A novel method to enhance the gettering efficiency in p-type Czochralski silicon by a sacrificial porous silicon layer*

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Abstract: A new two-step phosphorous diffusion gettering (TSPDG) process using a sacrificial porous silicon layer (PSL) is proposed. Due to a decrease in high temperature time, the TSPDG (PSL) process weakens the deterioration in performances of PSL, and increases the capability of impurity clusters to dissolve and diffuse to the gettering regions. By means of the TSPDG (PSL) process under conditions of 900 ℃/60 min + 700 ℃/30 min, the effective lifetime of minority carriers in solar-grade (SOG) Si is increased to 14.3 times its original value, and the short-circuit current density of solar cells is improved from 23.5 o 28.7 mA/cm^2, and the open-circuit voltage from 0.534 to 0.596 V along with the transform efficiency from 8.1% to 11.8%, which are much superior to the results achieved by the PDG (PSL) process at 900 ℃ for 90 min.

Key words: two-step phosphorous diffusion gettering; effective lifetime; porous silicon layer; solar-grade Si

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1. Introduction

Solar-grade (SOG) Si is the most important material for fabricating solar photovoltaic cells due to its low-cost. However, this material contains a high concentration of transition metal, such as iron (Fe), copper (Cu) or gold (Au), with typical concentrations of about 10^{11} cm^{-3}, which may degrade the characteristics of solar cells[1−3]. Phosphorous diffusion gettering (PDG)[3] and porous silicon gettering[4] are two of the most effective applied schemes to improve performances of Si materials and cell efficiency. PDG using a sacrificial porous silicon layer (PSL) has been found to be an efficient procedure to improve the bulk diffusion lengths of a minority charge carrier in p-type Czochralski (CZ) silicon[5−7]. Khedher *et al*[5]. have found the optimum gettering conditions to be 900 ℃/90 min for the conventional PDG (PSL). The main disadvantage of this process, i.e., high temperature processing for a long time, may lead to deterioration in the performances of PSL[8], influencing the gettering effect. A new two-step phosphorous diffusion gettering (TSPDG (PSL)) method was proposed to improve the gettering effect of PDG (PSL). By an appropriate decrease in the gettering time at high temperature and an adoption of a treatment step at low temperature, the TSPDG (PSL) process weakens the factors limiting the gettering efficiency of PSL and improves the ability of defect clusters to dissolve and diffuse to gettering regions. After the same whole gettering time, the TSPDG (PSL) process has a better gettering effect than that of the conventional PDG (PSL) process, provided that the gettering time at high temperature is long enough to ensure that the impurity clusters dissolve and diffuse to the gettering regions. Experimental results show that by means of the TSPDG (PSL) process under conditions of 900 ℃/60 min + 700 ℃/30 min, the effective lifetime ($\tau_{\rm eff}$) of minority carriers in SOG-Si is increased to 14.3 times its original value, and the short-circuit current density ($J_{\rm sc}$) of solar cells is improved from 23.5 to 28.7 mA/cm^2, the open-circuit voltage ($V_{\rm oc}$) from 0.534 to 0.596 V along with the transform efficiency (η) from 8.1% to 11.8%, which are much superior to the results achieved by the PDG (PSL) process at 900 ℃ for 90 min.

2. Experiments

The p-type (100) orientation CZ SOG-Si doped with boron was used as the original wafers to study the influence of the TSPDG (PSL) process on the performance of SOG-Si material and photovoltaic cells. Its thickness is about 330 μm and its resistivity is about 1–2 Ω·cm. Each wafer was divided into many pieces to minimize the variation resulting from different wafers. The main technological processes are as follows.

2.1. TSPDG (PSL) process

(1) Porous silicon layers were elaborated on both sides of the samples by the stain-etching technique using $HF/HNO_3/H_2O$ solution, and the volume composition of the solution was 1:3:5. (2) A $POCl_3$ acetone liquid source with a ratio of 1:5 was spread out onto the samples by the spinning technique. (3) Samples were dried at 200 ℃ for evaporating solvent and steadying PSL. (4) Samples were thermally treated at 900 ℃ for high temperature time ($t_{\rm H}$), then the gettering temperature was slowly decreased to 700 ℃ at the rate of 4–5 ℃/s, and samples were treated at 700 ℃ for low temperature time ($t_{\rm L}$). The whole gettering time was controlled at 90 min during which $t_{\rm H}$ was controlled at 15, 30, 45 and 60 min, respectively. All heat treatments were carried out in an infrared (IR) furnace in a N_2 atmosphere. (5) Samples were chemically cleaned to remove the PSLs.

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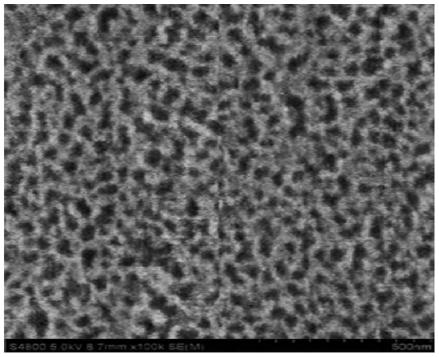
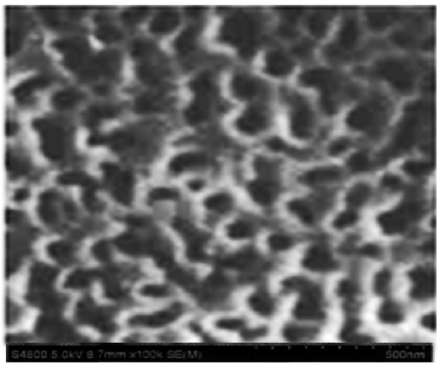


(a)



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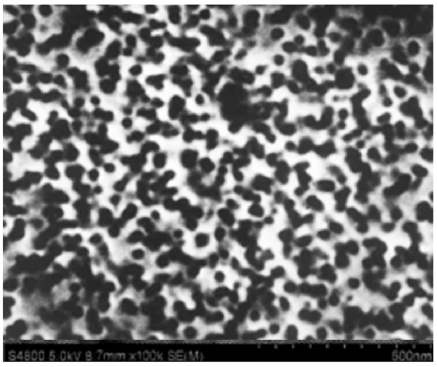

(c)

Fig. 1. Surface morphology of PSLs. (a) Before gettering. (b) After the PDG process at 900 ℃ for 90 min. (c) After the TSPDG process under conditions of 900 ℃/60 min + 700 ℃/30 min.

2.2. Solar cell process

Solar cells were fabricated from SOG-Si wafers purified by PDG (PSL) at 900 ℃ for 90 min and the TSPDG (PLS) process under conditions of 900 ℃/60 min + 700 ℃/30 min, respectively. The area of solar cells was 2.5 × 2.5 cm^2. After the gettering regions were removed, samples were immersed in a 2% NaOH solution with a temperature of 85 ℃ for 30 min in order to form the surface texture. Then, the N^+/P junction with a sheet resistance of about 30 Ω·cm was formed by phosphorus diffusion carried out at 870 ℃ from a $POCl_3$ liquid source in an open tubular furnace for 50 min. Aluminium was deposited on both sides of the samples, and these were annealed for 30 min at 400 ℃ in a N_2 atmosphere to form ohmic contacts. Aluminium front contacts were chemically etched using the photolithographic process with the front contact mask to receive the incident light.

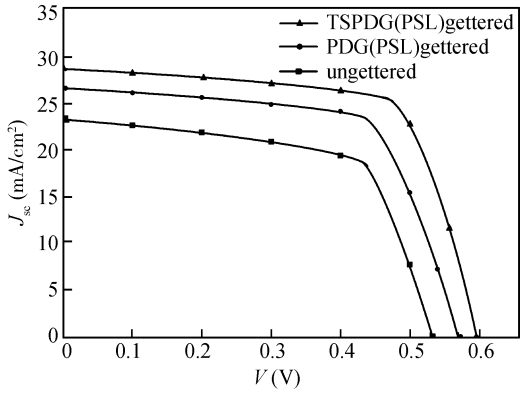

Fig. 2. Photovoltaic characteristic parameters of different solar cells.

Table 1. τ_n/τ_0 of minority carriers before and after different gettering processes.

Treated condition	τ_n/τ_0
Ungettered sample (reference)	1
Sample gettered by PDG (PSL) at 900 ℃ for 90 min	7.8
Samples gettered by TSPDG (PSL) under conditions of 900 ℃/15 min + 700 ℃/75 min	1.1
Samples gettered by TSPDG (PSL) under conditions of 900 ℃/30 min + 700 ℃/60 min	3.2
Samples gettered by TSPDG (PSL) under conditions of 900 ℃/45 min + 700 ℃/45 min	10.4
Samples gettered by TSPDG (PSL) under conditions of 900 ℃/60 min + 700 ℃/30 min	14.3

3. Results and discussion

Before and after different gettering processes, the τ_{eff} of minority carriers was measured using a microwave detected photoconductivity decay (μ-PCD) method with a pulse laser of 904 nm. Before measurements, the surfaces of the samples were passivated by immersing them in a dilute HF solution. The ratio of the finial effective lifetime τ_n to its original value τ_0 is shown in Table 1.

SEM (Hitachi S-4800) was used to analyze the influence of different gettering methods on the performances of PSL, and the surface morphologies of some samples are shown in Fig. 1.

J_{sc}, V_{oc}, FF and η of the solar cells were measured at room temperature using a solar simulator calibrated under AM1.5 illumination. Figure 2 shows the photovoltaic characteristic parameters of different solar cells.

Because of lattice expansion, the lattice constant of the PSLs along the surface direction usually exceeds that of the initial SOG-Si. This may lead to an elastic lattice deformation in the P-doped PSLs/Si interface and a large amount of dangling bonds in the PSLs during the gettering process. The state of impurities captured by dangling bonds in the PSLs is steadier than that in the Si compound[5−8], so PSLs are efficient gettering centers to capture impurities during thermal treatment. Table 1 demonstrates that both the PDG (PSL) and the TSPDG (PSL) process with t_H longer than 15 min can remove impurities efficiently so that τ_{eff} of minority carriers was largely improved. In particular, after treatment of the TSPDG (PSL) process under conditions of 900 ℃/60 min + 700 ℃/30 min, the τ_{eff} of minority carriers is increased to 14.3 times its orig-

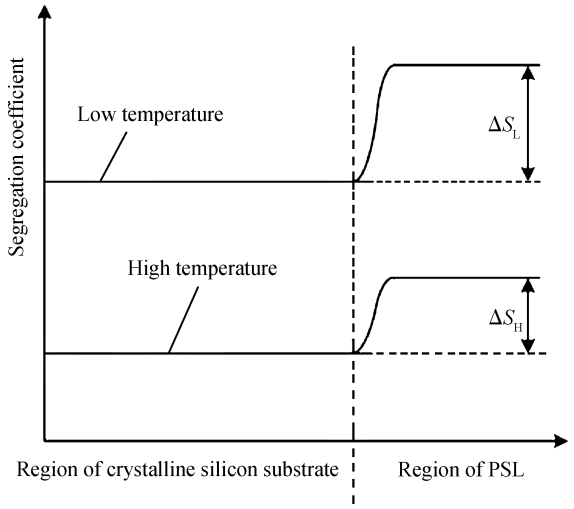

Fig. 3. Variation in the segregation coefficient at different temperatures.

inal value, which is far superior to the result 7.8 times of the conventional PDG (PSL) at 900 ℃/90 min. This is mainly because the performances of the PSL, such as the pore diameter and coarsening of the pore texture, may affect the gettering efficiency ($\eta_{\rm get}$). The reported experimental and simulated data reveal the following relationship among the average pore diameter $d_{\rm pore}$, the annealing temperature T and the annealing time t, as follows[9],

$$d_{\rm pore} \propto {\rm e}^{-0.2/kT}, \tag{1}$$

$$d_{\rm pore} \propto t^{1/4}. \tag{2}$$

The annealing of the PSL at high temperature for a long duration can increase the mean pore diameter, thereby reducing the total surface area and the coarsening of the PSL. Moreover, it is possible for the pores to collapse[10]. $\eta_{\rm get}$ using the PSL is directly proportional to the gradient of vacancy concentration $\Delta\varepsilon(R)$ from the interface to the top of the porous silicon layers to some extent, $\Delta\varepsilon(R)$ is expressed as[11]

$$\Delta\varepsilon(R) = \varepsilon_{\rm R}(R) - \varepsilon + \varepsilon_{\rm Gr}(p), \tag{3}$$

where ε is the vacancy concentration of the lattice, $\varepsilon_{\rm Gr}$ is an additional vacancy concentration and $\varepsilon_{\rm R}$ is the vacancy concentration at the rim of the pore. The vacancy concentration near a large pore is lower than that near a small pore, therefore the vacancy concentration $\Delta\varepsilon$ and $\eta_{\rm get}$ decreases with increasing pore radius.

With the increase in treatment time at 900 ℃, some small pores connect with each other and become a large pore, the mean pore diameter $d_{\rm pore}$ becomes larger, and the total surface of the pores becomes small. These are factors limiting the increase in $\eta_{\rm get}$. While comparison of Figs. 1(c) and 1(b) indicates that the above disadvantageous factors were weakened after the TSPDG (PSL) process because the treatment time at 900 ℃ was shortened, so the gettering effect of the TSPDG (PSL) under conditions of 900 ℃/60 min + 700 ℃/30 min are better than that of the PDG (PSL) at 900 ℃ for 90 min.

Based on the proposed segregation gettering model, the gettering procedure includes three steps: (1) the impurities dissolve; (2) the dissolved impurities diffuse quickly to the PSLs; (3) the impurities are trapped in the PSLs. The optimum gettering result could be the result of competition between the release of impurities from the bulk and a capture of impurities in the gettering layer. The gettering efficiency $\eta_{\rm get}$ is directly proportional to the segregation coefficient between the Si substrate and the gettering regions PSLs[11]. As shown in Fig. 3, the difference in segregation coefficients $\Delta S_{\rm H}$ of the impurity atoms between the regions of crystalline silicon substrate and the PSL at low temperature is larger than that at high temperature[12]. The following treatment step at 700 ℃ of the TSPDG (PSL) makes the $\Delta S_{\rm H}$ of impurity atoms increase obviously. So, the gettering efficiency will be improved.

Due to improved gettering efficiency, as shown in Fig. 2, the TSPDG (PSL) process under conditions of 900 ℃/60 min + 700 ℃/30 min improves $J_{\rm sc}$ of the solar cells from 23.5 to 28.7 mA/cm^2, $V_{\rm oc}$ from 0.534 to 0.596 V and η from 8.1% to 11.8%, which are far superior to the result improved by the PDG (PSL) process at 900 ℃ for 90 min. The new method is simple and compatible with fabrication technology of solar cells to ameliorate SOG-Si based solar cells.

4. Conclusions

As a result of an appropriate decrease in the gettering time at 900 ℃ and an adoption of a gettering step at 700 ℃, the TSPDG (PSL) process weakens the deterioration of performances of the PSL, improves the $\Delta\varepsilon$, and increases the $\Delta S_{\rm H}$ between the substrate material and the PSL gettering regions. So, within the same whole gettering time of 90 min, the TSPDG (PSL) process has a better gettering effect than that of the conventional PDG (PSL) process at 900 ℃, provided that the gettering time at 900 ℃ is long enough to ensure that the impurity clusters dissolve and diffuse to the gettering region. The TSPDG (PSL) process under conditions of 900 ℃/60 min + 700 ℃/30 min can increase the $\tau_{\rm eff}$ of minority carriers in SOG-Si to 14.3 times its original value, improve $J_{\rm sc}$ of solar cells from 23.5 to 28.7 mA/cm^2, $V_{\rm oc}$ from 0.534 to 0.596 V and η from 8.1% to 11.8%,which are far superior to the best result achieved by the PDG (PSL) process. The new method is simple and compatible with the fabrication technology of solar cells to ameliorate SOG-Si based solar cell performances.

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