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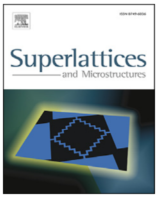

Aluminum-doped crystalline silicon and its photovoltaic application

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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], δ/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

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