Influence of the initial transient state of plasma and hydrogen pre-treatment on the interface properties of a silicon heterojunction fabricated by PECVD*

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Abstract: Amorphous/crystalline silicon heterojunctions (a-Si:H/c-Si SHJ) were prepared by plasma-enhanced chemical vapor deposition (PECVD). The influence of the initial transient state of the plasma and the hydrogen pre-treatment on the interfacial properties of the heterojunctions was studied. Experimental results indicate that: (1) The instability of plasma in the initial stage will damage the surface of c-Si. Using a shutter to shield the substrate for 100 s from the starting discharge can prevent the influence of the instable plasma process on the Si surface and also the interface between a-Si and c-Si. (2) The effect of hydrogen pre-treatment on interfacial passivation is constrained by the extent of hydrogen plasma bombardment and the optimal time for hydrogen pre-treatment is about 60 s.

Key words: silicon heterojunction; PECVD; interface properties; initial transient state of plasma; hydrogen plasma pre-treatment

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1. Introduction

Heterojunction with intrinsic thin-layer (HIT) solar cells are of great interest for photovoltaic development due to their low-cost fabrication and high efficiency[1, 2]. For an HIT solar cell, a layer of a-Si:H with a thickness of about 5 nm is deposited on top of c-Si. The properties of the a-Si:H(i)/c-Si interface are decisive to the eventual device performance[3−5]. For PECVD processing, during the initial transient stage, the concentration and the temperature of plasma are quite unstable[6−9]. For example, after starting the glow discharge, the intensity of the excited SiH radicals decreases and then levels off, and for different chambers, the initial transient state of plasma takes place over periods ranging from 2 to 60 s[6]. It is clear that the interfacial properties between a-Si:H(i)/c-Si depend on the initial transient state of plasma directly[8], and the performance of HIT cells relies on the precise control of the initial processing stage in particular. Before depositing a layer of a-Si:H on c-Si, hydrogen pre-treatment is often used to passivate the surface of c-Si. This is mainly because H atoms can etch the c-Si surface to remove the defective parts and terminate the dangling bonds as well. It has been reported that proper hydrogen pre-treatment using hot-wire chemical vapor deposition (HWCVD) is beneficial for the surface passivation of c-Si and enhances the performance of an HIT solar cell[10, 11]. Considering the bombardment of hydrogen plasma in PECVD, the effect of the hydrogen plasma pre-treatment on the surface passivation of c-Si still needs further study.

In this paper, intrinsic and boron-doped a-Si:H films were deposited by PECVD to form silicon heterojunctions. To prevent the initial transient state of the plasma from affecting the film deposition, a shutter was used to shield the substrate during the initial unstable plasma stage. We investigated the effects of the shutter shielding time ($t_{\rm s}$) and hydrogen plasma pre-treatment time ($t_{\rm H}$) on the interfacial properties between a-Si:H/c-Si by minority carrier lifetime measurements and the dark I–V characteristics of the heterojunction with the structure of Ag/a-Si:H(p)/a-Si:H(i)/c-Si(n)/Ag.

2. Experimental

All samples were prepared on c-Si substrates (CZ, N-type, 1–3 Ω·cm) with (100) surface orientation. Before texturization, the saw damages of c-Si wafers were removed by a 20 wt% NaOH solution for 20 min at 75 ℃. Then, the wafers were textured by NaOH and NaClO solutions, respectively. The texturization conditions are listed in Table 1. The average height of the pyramids on the c-Si surface textured by NaClO solution is around 3 μm, which is smaller than the one obtained by NaOH solution (about 10 μm), as shown in Fig. 1. After that, the wafers were RCA cleaned. All the Si films were deposited by PECVD in a triple-chamber system. Before deposition, the natural oxide layer on the c-Si surface was removed by 2% HF solution for 60 s. The c-Si was shielded by a shutter when starting the glow discharge. After $t_{\rm s}$, the shutter was withdrawn and the a-Si:H(i) layer began to be deposited. The deposition conditions are summarized in Table 2 and the conditions for hydrogen plasma pre-treatment are shown in Table 3. In order to study the interfacial properties, we deposited an a-Si:H(i)

Table 1. Conditions for NaOH and NaClO texturizaiton.

Solution	Concentration (wt%)	Additives	Temperature (℃)	Time (min)
NaOH	1.4	3wt% Na_2SiO_4 +8V% C_2H_5OH	75	60
NaClO	1	15V% C_2H_5OH	80	110

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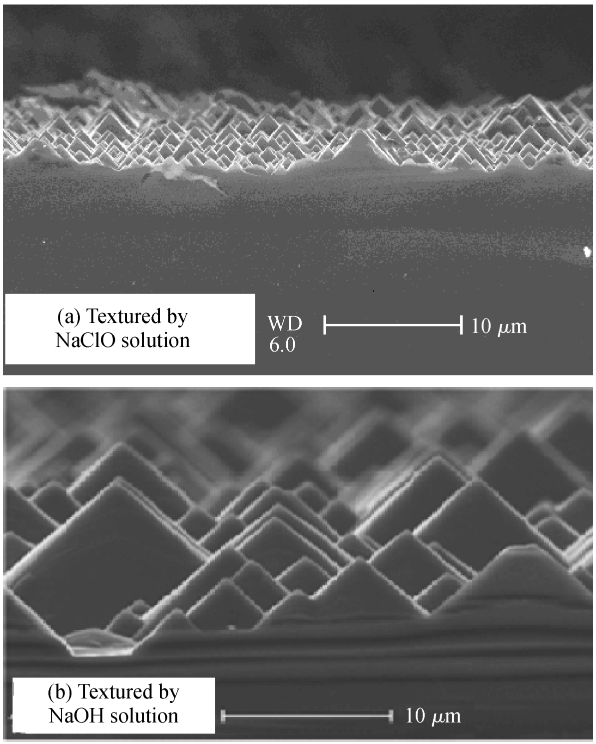

Fig. 1. SEM image of textured c-Si surface.

Table 2. Deposition conditions for the Si thin films.

Type	T_s (℃)	H_2 (sccm)	SiH_4 (sccm)	B_2H_6 (sccm)	Pressure (Pa)	Power (W)
a-Si:H(i)	140	16	2	—	150	6
a-Si:H(p)	170	10	2	10	200	10

Table 3. Conditions for the hydrogen plasma pre-treatment.

T_s (℃)	H_2 (sccm)	Pressure (Pa)	Power (W)
140	18	230	6

layer with a thickness of about 20 nm on c-Si substrate, which is thicker than that of the a-Si:H(i) layer in the HIT cell. The thickness of the a-Si:H(p) layer is about 15 nm. The heterojunction was fabricated with a Ag/a-Si:H(p)/a-Si:H(i)/c-Si(n)/Ag structure. The minority carrier lifetime was measured by a WT-2000 wafer scanner and the dark I–V characteristics of the heterojunction were obtained at 300 K.

3. Results and discussion

3.1. Initial transient state of plasma

The c-Si substrates were textured by NaOH solution in this work. It is clear that the interface properties between a-Si:H(i)/c-Si are affected by the chamber history (such as cross-contamination, remaining impurities and silicon powder) and the initial transient state of plasma as well[12]. Here, we studied the influence of t_s on the interface properties of a-Si:H(i)/c-Si. Figure 2 shows the dependence of minority carrier lifetime (τ) for a-Si:H(i)/c-Si on t_s. When $t_s < 100$ s, τ decreases with increasing t_s, indicating that removing the shutter during the initial transient state of plasma results in a re-distribution of electric field and may make the plasma more unstable. When $t_s > 100$ s, τ increases obviously with increasing t_s and reaches the maximum value at $t_s = 150$ s. It presents that, for our experimental condition, the plasma equilibrium time (including the initial transient time and the unstable time resulted from the shutter removed) exceeds 100 s, which is quite consistent to the result reported by Nunomura *et al.*[13].

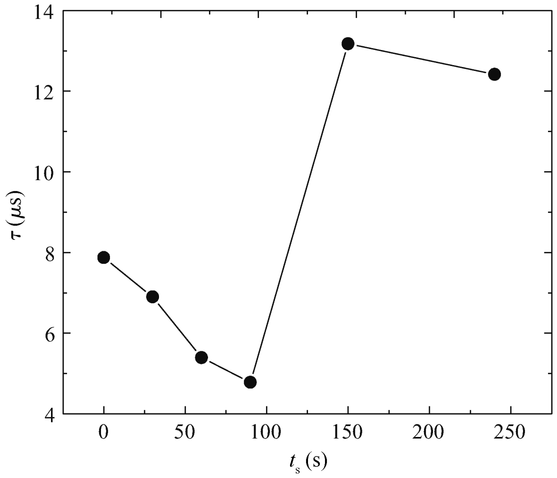

Fig. 2. Dependence of τ for a-Si:H(i)/c-Si on t_s.

Dark I–V measurements were undertaken to analyze the interface properties of the heterojunction. The dark I–V characteristics could be fitted according to the following double-diode equation:

$$
\begin{aligned}
I = {} & I_{01}\left[\exp\frac{q(V-IR_s)}{n_1kT}-1\right] \\
& + I_{02}\left[\exp\frac{q(V-IR_s)}{n_2kT}-1\right] \\
& + \frac{V-IR_s}{R_p},
\end{aligned}
\quad (1)
$$

where I_{01} and I_{02} are the diffusion saturation current and generation–recombination saturation current, n_1 and n_2 are the diffusion diode factor and generation–recombination diode factor, q is the electron charge, k is Boltzmann's constant, T is the temperature, R_s is the series resistance and R_p is the shunt resistance. The first diode with $n_1 = 1$ expresses the diffusion process within the heterojunction at room temperature. With the second diode, the different recombination mechanisms are considered, where the theoretically calculated ideality factor comes to $n_2 = 2$[14–16].

From the dark I–V curves, we can recognize four different voltage regions (Fig. 3): (1) $V < 0.15$ V, the dark current is mainly determined by the shunt resistance R_P; (2) $0.15 < V < 0.3$ V (the second term of Eq. (1)), the generation–recombination current predominates; (3) $0.3 < V < 0.5$ V (the first term of Eq. (1)), the diffusion current is dominant; (4) $V > 0.5$ V, the dark current is controlled by the series resistance R_S. So, by fitting the dark I–V curve, the parameters can be extracted. In this paper, our interest is focused on the interfacial property of the heterojunction, the generation–recombination current in the depletion region, which is related to the interfa-

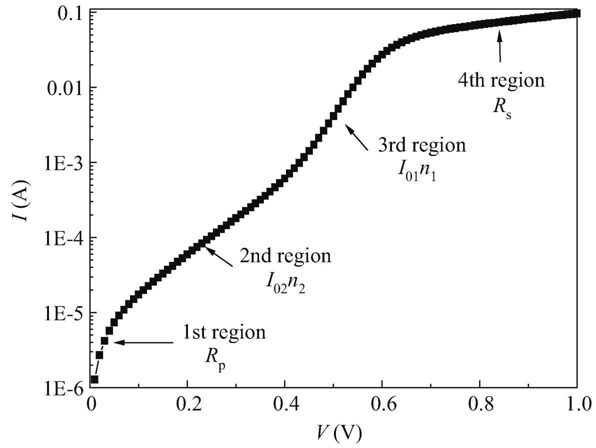

Fig. 3. Dark I–V curve with different regions.

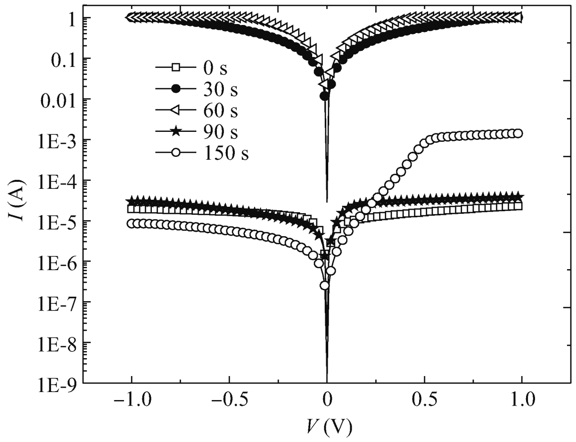

Fig. 4. Dark I–V curves of the heterojunctions with different t_s.

cial property, is mainly studied and only parameters n_2 and I_{02} are fitted. The derivation of the theoretically assumed value is basically attributed to the interface and surface recombination.

Figure 4 shows the dark I–V curves for heterojunctions with different t_s. As is shown, when t_s is short, the diode properties of the heterojunctions are bad, especially for the samples with t_s = 30 s and 60 s. These two curves are symmetrical, meaning that the performance of the heterojunctions is just like a resistance. The dark I–V curve for the sample with t_s = 150 s indicates the best interface properties of them all. The results shown in both Figs. 2 and 4 have clearly certified that, if t_s < 100 s, the plasma process cannot be stable enough to deposit, which may result in a negative effect on the interface properties of the heterojunctions.

3.2. Hydrogen plasma pre-treatment

The c-Si substrates were textured by NaClO solution here. Figure 5 shows the dependence of τ on t_H. It is obvious that τ decreases when the process of hydrogen plasma pre-treatment is added, and the value of τ is sensitive to t_H. The sample with $t_H = 60$ s has the best value of τ among the samples with the hydrogen plasma pre-treatment process, implying the optimal value of t_H is 60 s, which is consistent with the result obtained by HWCVD reported by Zhang *et al.*[11].

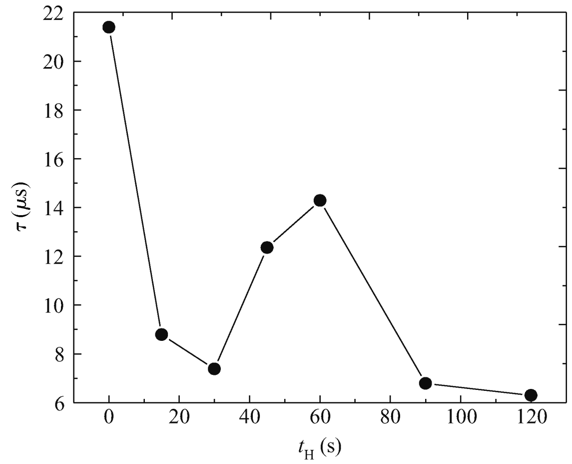

Fig. 5. Dependence of τ for a-Si:H(i)/c-Si on t_H.

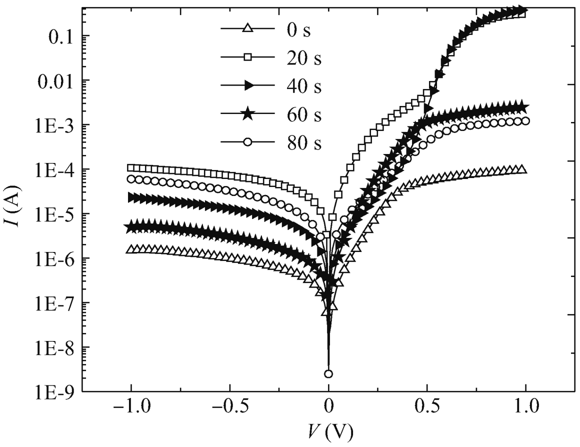

Fig. 6. Dark I–V curves of the heterojunctions with different t_H.

Table 4. The fitted parameters from the dark I–V curves (0.15 V < V < 0.3 V).

t_H (s)	n_2	I_{02} (μA)
0	2.17	0.12
20	3.65	47
40	2.72	2.1
60	2.51	1.2
80	3.4	6.5

To further study the influence of hydrogen plasma pre-treatment on the properties of the a-Si:H(i)/c-Si interface, we measured the dark I–V curves for heterojunctions with different t_s, as shown in Fig. 6. The parameters n_2 and I_{02} were fitted and listed in Table 4. The values of n_2 and I_{02} for the sample with $t_H = 0$ are smallest and nearest to the ideal value implying the best interface properties. When $t_H > 0$, the values of n_2 and I_{02} decrease obviously, meaning that the interface properties become worse after H plasma treatment. Especially for the one with $t_H = 20$ s, the dark I–V curve is S-shaped and the value I_{02} is 1–2 order larger than others. The values of n_2 and I_{02} for the sample with $t_H = 60$ s are the smallest among all the samples with $t_H > 0$, showing that 60 s is the optimal value of t_H.

The results (shown in Figs. 5, 6 and Table 4) may indicate that:

(1) The energy of the H atoms obtained from PECVD process is much greater than that obtained from HWCVD process. They not only bombard the reactor's wall and the substrate then cause contamination to the wafer, but also etch the c-Si wafer directly and create new defects there.

(2) The optimal time of hydrogen plasma pre-treatment obtained by the minority carrier lifetime measurements and the dark $I-V$ curves are both 60 s, which is consistent with the result by HWCVD. It means that hydrogen plasma pre-treatment with proper t_H can also reduce the surface defect density of c-Si (mainly through the saturation of the dangling bonds at the c-Si surface). If the negative effects of the hydrogen plasma bombardment can be suppressed, the positive effects of the hydrogen plasma on passivation may be demonstrated.

4. Conclusions

Avoiding the effects of the initial transient state of plasma on the deposition of the a-Si:H(i) thin film is critical to the performance of a Si heterojunction. Using a shutter to shield the substrate during the unstable plasma stage is an easy and effective way to realize this. $t_s > 100$ s (in our experimental conditions) can improve the interface properties between a-Si:H(i)/c-Si; removing the shutter during the initial transient state of plasma will worsen the interface properties, which may be caused mainly by the redistribution of the electric field. The optimal value of hydrogen plasma pre-treatment time is 60 s. Its effects on the surface passivation of c-Si are constrained to hydrogen plasma bombardment.

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