論 文 の 内 容 の 要 旨

論文題目　　Property control of compensated Si for solar cells by Al co-doping

（Al 共ドープにより補償された太陽電池用 Si の特性制御）

氏　　名　　游　毓鋆

The photovoltaic (PV) industry has enjoyed rapid development for the past 17 years. The traditional methods for the SOG-Si such as the modified Siemens process, the Union Carbide process or the Ethyl corporation process cannot satisfy the continuing increased PV market because of their high cost, high energy consumption and low productivity. The recently developed metallurgical methods show lower cost and energy consumption. However the resulting Si by these methods always contains relatively high concentrations of B and P which limits the solar cell efficiency.

In Chapter 1, the compensation of donors and acceptors in semiconductors was introduced. Based on this kind of compensation, Si containing high concentration of B and P can still show good electrical properties if only the net doping density is low enough. Due to the different segregation coefficient between B and P, the resulting Si ingot always shows nonuniform net doping density after directional solidification. In order to eliminate the segregation coefficient difference between B and P and increase the performance of Si containing relatively high concentrations of B and P, an Al co-doping method was proposed for the first time.

In Chapter 2, Al was chosen as additive to eliminate the segregation coefficient difference between B and P. The amount of Al added to Si containing 1×10^{17} cm^{-3} of B and 2×10^{17} cm^{-3} of P was calculated as 1×10^{19} cm^{-3} based on the Scheil equation. More than 90% of the resulting ingot exhibited a net dopant concentration less than 1×10^{17} cm^{-3} and the polarity type inversion was suppressed.

The effect of Al ratio on the electrical properties of P-B-Al compensated Si was also studied. At the same net doping density, when the Al:(Al+B) $\leq$ 80%, the electrical properties of P-B-Al-compensated Si were as well or better than non-compensated Si (the only dopant was B) therefore Al ratio acceptable for solar cells was between 80% and 100% at maximum. The calculated Al ratio after Al co-doping method is lower than this limit, therefore this method is feasible to get good and uniform electrical properties.

In Chapter 3, non-compensated Si ingot and compensated Si ingots with and without Al co-doping were fabricated by directional solidification method.

After Al co-doping and directional solidification, the Si ingot showed resistivity ranged from 0.9 to 2.7 Ω•cm and minority carrier lifetimes ranged from 70 to 130 μs, which were well suited to the solar cells. Moreover, no less than 85.7% of the entire Si ingot was *p*-type and the carrier concentration ranged from 1.36×10^{16} to 3.99×10^{16} cm^{-3} which was quite narrow and low. In contrast to B-P-compensated Si, P-B-Al-compensated Si showed good electrical properties through the entire ingot height. Besides, severe decrease of the resistivity and increase of the carrier mobility at the top part and the trend inversion of the minority carrier lifetime was observed in the P-B-Al-compensated Si.

In Chapter 4, the effects of GBs on the electrical properties of the P-B-Al-compensated Si were studied to explain the properties degradation and the increase of the carrier mobility at the top part of the P-B-Al-compensated Si ingot.

The grain size increased *i.e.* GB length decreased along the ingot height in both SOG-Si and P-B-Al-compensated Si. All kinds of pure GBs are electrical inactive and have same recombination strengths. Therefore shorter GB length leads to fewer recombination centers and fewer barriers for moving carriers. In turn, in the SOG-Si, the resistivity decreased and the minority carrier lifetime increased as the grain size increased.

When the GBs are contaminated, the minority carrier lifetime is determined by the combination of GB length, total dopants concentration and GB types. In the P-B-Al-compensated Si, the grain size and the dopants concentration (especially Al concentration) increased along the ingot height. As to the GB type, the bottom sample showed highest ratio of random and small angle (SA) GBs, the middle sample showed lowest ratio of random and SA GBs and the top sample was in between. The random and SA GBs are easier to become strong recombination centers for minority carriers once they are contaminated. Therefore the minority carrier lifetime increased first and then decreased along the ingot height. Moreover the dopants segregation at GBs might affect the Fermi level of the GBs and hence the carriers might be easier to migrate through the GBs resulting in high carrier mobility and severe decrease of the resistivity at the top part of the ingot.

Heat treatment and quenching was used to eliminate the bad effects of the dopants segregation. The resistivity of the samples with Al:(Al+B)>80% increased to about 0.39 Ω•cm and the minority carrier lifetime increased to 50μs after heat treatment.

In Chapter 5, morphology control of the grains during the directional solidification was studied in order to further eliminate the bad effect of the grain morphology on the electrical properties.

Grains grown from side to center which have detrimental effects on the electrical properties

were effectively suppressed by decreasing the pulling rate. The grain size were controlled uniform by a two-step directional solidification method in which the pulling rate was set as 0.04mm/min at the first step and 0.2 mm/min at the second step. Moreover the electrical properties degradation at the top part was also relieved by this method. Finally, a modified graphite crucible which was coated with thermal insulating ceramic was used in the two-step method. The resulting ingot was longer than previous one and the morphology and electrical properties were also uniform. The improved two-step method has advantages in materials yield, morphology and properties control.

All the conclusions were summarized in Chapter 6 and based on these conclusions a new process for producing Si wafers for solar cells from MG-Si was established.

The advantage of the new process is that the upper limits for the remained B and P concentration after refining are about 0.78 ppm (1×10^{17} cm^{-3}) and 4.42 ppm (2×10^{17} cm^{-3}) respectively which are much higher than that for traditional SOG-Si, B (0.38 ppm) and P (0.79ppm). This avoids a repeating slag treatment and vacuum refining and hence reduces the cost and energy consumption. After Al co-doping and two-step directional solidification, uniform net doping density and grains along the entire ingot is achieved. The final heat treatment is conducted to remove the bad effects of the dopants segregation at GBs. Then Si wafers with good electrical properties are obtained.

Keywords: Dopants compensation; Segregation coefficient; Al co-doping; Directional solidification; Grain boundary segregation; Morphology control.