 2 shows the average lifetime of each wafer. Wafer A has the largest lifetime, followed by wafer B, and wafer C has the shortest. Figure 3 shows the distribution of the lifetimes of wafers A and C along the radius. In wafer C, the lifetime increases with the radial distance. At its edge, it has three times the lifetime than at its center. Conversely, wafer A has a fairly uniform lifetime of about 2300 μs. This indicates that the density of recombination centers in the innermost region of the 10-mm thick crystal is highest, and that the density decreases with the distance from the center. We annealed wafers C at between 750 and 900°C for 15 minutes, to study the thermal stability of the recombination center (dissociation annealing). The lifetime increased after annealing at above 800°C, as shown as solid line in Fig. 4. This indicates the elimination of the recombination center. We again annealed wafer C and wafers C with dissociation annealing to precipitate oxygen at 700°C for 72 hours, and measured the interstitial oxygen by infrared (IR) measurement. Results are shown in Fig. 4 as a dashed line. The amount of oxygen precipitation decreased by annealing at above 800°C, indicating the elimination of oxygen precipitates nuclei.

Grown-in H out-diffuses from 1-mm thick crystals during annealing at 750°C for 5 minutes because the hydrogen partial pressure in ambient gas is zero. It is also because the diffusion length of H during the annealing is 1.1-mm. However, the grown-in H in the innermost region of 10-mm thick crystals remains, due to the long distance from the surface. In the surface region of 10-mm thick crystal, the amount is lower than in the innermost region. However, it is higher than in the 1-mm thick crystal due to the flow of H from the innermost region to the surface. We recently found that the concentration of grown-in H decreased with increasing distance from center along the radius [3]. These show that the lifetime increases with decreasing grown-in H concentration. The annihilation temperatures of the recombination center and the oxygen precipitates nuclei are nearly equal, which indicates that origin of recombination centers and oxygen precipitates nuclei are same defects. It is known that hydrogen enhances oxygen diffusion, and this lead to the increased formation of oxygen-related aggregates such as TDs and carbon-oxygen complexes [4]. This effect is pronounced with hydrogen concentration [2,4]. The thermal stability of the recombination center is higher than in TDs. Therefore, we think that oxygen-related aggregates, whose formation are enhanced by grown-in H and which have higher thermal stabilities than that of TDs, act as a recombination center and nuclei of oxygen precipitates.

In summary, we studied the influence of grown-in H on the quality of the CZ Si crystal. Grown-in H degrades the electrical properties of the CZ Si crystal by enhancing the formation of recombination centers. The recombination centers have high thermal stabilities and are related with small oxygen aggregates acting as nuclei of oxygen precipitates. Reducing the hydrogen concentration in the ingot during crystal growth is important in improving the quality of CZ Si crystals.

[1] A. Hara et al. : 1993 SSDM p.1014. [2]A. Hara et al. : Proceeding of the 20th UCS symposium, p.110. [3] A. Hara et al. : The 41th Spring Meeting of Japan Society of Applied Physics 1994, 29p-ZD-5. [4] R.C. Newman et al. : J. Appl. Phys. 70, 3061 (1991). * present address Fujitsu Lab. Ltd. 10-1 Morinosato-Wakamiya, Atsugi 243-01, Japan TEL 0462-48-3111 (EXT. 3611) FAX 0462-48-5192

Table 1 Samples

Ingot	Type	Resistivity (ohm-cm)	Oxygen (x10^{18}cm^{-3})	Carbon (x10^{17}cm^{-3})
I	N	40	1.5	< 1
II	P	20	1.5	< 1
III	P	10	1.5	< 1

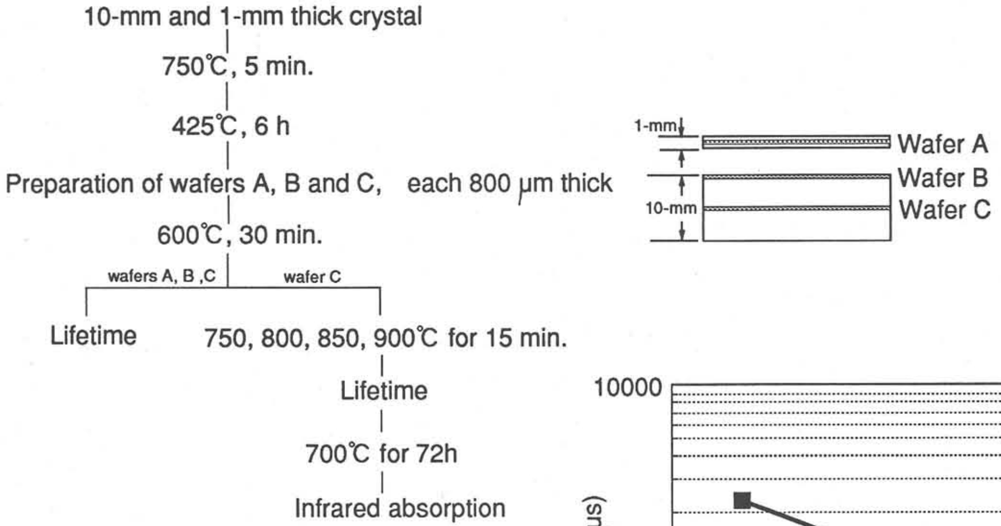

Fig. 1 Experiments

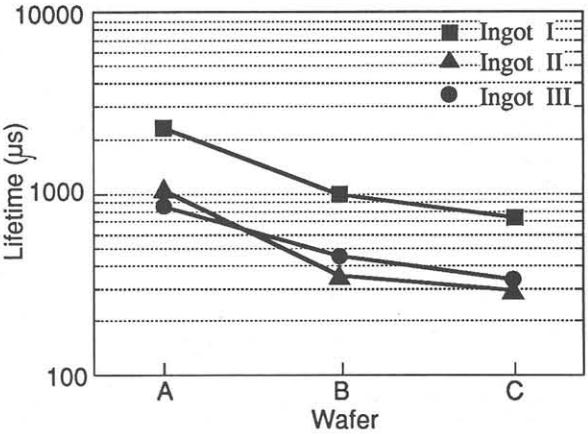

Fig. 2 Average lifetimes in wafers A, B, and C.

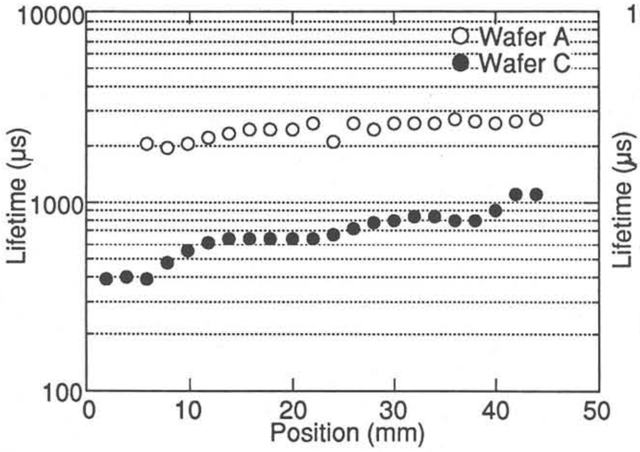

Fig. 3 Distribution of lifetimes along the radius. Ingot I was used.

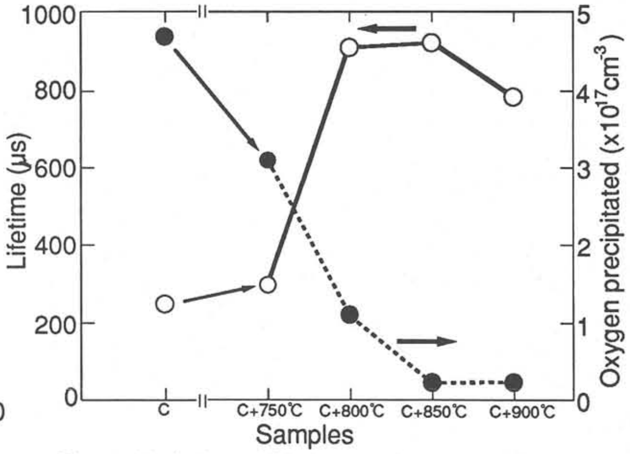

Fig. 4 Variation of lifetime and amount of oxygen precipitation on Ingot III. Lifetimes of wafer C and wafers C with dissociation annealing are shown (open circle). The amount of oxygen precipitation of wafer C and wafers C with dissociation annealing, after annealing at 700℃ for 72 hours, are shown (solid circle).