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Aluminum-doped crystalline silicon and its photovoltaic application

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ABSTRACT

The impact of Al doping with the concentrations in the range of 0.01—0.1 ppmw on the performance of silicon wafers and solar cells is studied. The effective segregation coefficient of impurity k_{eff} of Al in Si is obtained as 0.0029, which is calculated as 0.0027, supporting that Al should be totally ionized and occupy the substitutional sites in silicon and serve as the +1 dopant. It is found that the open-circuit voltages (U_{oc}), short-circuit currents (I_{sc}) and photo-electrical conversion efficiency of the Al-containing solar cells decrease with the increase of Al concentrations because of Al-related deep level recombination centers. The average absolute efficiency of Al-doped silicon solar cells is 0.34% lower than that of Ga-doped-only cells, and the largest difference can be about 0.62%. Moreover, Al doped silicon solar cells show no light induced efficiency degradation, and the average efficiency maintains above 17.78%, which is comparable at the final state to that of normal B-doped silicon solar cells.

1. Introduction

Since conventional fossil fuels are drastically decreasing, there is a strong demand for sustainable energy sources, among which photovoltaics (PV) based on solar cells is undoubtedly one of the cleanest ways to produce electricity. In PV industry, Si materials have been widely employed for the fabrication of commercial solar cells for decades, since it is the second most abundance in the earth's crust and meanwhile has excellent electrical and mechanical performances [1]. But, nowadays, most of Si raw materials used for solar cells are electronic-grade, which largely barriers the cost reduction for cell fabrication. So, to date, various methods of refining metallurgical grade (MG) Si have been proposed [2,3]. There are many approaches that have been developed to fabricate inexpensive silicon, i.e. the upgraded metallurgical grade (UMG) Si, such as the NEDO approach of Japan [4—6], pyro-metallurgical approach of Elkem [7], the aluminum solvent approach and so on.

The content of impurities in UMG Si is about 1 ppmw, and Al is commonly present whose concentration is usually 0.01—0.1 ppmw [8]. As is known, Al atoms can occupy substitutional sites in silicon lattice with the ionization energy of 0.057 eV, which in fact forms shallow acceptors. Recent literatures have reported that Al can introduce deep energy level

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defects, which are speculated to have something to do with Al–O complexes with the energy level of E_v+0.45 eV [9]. However, there is few researches showing the impact of Al with the concentration in the range of 0.01–0.1 ppmw on the performance of silicon wafers and solar cells, which is essential for the industry to know whether such kind of silicon raw material can be employed or not.

In this paper, the impact of Al doping on the performance of silicon wafers and solar cells is studied by an Al–Ga co-doped silicon ingot. The results show that Al concentrations increase in the ingot with the crystallographic direction and the performance degradation of silicon wafers and solar cells becomes heavier with the increase of Al concentrations. Finally, the Al doped silicon solar cells shows no light induced efficiency degradation and a comparable efficiency at the final state to that of normal B-doped silicon solar cells.

2. Experiments

The Al concentration of 0.01–0.1 ppmw cannot lead to an eligible resistance for solar cells, so Ga is added into the ingots to adjust the resistance and avoid the unwanted negative effects. Using the same thermal parameters for crystal growth, an ⟨100⟩ oriented, 165 mm diameter, Al and Ga co-doped Czochralski (CZ) ingot was fabricated with a Ga-doped-only ingot as reference. Table 1 lists all the parameters used for the above-mentioned two CZ-ingots. The CZ-ingots were cut into wafers with the thickness of 180 μm or 2 mm for different measurements. First, 2 mm thick samples were annealed at 650 °C in Ar ambient to eliminate grown-in thermal donors and then the resistivity of them were tested by a Four-point Probe (Sevenstar, D41-11D/ZM). Secondary ion mass spectra (SIMS) were used to analyze dopant concentrations in the samples, which were compared to the resistivity. Then, after polishing 2 mm thick samples to shiny surfaces, Fourier transformation infrared spectrometry (FTIR, Bruker, IFS 66v/S) was used to measure the content of interstitial oxygen [O_i] [10] with a calibration coefficient of 3.14×10^{17} cm^{-2}. The effective minority carrier lifetime was measured by quasi-steady state photoconductance (QSSPC, Sinton, WCT-120) [11] after 900 °C phosphorus diffusion gettering (PDG) and surface passivation by plasma enhanced chemical vapor deposition (PECVD) SiNx films. The excess carrier density was set the same about 1×10^{14} cm^{-3}. Finally, 180 μm thick wafers together with normal 180 μm thick B-doped-only wafers were fabricated into solar cells using standard online processes, and their performance under illumination was compared with simulated results using PC1D [12], in which minority carrier lifetime results were taken as the only variable.

3. Results and discussions

3.1. Segregation of Al in silicon ingot

Fig. 1 shows the resistivity, [O_i] and the concentrations of Al and Ga of the silicon wafers cut from different positions of the ingots. It can be seen that the concentrations of Al and Ga increase along the crystallographic direction due to their segregation coefficients that are far smaller than 1. Since the segregation coefficient of oxygen in silicon is larger than 1, the [O_i] should decrease along the crystal growth direction. According to the Eq. (1),

$$C_S = k_{eff}C_0(1 - g)^{k_{eff} - 1} \tag{1}$$

where C_S the impurity concentration at the solid-liquid interface, C_0 the initial impurity concentration before segregation, k_{eff} the effective segregation coefficient of impurity, g the solidification percentage. k_{eff} of Al in Si can be obtained as 0.0029 (assuming k_{eff} of Ga is 0.0085), deviating 45% from the ideal segregation coefficient reported in the previous reference [13]. This difference should be a result of the impurity-rich layer at the solid-liquid interface during the crystal pulling. According to Burton-Prim-Slichter (BPS) theory [14], the relationship between k_{eff} and k_0 is given by:

$$k_{eff} = \frac{k_0}{k_0 + (1 - k_0)\exp\left(-\frac{v\delta}{D}\right)} \tag{2}$$

where v is the growth velocity, δ and D are the thickness of impurity border and the diffusion coefficient of impurity in silicon melt, respectively. According to the results of Kodera [15] and Tiller [16], $\delta/D = 120$ s/cm in the case of 1.1 mm/min growth velocity. Then the effective segregation coefficient is estimated to be 0.0027, which is in agreement with the measured one. From this measured k_{eff}, it can be inferred that most of Al impurities can be precluded out of silicon ingot by segregation when the Al content in silicon raw material is below 1 ppmw.

Table 1
Parameters of the two CZ-Si ingots.

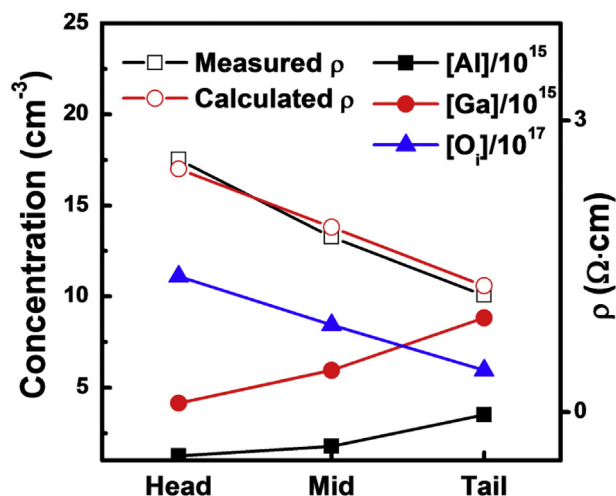| Dopant	Mass (kg)	Effective length (mm)	Target ρ@head (Ω cm)	[Al]@head (cm^{-3})
Ga1.07 g, Al 0.28 g	30	395	2	1×10^{15}
Ga1.25 g	30	422	2	0

Fig. 1. Resistivity, interstitial oxygen concentration measured by FTIR and aluminum and gallium concentrations measured by SIMS in the Al/Ga-codoped CZ Si ingot.

Al and Ga are both elements of the group III and they can serve as +1 p-type dopant in silicon when they occupy the substitutional sites in silicon. Assuming Al and Ga atoms are both ionized and located at the substitutional sites, the resistivity of silicon wafer is calculated based on the SIMS measurements. In Fig. 1, the calculated resistivity complies well with the measured one, supporting the assumption that Al and Ga are totally ionized. In other words, when the Al concentration is in the range below 1 ppmw, Al should be totally ionized and occupy the substitutional sites in silicon and it also serves the +1 dopant.

3.2. Effect of Al on the property of crystalline silicon materials and solar cells

Fig. 2 compares the effective minority carrier lifetime before and after PDG. Meanwhile, Fig. 2 also provides the data of the Ga-doped-only silicon wafers. It can be seen that, with comparison to the Ga-doped-only wafers, the wafers containing Al has lower lifetime. In addition, in the as-grown samples, the lifetime demonstrates the declining tendency with the increase of Al concentrations. This indicates that Al doping brings in minority carrier recombination centers in silicon and consequently leads to the reduction of minority carrier lifetime. Also, the concentration of these centers is proportional to the Al concentration. After PDG, the carrier lifetime of samples were improved. It has been well known that on one hand, PDG can eliminate the deteriorating metallic impurities, and on the other hand, the defects related to Al–O complexes might be caused by the capture of O-related clusters of substitutional Al, for example, O_{2i}, O_{3i} and so on [13]. Due to the close collation between
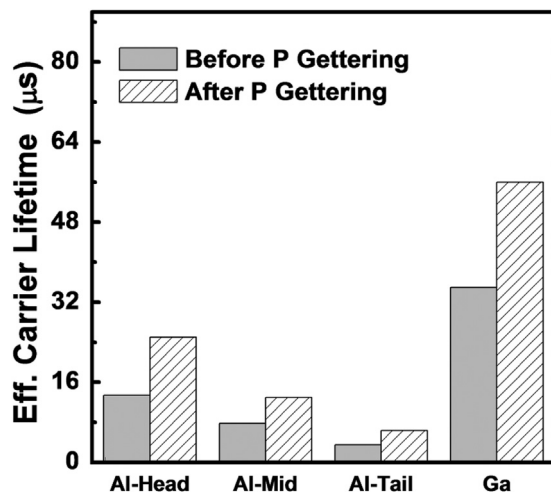

Fig. 2. Effective carrier lifetime of the silicon wafers from different positions of the Al/Ga-codoped ingot before and after phosphorus diffusion gettering. As a reference, the figure also depicts those of the Ga-doped silicon.
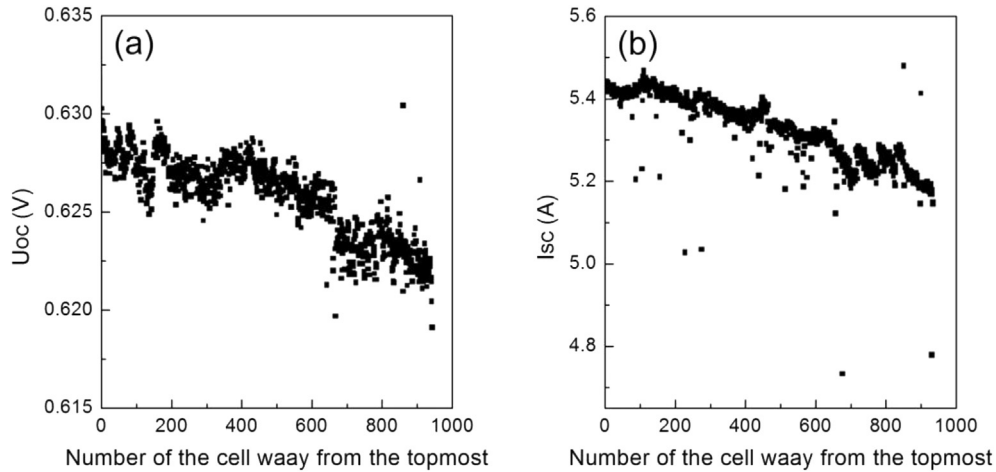
Fig. 3. Distribution of U_{oc} and I_{sc} for the Al/Ga-codoped silicon solar cells as a function of the wafer position in the ingot.

oxygen clusters and the thermal history that one sample may experience, the high temperature process may crack the O-related clusters, decrease the cluster concentration and finally reduce the Al−O complexes [17].

About thousands of silicon wafers along with the Al/Ga co-doped silicon ingot were fabricated to solar cells in our experiments, which were tested in sequence. Fig. 3 shows the open-circuit voltage (U_{oc}) and short-circuit current (I_{sc}) of the Al-containing solar cells as a function of wafer positions. It can be seen that U_{oc} and I_{sc} decrease along the crystal growth direction. This may be ascribed to the Al concentration increase and thus the relative defect concentration increase. But the U_{oc} and I_{sc} are related to not only base materials but also solar cell processes, which should be also taken into account. Fig. 4 shows the impact of solar cell processes on the parameters of Al-containing solar cells, mainly the series resistance (R_s), shunt resistance (R_{sh}) and fill factor (*FF*). It can be seen that all the values of R_s are under the similar level and the values of R_{sh} are basically above 100 Ω. According to the simulation performed by PC1D [12], R_s and R_{sh} mentioned in this study have little impact on the solar cell performance. *FF* is usually determined by R_s and R_{sh}, so the variation of *FF* in Fig. 4 is very small and *FF* can be thus considered as constant. In other word, the negative deviation in U_{oc} and I_{sc} is caused by the increase of Al concentration, instead of the solar cell processes.

Fig. 5 shows the photo-electrical conversion efficiency of the Al/Ga-codoped silicon solar cells, compared to that of the Ga-doped-only ones. One can see that the cells based on the Al-containing wafers from the head position of the ingot already have lower efficiency, with comparison to that of the Ga-doped-only silicon solar cells. With the increase of Al concentrations, the efficiency gradually decreases. As a result, the averagely absolute efficiency of Al-containing silicon solar cells is about 0.34% lower than that of the Ga-doped-only cells, and the largest difference can be about 0.62%. Using PC1D [12] to simulate the practical parameters of solar cells, we found that the calculated efficiency is mostly close to the experimental one when the minority carrier lifetime results obtained from the QSSPC test are taken as the only variable, as shown in Fig. 5. Therefore, it can be inferred that the efficiency reduction of Al-containing solar cells is principally caused by the reduction of carrier lifetime in the silicon ingot. According to Ref. [18], Al doping introduces deep energy level recombination centers in silicon, lowering the lifetime of silicon wafers and consequently results in the decrease of silicon solar cell performance.

3.3. LID of Al-doped silicon solar cells

Fig. 6 shows the LID behaviors of Al/Ga co-doped silicon solar cells under long time illumination. It can be seen that there is negligible efficiency loss for the Al-containing solar cells after illumination, and the average efficiency maintains above 17.78%. This indicates that Al can only introduce lifetime reduction once while there are no secondary deep energy level defects under light-induced excess carriers. The previous reference [19] reported the obvious LID effect in Al-containing silicon, which is contradicted against our results. In fact, the Al-containing Si reported in Ref. [16] was co-doped by B and the existence of B in CZ-silicon will definitely cause LID. In the B-free silicon ingot, we believe that Al can lead to no efficiency degradation. From Fig. 6, it can be seen that the B-doped-only CZ silicon solar cells have efficiency decrease from 18.18% before illumination to 17.59% after sunlight illumination, with the absolute efficiency reduction of 0.59%. Therefore, it can be induced that the performance of Al-containing solar cells is superior to that of B-doped cells after LID effect.

Due to the resistance requirement of silicon ingots and the very small segregation coefficient of Ga, UMG silicon is rarely doped by Ga and the main *p*-type dopant is B. Because of the existence of Al, Al could take place of portion of B and less B can be doped for crystal growth, leading to the slighter LID in silicon solar cells. Considering the consequence of Al doping from the aspects of direct efficiency degradation and LID, it can be concluded that the negative effect brought by Al doping on silicon solar cell efficiency is offset by the zero LID under illumination. Therefore, silicon ingots containing 0.01−0.1 ppmw Al
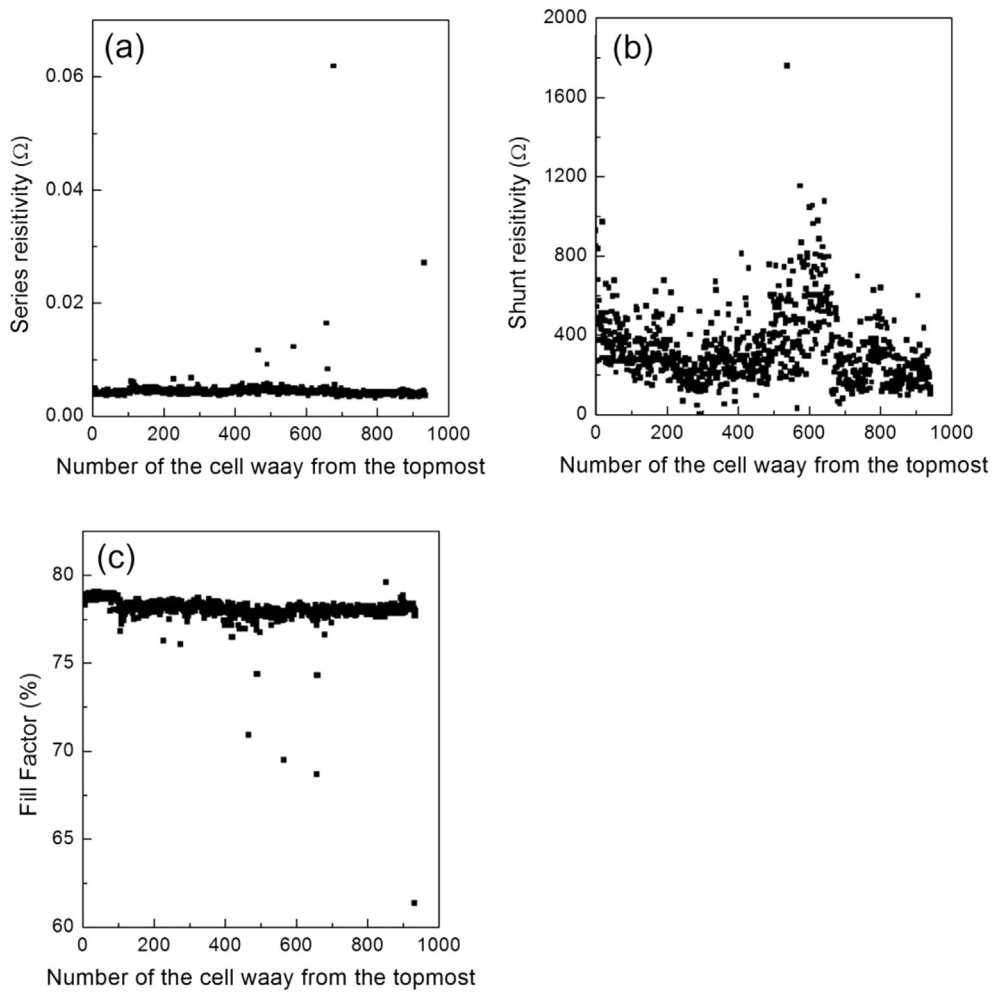
Fig. 4. Distribution of R_s, R_{sh} and FF for the Al/Ga-codoped silicon solar cells as a function of the wafer position in the ingot.
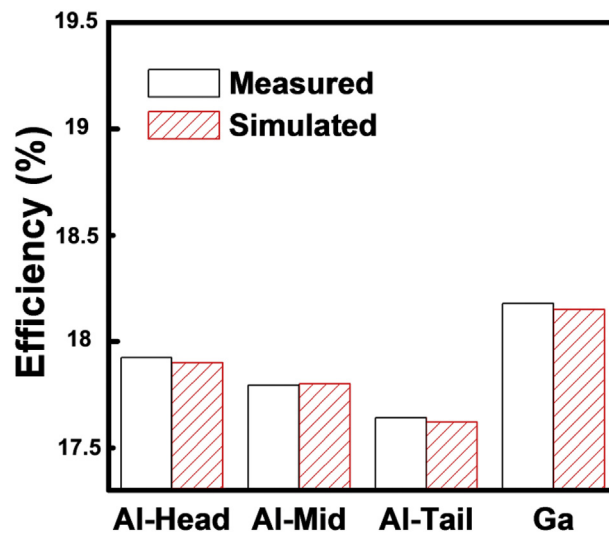

Fig. 5. Efficiencies of the Al/Ga-codoped and Ga-doped silicon solar cells (Experiments and simulations).
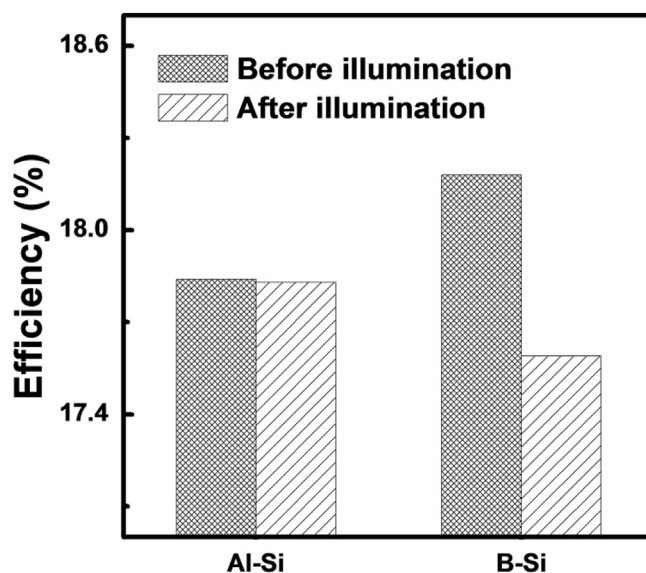
Fig. 6. Efficiency degradation of the Al/Ga-codoped and B-doped silicon solar cells under illumination.

can be employed as the substrate for solar cells. According to the segregation coefficient of Al in silicon, the upper limit of Al concentration in silicon should not exceed 50 ppma, which is in accordance to the estimation in Ref. [8].

4. Conclusions

The impact of Al doping with the concentrations in the range of 0.01–0.1 ppmw on the performance of silicon wafers and solar cells is studied by an Al–Ga co-doped silicon ingot. The results show that Al concentration increases in the ingot with the crystallographic direction. But the performance degradation of silicon wafers and their solar cells becomes severer with the increase of Al concentrations. Finally, the Al doped silicon solar cells shows no light induced efficiency degradation and a comparable efficiency at the final state to that of normal B-doped silicon solar cells.

Acknowledgements

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