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# Growth and characterization of *n*-type polycrystalline silicon ingots

Koji Arafune *, Mami Nohara, Yoshio Ohshita, Masafumi Yamaguchi

*Toyota Technological Institute, 2-12-1 Hisakata, Tempkaku, Nagoya 468-8511, Japan*

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ABSTRACT

*n*-type polycrystalline silicon ingots were grown by directional solidification, and the grown ingots were sliced to wafers. The wafers were subjected to phosphorus gettering and hydrogen passivation. The minority carrier lifetimes of wafers before and after the processes were measured. The average lifetimes of the wafers after both the processes were improved by a factor of 2–3 times compared to those of as-grown wafers. The wafers were etched with a Secco solution to detect crystallographic defects. The effect of phosphorus gettering in the region where many etch-pits were observed is lower than that in the other region. On the contrary, the effect of hydrogen passivation in the region where many etch-pits were observed is higher than that in the other region.



## 1. Introduction

Crystalline silicon solar cells mainly use *p*-type polycrystalline silicon (pc-Si) and single crystalline silicon wafers doped with boron. However, a serious problem was observed in solar cells made of B-doped *p*-type silicon. The performances of the solar cells degrade by exposure to light. It could be attributed to the formation of boron–oxygen complex, which is highly recombination active [1]. A simple solution to the degradation problem is to use *n*-type silicon. In addition, *n*-type Si was reported to be a high-diffusion-length material due to the reduced recombination activity of metal impurities compared to *p*-type silicon [2]. Therefore, recent solar cell research has focused on material and process requirements for *n*-type solar cells. In fact, the researches and developments of solar cells based on *n*-type Si substrates become active within 2–3 years, and several solar cell structures, such as boron-diffused emitter type, aluminum-alloyed emitter type, and amorphous silicon hetero-junction type, have been reported. However, the roles of impurities and defects in *n*-type pc-Si were still unknown. In this study, *n*-type pc-Si ingots were grown by the directional solidification technique. The wafers sliced from the grown ingot were subjected to phosphorus gettering and forming gas annealing to reduce impurities and defects. Then effectiveness of both processes on the improvement of pc-Si quality was discussed through minority carrier lifetime measurements.

## 2. Experimental procedure

The growth experiment was carried out in the traveling heater furnace. The silicon feedstock we used in the present study was off-specification of electronics grade feedstock. The feedstock with phosphorus as *n*-type dopant was melted in a quartz crucible coated with $Si_3N_4$. Argon gas was passed from the top of the furnace to avoid contamination from the gas phase. *n*-type pc-Si ingots were grown by the successive relaxation of supercooling method that was developed by the authors [3]. The resistivity of the ingot was from 4 to 1 Ω cm. The grown ingot was cylindrical in shape with a diameter of 15 cm and a height of 10 cm. The grown ingots were vertically cut into two half-cylinders. Then the half-cylinder was cut and sliced to $5 \times 5$ cm$^2$ wafers with a thickness of 300 μm. Saw-induced damage layers were etched in a mixture of nitric and hydrofluoric acids. The distribution of minority carrier lifetime was measured with a spatial resolution of 1 mm using the laser/microwave photoconductance decay (μ-PCD) method. The wafer surface was passivated with iodine–ethanol solution for lifetime measurements. In order to remove metal impurities, the wafers were subjected to phosphorus gettering by $POCl_3$ diffusion. The phosphorus diffused layers with a sheet resistance value of about 40 Ω/sq. were etched before lifetime measurements. Furthermore, the gettered wafers underwent a forming gas (90% $N_2$, 10% $H_2$) annealing to reduce the recombination-active defects by hydrogen passivation. The processed wafers were etched with a Secco solution [4] for 5 min to evaluate the distribution of defects. Crystallographic orientation analysis was performed using the electron backscatter diffraction (EBSD) measurements.

## 3. Results and discussion

The resistivity of the ingot is slightly lower than what we expected. It is well known that the $Si_3N_4$ coating material dissolved into molten silicon during crystal growth. Therefore, we considered that a part of dissolved nitrogen act as *n*-type dopants. Fig. 1 shows dopant concentration distribution as a

* Corresponding author at: Division of Environment and Energy, Department of Mechanical and system Engineering, University of Hyogo, 2167 Shosha, Himeji 671-2280, Japan. Tel./fax: +81 79 267 4845.
*E-mail address:* arafune@eng.u-hyogo.ac.jp (K. Arafune).

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function of fraction solidified, $z$. Here, $z = 0$ and 1 correspond to the bottom and top of the ingot, respectively. Closed circles are dopant concentrations estimated using the measured resistivity. The lines are calculated concentrations using Scheil's equation. Here, we used the values of the segregation coefficients of nitrogen and phosphorus as 0.0007 and 0.35 [5], respectively. The initial phosphorus concentration is determined using charged phosphorus concentration. The calculated result indicates that nitrogen concentration at the bottom of the ingot is about $2.5 \times 10^{14}$ atoms/cm$^3$, and the nitrogen concentration exceeds its solubility limit near the top of the ingot. It is ensured by the fact that $Si_3N_4$ precipitates were observed at the top of the ingot. Therefore, it could be considered that nitrogen plays a role of the dopant. Since the size of the crucible used in this study is small compared with the industry scale, the dissolution of nitrogen could not be negligible. However, even in the industrial case, the effect of nitrogen on the carrier concentration becomes large because of the shortage of silicon feedstock. Usually, the peripheral region of the grown ingot is cut off due to higher impurity concentration, and the cut-off region is used again as a feedstock. Therefore, nitrogen concentration in molten silicon increases and affects carrier concentration.

Fig. 2 shows average lifetime distributions of the as-grown, phosphorus gettered, and forming-gas-annealed samples as a function of fraction solidified. Regarding the as-grown samples, the average lifetimes at the middle of the ingot were about 60 μs. The lifetimes at the top and bottom of the ingot show low values due to the high concentration of metal impurities compared to those at the middle. The average lifetimes at the middle of the ingot after phosphorus gettering were about 120 μs. After phosphorus gettering and forming gas annealing, the average lifetime was improved by a factor of 2–3 times compared to that of the as-grown samples.

To clarify the effect of both processes on lifetime, we defined the following equations:

$$\frac{1}{\tau_{FGA}} = \frac{1}{\tau_{bulk}} \tag{1}$$

$$\frac{1}{\tau_{P\text{-}getter}} = \frac{1}{\tau_{bulk}} + \frac{1}{\tau_{defect}} \tag{2}$$

$$\frac{1}{\tau_{as\text{-}grown}} = \frac{1}{\tau_{bulk}} + \frac{1}{\tau_{defect}} + \frac{1}{\tau_{impurity}} \tag{3}$$

Here, $\tau_{FGA}$ is lifetime of both the phosphorus gettering and the forming gas annealing processed sample. $\tau_{P\text{-}getter}$ is lifetime of the phosphorus gettering processed sample. $\tau_{as\text{-}grown}$ is lifetime of the as-grown sample. $\tau_{defect}$ is the Shockley–Read–Hall (SRH) lifetime of the defects that were neutralized by forming gas annealing. $\tau_{impurity}$ is the SRH lifetime of impurities removed by phosphorus gettering. Using Eqs. (2) and (3), $\tau_{impurity}$ can be obtained. In the same way, $\tau_{defect}$ can be obtained using Eqs. (1) and (2). The effective trap density, $N^*$ [1/μs], is defined as follows:

$$N^* = \frac{1}{\tau} \tag{4}$$

The effective trap density is calculated at each measurement point. Fig. 3 shows the averaged effective trap densities of removed impurities, $N^*_{impurity}$, neutralized defects, $N^*_{defect}$, and remained bulk defects, $N^*_{bulk}$, as a function of the fraction solidified. $N^*_{impurity}$ and $N^*_{defect}$ mean the degree of improvements by the phosphorus gettering and forming gas annealing, respectively. $N^*_{impurity}$ at the bottom and top of the ingot are higher than those at the middle of the ingot. Assuming that metal impurity removed by phosphorus gettering was iron, the removed iron concentration was estimated using traditional Shockley–Read–Hall statistics and using energy level and capture cross-section for interstitial iron [6]. The removed iron concentrations in the bottom, middle, and top regions were about $1 \times 10^{14}$, $4 \times 10^{12}$, and $1 \times 10^{15}$ atoms/cm$^3$, respectively. These values are almost the same as those in $p$-type pc-Si ingot grown by the SRS method. Regarding

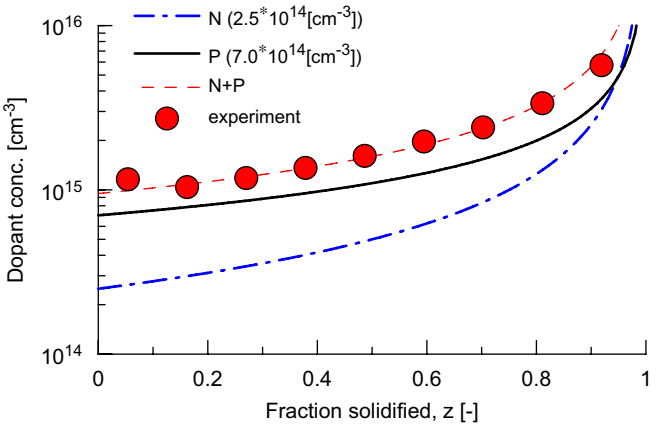


**Fig. 1.** Estimated and calculated dopant concentration distribution.

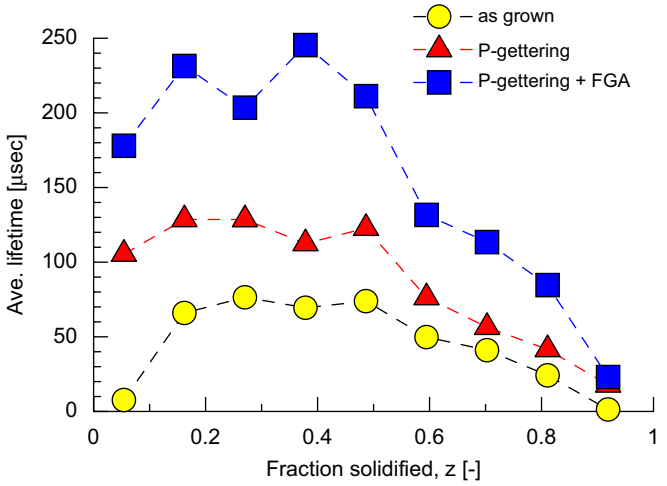


**Fig. 2.** Average lifetime distributions of as-grown, phosphorus gettered, and forming-gas-annealed wafers.

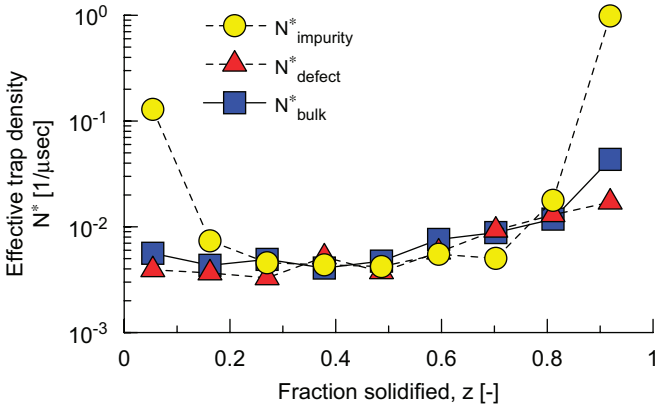


**Fig. 3.** Averaged effective trap density of removed impurities, neutralized defects, and remained bulk defects as a function of fraction solidified.