Research Article

Effect of the Phosphorus Gettering on Si Heterojunction Solar Cells

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To improve the efficiency of crystalline silicon solar cells, should be collected the excess carrier as much as possible. Therefore, minimizing the recombination both at the bulk and surface regions is important. Impurities make recombination sites and they are the major reason for recombination. Phosphorus (P) gettering was introduced to reduce metal impurities in the bulk region of Si wafers and then to improve the efficiency of Si heterojunction solar cells fabricated on the wafers. Resistivity of wafers was measured by a four-point probe method. Fill factor of solar cells was measured by a solar simulator. Saturation current and ideality factor were calculated from a dark current density-voltage graph. External quantum efficiency was analyzed to assess the effect of P gettering on the performance of solar cells. Minority bulk lifetime measured by microwave photoconductance decay increases from 368.3 to 660.8 μ s. Open-circuit voltage and short-circuit current density increase from 577 to 598 mV and 27.8 to 29.8 mA/cm², respectively. The efficiency of solar cells increases from 11.9 to 13.4%. P gettering will be feasible to improve the efficiency of Si heterojunction solar cells fabricated on P-doped Si wafers.

1. Introduction

Solar cells have attracted great attention as a promising alternative energy source and various ways have been investigated to improve their performances. To obtain high-efficiency solar cells, minority carriers should have a long lifetime and a low recombination velocity [1]. Currently, single-, multicrystalline or amorphous silicon-based solar cells show high efficiency because of their reliability, scalability, and performance. However, metal impurities incorporated in Si wafers, such as Fe, Ni, and Cu, are highly mobile, diffuse over long distances, and act as a recombination center [2–4]. Furthermore, solar cell performance is largely limited by the regions of poorest material quality [4]. Such recombination center in the wafers deteriorates carrier

collection efficiency. Therefore, impurity gettering has been widely studied to reduce their deleterious effect. Several methods have been investigated, including spontaneously occurring and intentionally formed sinks for the transition metals—at the surface and bulk. Depending on where we capture metal impurities, it is classified to intrinsic and extrinsic gettering. Intrinsic gettering is involving the metal impurity trapping sites mainly in the bulk region. External gettering is that generating stress silicon lattice which acts as a sink by external means such as abrasion grooving or phosphorus diffusion. Extrinsic impurity gettering in Si wafers is appropriate since solar cells employ the whole bulk region which is used as generation points. Furthermore, generated carriers move through the bulk region to electrodes, less recombination sites in bulk goes to better efficiency of solar

cells. Among extrinsic gettering, phosphorus (P) gettering is widely studied because it can be easily prepared by the diffusion of P [5–9].

Si heterojunction solar cells are one of important high efficiency solar cells showing a high open-circuit voltage and a low absorption in the emitter region.

Amorphous Si thin film has a large energy bandgap; Si heterojunction solar cells show a high open-circuit voltage and a low absorption in the emitter region. Since most light is absorbed in the bulk region of heterojunction silicon solar cells, it is important to have less recombination sites at the bulk region which reduce the diffusion length of excess carriers and collection efficiency.

In this work, we introduced extrinsic P gettering into the fabrication process of Si heterojunction solar cells and investigated the effect of P gettering on the performance of solar cells.

2. Experimental

Low-quality n-type monocrystalline Si wafers with the thickness of 170 μm were doped by P into (100) plane and showed the resistivity of 3–5 Ωcm . They underwent saw damage etching (SDE). Then, an aqueous hydrochloric acid and peroxide mixture (HPM) were used to remove metal particles from their surfaces. After finishing each process, the Si wafers were rinsed with DI water. We skipped texturing process to eliminate unwanted process variables.

P gettering has been reported to occur at an optimum temperature as it relies on the transportation of released impurities towards a segregation region near the surface of the samples [10]. Hence, the temperature and duration of P diffusion were expected to affect the gettering efficiency. Therefore, Si wafers were gettered at 750, 800, 850, and 900°C for 30 minutes in a quartz tube furnace, while a reference sample was not gettered. The resistivity of P-gettered Si wafer was measured at 9 points. Phosphosilicate glass (PSG) layers were removed in buffered oxide etch (BOE) solution. To remove the gettered layers where impurities were assumed to be gathered, samples were immersed in potassium hydroxide (KOH) solution for 5 minutes to etch back. The reference underwent the same etch-back process. Bulk lifetime was measured by iodine passivation using microwave photoconductance decay ($\mu\text{w-PCD}$).

Si heterojunction solar cells of $1 \times 1 \text{ cm}^2$ were fabricated after finishing P gettering. 10 nm intrinsic a-Si:H films were deposited by hot wire chemical vapor deposition (HWCVD) using silane (SiH_4) and H_2 as precursor gases. 10 nm P-doped and 20 nm n-doped a-Si:H films were then formed by plasma enhanced CVD (PECVD) using SiH_4 , H_2 , and diborane (B_2H_6) or phosphine (PH_3). After deposition of intrinsic a-Si:H films, front and back electrodes were formed by evaporation. Finally, edge isolation process was carried out in a 4:1 (HCl:DI water) mixed solution. Processing sequence is described in Figure 1. Generally, it is hard to detect metal impurities concentration in crystalline silicon wafer because of the detection limit. Therefore, we analyzed

wafer characteristics and cell characteristics to deduce the P gettering effect. The saturation current and ideality factor of Si heterojunction solar cells were calculated from their dark currents and voltages. Short-circuit current density, open circuit voltage, and fill factor of the solar cells were measured using a solar simulator. External quantum efficiency was analyzed between 400 to 1100 nm wavelength to assess the electron-hole separation and collection at the bulk region.

3. Results and Discussion

The resistivity of Si wafers is 3–5 Ωcm before P gettering. The sheet resistances of P-gettered samples as a function of gettering temperature are shown in Figure 2. Resistivity of gettered sample abruptly decreases at 800°C from 2.7 to 0.9 Ωcm . With the increasing gettering temperature, the resistivity decreases since the rate of P incorporation into substitutional sites of Si is enhanced by increased thermal activation at higher gettering temperature.

The minority carrier lifetime and diffusion length as a function of gettering temperature are shown in Figure 3. The bulk lifetime of the nongettered reference sample is 368.3 μs . Those of the gettered samples at 750, 800, 850, and 900°C are 615.4, 660.8, 343.0, and 301.4 μs , respectively. While the bulk lifetime shows the longest value at 800°C, which is 292.5 μs higher than that of the nongettered sample, the bulk lifetime shows the shortest value at 900°C, which is 56.0 μs shorter than that of the nongettered sample. Average diffusion length varies between 610.5 and 886.5 μm depending on gettering temperature. The diffusion lengths of the gettered samples at 750 and 850°C are 835.9 and 634.6 μm , respectively. While the diffusion length shows the longest value at 800°C, the diffusion length shows the shortest value at 900°C.

Figure 4 shows the mapping of bulk lifetime and its probability distribution for (a) nongettered sample and gettered samples at (b) 750, (c) 800, (d) 850, and (e) 900°C. The nongettered sample shows that over 90% of the substrate has a bulk lifetime below 407.4 μs and its 10% has a bulk lifetime below 195.0 μs . Its 80% has bulk lifetime between 195.0 and 407.4 μs , while 90% of the substrate for the sample gettered at 800°C shows a bulk lifetime over 501.2 μs . The mapping of bulk lifetime and its probability distribution of the samples gettered at 750 and 800°C are similar, though the sample gettered at 750 shows widely distributed values as compared with those of 800°C.

The variation of lifetime and its probability distribution by gettering temperature can be explained by the diffusion-induced gettering of impurities as shown in Figure 5 [9]. When thermal activation energy is given in Si wafer, impurities are released from energetic binding and diffused through Si wafer. Then they are finally captured where the emitter acted as a sink. Here, experiment data shows that there is an optimized temperature of gettering. Metal impurities elimination efficiency of P gettering depends on the transport of impurities and solubility segregation. It was reported that there is competing effectiveness of two processes responsible for segregation gettering, that is, impurity transport and solubility segregation, the latter

FIGURE 1: Processing sequence of samples for analysis.

FIGURE 2: Resistivity as a function of gettering temperature.

FIGURE 3: Bulk life time and bulk diffusion length as a function of gettering temperature.

process being characterized by a decreasing segregation coefficient with increasing temperature [8, 11]. At high temperature, metal solubility is large, so required time for precipitation at the gettered region becomes long. However, if the gettering temperature is too high, crystallographic

defects are formed [12]. Gettering temperature should be decided after considering the diffusion, precipitate, and segregation of metal impurities.

FIGURE 4: Continued.

FIGURE 4: Mapping of bulk lifetime and its probability distribution for (a) nongettered sample and gettered samples at (b) 750, (c) 800, (d) 850, and (e) 900°C.

Figure 6 shows the illuminated current-voltage curves of nongettered and gettered samples. The sample gettered at 800°C shows the highest V_{oc} and J_{sc} values, 598 mV and 29.8 mA/cm², respectively. The samples gettered at 850 and 900°C do not show better properties than those of nongettered sample. For all the samples, V_{oc} values are between 581 and 598 mV, and J_{sc} values are between 27.1 and 29.8 mA/cm². Fill factor is calculated from the current-voltage curves. With the increasing gettering temperature, the fill factor slightly increases up to 800°C and then slightly increases up to 900°C. The sample gettered at 800°C shows the highest value of 75.3%.

P gettering was undertaken to suppress recombination due to impurities in the bulk region before the fabrication of Si heterojunction solar cells. As P gettering mainly affects the bulk or base region of the cells, we focus on variations in characteristics of quasineutral region than emitter region.

From the dark current-voltage curves, ideality factor and saturation current can be calculated. J_0 is obtained by extrapolation to $V = 0$ [12]. Calculated saturation current and ideality factor as a function of gettering temperature are shown in Figure 7. The nongettered sample has a saturation current of 1.5×10^{-8} mA/cm² in its quasi-neutral region. With the increasing gettering temperature, the saturation current decreases up to 800°C and then increase up to 900°C. The sample gettered at 800°C shows the lowest value of 0.5×10^{-8} mA/cm². Ideality factors were calculated from the relationship [13]

$$n = \frac{q}{l_n m k T} = \frac{q}{2.3 m k T}. \quad (1)$$

In the quasi-neutral region, the ideality factor of nongettered sample is 1.65. With the increasing gettering temperature, the ideality factor decreases up to 800°C and then increases up

FIGURE 5: Sketch of the basic principle of diffusion-induced gettering of impurities.

FIGURE 6: Illuminated current density-voltage curves of nongettered and gettered samples.

to 900°C; this is the same tendency with the dependence of saturation current on the gettering temperature. The sample gettered at 800°C shows the lowest value of 1.56.

External quantum efficiency (EQE) plots of the Si heterojunction solar cells are shown in Figure 8. We consider response to wavelength between 420 to 1100 nm corresponding to the signal from the bulk region. Responses of 750 and 800°C gettered samples show higher signal than that of the nongettered sample. The sample gettered at 800°C shows a superior response over all the wavelengths. However, samples gettered at 850°C and 900°C show a worse response than that of nongettered sample.

Ideality factors, J_0 , V_{oc} , J_{sc} , fill factors, and efficiencies are summarized in Table 1. The dependences of these parameters on the gettering temperature as described above explain that the sample gettered at 800°C show the best value, and then

FIGURE 7: Calculated saturation current and ideality as a function of gettering temperature.

FIGURE 8: External quantum efficiency (EQE) of nongettered and gettered samples.

the optimized P gettering temperature as a process parameter is to be chosen at 800°C.

4. Conclusions

Extrinsic phosphorus gettering was performed at 750, 800, 850, and 900°C to make high quality of silicon substrates for heterojunction solar cells. 800°C gettered sample shows the best characteristics. Their minority bulk lifetimes are

TABLE 1: Properties of Si heterojunction solar cells.

Gettering temperature (°C)	Ideality factor	J_0 (10^{-8} mA/cm ²) Quasi-neutral region	V_{oc} (mV)	J_{sc} (mA/cm ²)	FF (%)	Efficiency (%)
Nongettered	1.65	1.4	577	27.8	73.9	11.9
750	1.61	1.3	583	29.6	72.2	12.5
800	1.56	0.5	598	29.8	75.3	13.4
850	1.68	1.4	581	27.1	73.7	11.6
900	1.90	7.4	572	27.1	70.3	10.9

improved from 368.3 to 660.8 μ s. V_{OC} and J_{SC} increase from 577 to 598 mV and from 27.8 to **29.8** mA/cm². Saturation current and ideality factors decrease to 0.5×10^{-8} mA/cm² and 1.56, respectively. It results in efficiency improvement of silicon heterojunction solar cells. While properties of above 850°C gettered samples show degradation, we consider that optimized temperatures exist for extrinsic phosphorus gettering. Through this study, we found the possibility to improve the Si heterojunction solar cells by P gettering.

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