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Effects of defects and impurities on minority carrier lifetime in cast-grown polycrystalline silicon

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Abstract

The grain size distribution of B-doped cast-grown polycrystalline Si could not explain the minority carrier lifetime map. The lifetime was not mainly determined by the grain boundary recombination, since the grain size of the present cast-grown polycrystalline Si exceeded 1 cm and was large enough as compared with the minority carrier diffusion length (0.25 μm). In the region where lifetime was relatively short, there were many defects, which appeared as etch-pit by the Secco etching. The relationship between the etch-pit density and the minority carrier lifetime suggested that these defects acted as a recombination center and that they mainly determined the lifetime. There were many C atoms ($>10^{17}\,cm^3$), which exist as substitutional impurities, in the as-grown wafer. The thermal annealing induced the C segregation, which might deteriorate the solar cell performance through the cell fabrication processes.

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Keywords: A1. Segregation; A1. Cast; A2. Growth from melt; B2. Semiconducting silicon; B3. Solar cells

1. Introduction

Recently, the solar cell industry is growing at about 20% per year and crystalline silicon (Si) solar cells become dominant. Especially, the polycrystalline Si cells are exceeding 50% in the crystalline solar cell market, because the polycrystalline Si wafer is low cost, and relatively better conversion efficiencies can be achieved. Therefore, to improve the conversion efficiency and to reduce the cost, the polycrystalline Si solar cells are more important for the further growth of the solar market. So far, since the grain boundary acts as recombination centers and determines the solar cell performances of polycrystalline Si, increasing the grain size of polycrystalline Si

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crystal has improved the conversion efficiency [1–4]. Now, the cast-grown Si, which has a significantly larger grain size exceeding 1 cm, was obtained. Since the grain size is large enough as compared with the minority carrier diffusion length, the high conversion efficiency over 20% can be expected. However, it has not been achieved. This result indicates that the grain boundaries do not play an important role in deteriorating the solar cell performances, and that the defects and impurities in a grain determine the conversion efficiency. Therefore, to improve the solar cell performances of the cast-grown polycrystalline Si, it is important to understand the effects of defects and the impurities in the grain on the electrical properties and to reduce the amounts of those that strongly decrease the conversion efficiency.

In the present work, we studied the effects of defects and impurities in the grain on the minority carrier (electron) lifetime in B-doped cast-grown polycrystalline silicon. The distribution of the grain size could not explain that of the minority carrier lifetime map. The short minority carrier lifetime region did not correspond to a small grain region. This indicated that the lifetime of the small region was not mainly determined by the grain boundary recombination. In the grain, there were many slip and twin boundaries, but they were not the recombination centers. On the other hand, the defects which appeared as etch-pit by the Secco etching, shortened the minority carrier lifetime. In the present cast-grown Si crystal, there are large amounts of oxygen (O) and carbon (C). A large amount of substitutional C would be precipitated by the thermal annealing, resulting in the deterioration of the solar cell performances. Then, the effects of the annealing temperature on the amount of segregated C were studied.

2. Experimental procedure

The cast polycrystalline Si grown at JFE steel corporation was used in this study. Wafers were boron-doped (10^{16}–$10^{17}\,cm^{-3}$) with a resistivity of 0.4–0.8 Ω cm. The wafer thickness was 350 μm and the size was 50 mm $\times$ 50 mm. The cooling rate was slow as compared with that of Czochralski growth. The maximum grain size exceeded 1 cm. The average diffusion length of the electron was 250 μm, and the conversion efficiency over 18% was obtained by using this wafer as a solar cell material [5]. Before measurements, the saw-induced damaged layer was etched off by the HNO_3/HF solution. For lifetime measurements, the Si surface was passivated by iodine (I). The lifetime mapping was obtained by laser microwave photoconductance decay (PCD) measurement. The step size used for generating the lifetime mapping was 1 mm and 523 nm He–Ne laser was used as carrier injection source. The wafer surface was Secco etched for 10 min and it was studied by the optical microscopy. Some defects were observed by the cross-sectional transmission electron microscopy (TEM) and transmission electron diffraction (TED). The numbers of the interstitial oxygen (O) and substitutional carbon (C) in the cast-grown crystal were determined by the Fourier-transform infrared spectroscopy (FTIR). For FTIR measurements, the polished wafers were used. The two-step thermal annealing of the wafer was carried out using the hot wall furnace with an N_2 ambient. The first annealing condition was 300–1100 °C/24 h, and then 1100 °C/24 h. The effects of first-step annealing temperature on the amount of precipitated C were studied.

3. Results and discussion

The minority carrier lifetime, which was obtained by PCD measurement, varied from 15 to 360 μs in the wafer. However, the distribution of the grain size cannot explain the minority carrier lifetime map. The short minority carrier lifetime region did not correspond to a small grain region. The plan-view optical microscope image of the polycrystalline Si surface after the Secco etching is shown in Fig. 1(a). Here, a relatively longer lifetime was obtained. There are many line-shaped structures. Cross-sectional TEM images and the TED patterns obtained from the region A are shown in Fig. 2. The simple TED pattern indicates that it is sliped. It would be created as a result of thermo-mechanical stress during the crystal

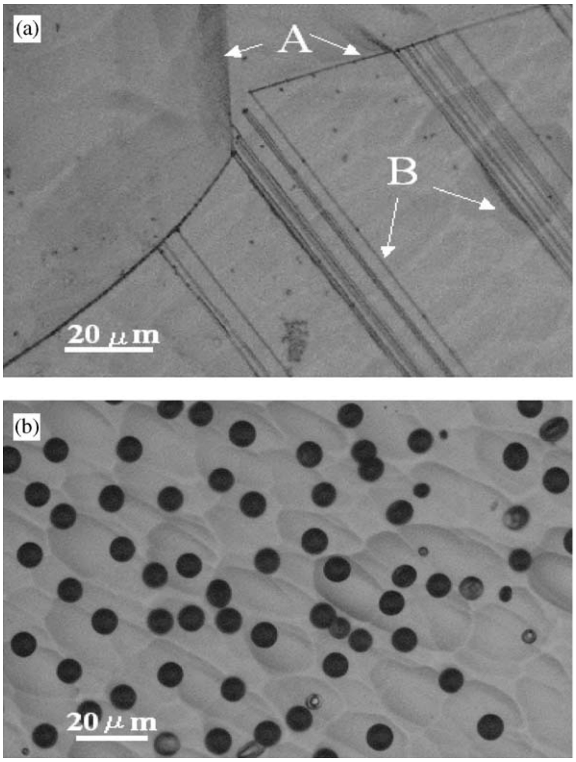

Fig. 1. Plan-view optical microscope images of the Secco etched surface: (a) relatively longer lifetime region, A; slip, B; twin boundary, (b) shorter lifetime region.

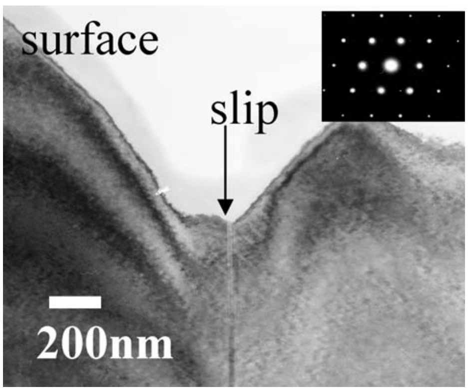

Fig. 2. Cross-sectional TEM image and TED pattern of slip.

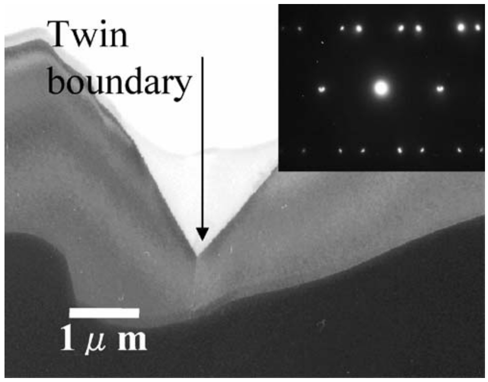

Fig. 3. Cross-sectional TEM image and TED pattern of twin.

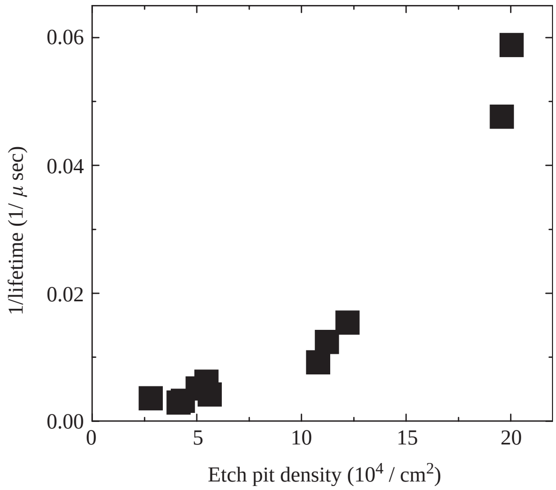

Fig. 4. Relationship between the minority carrier lifetime and the etch-pit density.

growth. The TEM image and TED pattern from the region B suggest that it has a twin boundary (Fig. 3). Electron beam-induced current (EBIC) image did not show the contrast near these structures, concluding that both of them did not deteriorate the minority carrier lifetime. On the other hand, in the region where the minority carrier lifetime was relatively short, there are many etch-pit in the grain (Fig. 1(b)). The relationship between the etch-pit density and the minority carrier lifetime is shown in Fig. 4. The lifetime dramatically decreases as the number of the etch-pit increases. The grain size exceeded 1 cm. It is large enough as compared with the diffusion length of the electron and the lifetime is not mainly limited by the grain boundary recombination. Then the defects, which appeared as etch-pit by the etching, acted as recombination centers, and mainly determined the minority carrier

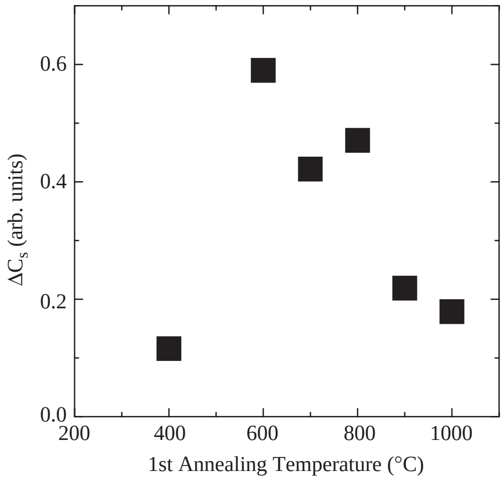

Fig. 5. Effects of two-step annealing on the segregation of the substitutional C. C segregation efficiently occurred by the first step 600 °C annealing.

(electron) lifetime in the present cast-grown polycrystalline Si.

The amounts of residual O and C in the cast-grown polycrystalline Si were evaluated to be about $1 \times 10^{17}\,cm^{-3}$ and $2 \times 10^{17}\,cm^{-3}$, respectively. Here, they were determined by analyzing the two peaks in the FTIR spectrum, one peak was around $1100\,cm^{-1}$ and the other was $607\,cm^{-1}$ that corresponded to the O at the interstitial site and the C at the substitutional site. The concentration of interstitial O was relatively low as compared with that in a Czochralski-grown Si wafer. However, the concentration of C was almost the solubility limit at the melting point. These C atoms might be mainly contaminated from the carbon heater during the melting and crystallizing processes. The solar cell fabrication process will induce the segregation of these super-saturated C through the thermal annealing. Then, the effects of thermal annealing on the C precipitation were studied. When the wafer was annealed at 1100 °C/48 h, C segregation slightly occurred. On the other hand, the relatively large amount of C was segregated by the two-step annealing. The relationship between the first annealing temperature and the decrease in the C peak intensity after the second annealing is shown in Fig. 5. When the wafer was annealed at 600–800 °C as a first-step, the larger amount of C atoms was segregated after the second-step 1100 °C annealing. This result suggested that not only the annealing temperature, but also the annealing history would determine the amount of segregated C.

4. Conclusion

Effects of defects in the grain on the minority carrier lifetime of the B-doped cast-grown polycrystalline Si were studied. The grain size of the cast-grown polycrystalline Si was large enough (>1 cm) as compared with the electron diffusion length (0.25 μm), and the minority carrier lifetime was not mainly limited by the grain boundary recombination. On the other hand, in the region where the lifetime was relatively short, there were many etch-pit appeared by the Secco etching, which acted as a recombination center and determined the minority carrier lifetime. There were large amount of C ($>10^{17}\,cm^3$) in the crystal. Some of them were segregated by the thermal annealing, suggesting that the solar cell performances would be deteriorated by the C segregation through the solar cell fabricating processes.

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