CHIN. PHYS. LETT. Vol. 34, No. 3 (2017) 038101

Significant Improvement of Passivation Performance by Two-Step Preparation of Amorphous Silicon Passivation Layers in Silicon Heterojunction Solar Cells *

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(Received 23 November 2016)

The key feature of amorphous/crystalline silicon heterojunction solar cells is extremely low surface recombination, which is related to superior passivation on the crystalline silicon wafer surface using thin hydrogenated amorphous silicon (a-Si:H) layers, leading to a high open-circuit voltage. In this work, a two-step method of a-Si:H passivation is introduced, showing excellent interface passivation quality, and the highest effective minority carrier lifetime exceeds 4500 µs. By applying a buffer layer deposited through pure silane plasma, the risk of film epitaxial growth and plasma damage caused by hydrogen diluted silane plasma is effectively reduced. Based on this, excellent passivation is realized through the following hydrogen diluted silane plasma process with the application of high density hydrogen. In this process, hydrogen diffuses to a-Si/c-Si interface, saturating residual dangling bonds which are not passivated by the buffer layer. Employing this two-step method, a heterojunction solar cell with an area of 239 cm^2 is prepared, yielding to open-circuit voltage up to 735 mV and total-area efficiency up to 22.4%.

PACS: 81.05.Gc, 88.40.H−, 88.40.jj, 88.40.hj DOI: 10.1088/0256-307X/34/3/038101

Silicon heterojunction (SHJ) solar cells enable high energy conversion efficiencies with industrial processing.[1] In 2016, a new world record of SHJ solar cell conversion efficiency at 26.3% was reported by Kaneka. The key feature of the high performance SHJ solar cells is the ability to allow extremely low recombination which results in high open-circuit voltage ($V_{\rm OC}$).[2] Given the excellent quality of monocrystalline Si (c-Si) wafers, charge carrier recombination losses occur principally at the c-Si surface.[3] Therefore, the performance of SHJ solar cells critically depends on the deposition condition of intrinsic thin hydrogenated amorphous silicon (a-Si:H) films, which has an effect on interface and film quality.

The a-Si/c-Si interface has been widely studied, and appropriate treatment including long-time low temperature annealing[4] and hydrogen plasma treatment[5−8] has been confirmed effective in improving passivation quality. These results indicate that such improvement comes from the saturation of dangling bonds with hydrogen.[4−6,9,10] Additionally, many studies have revealed that hydrogen produces effective chemical annealing on a-Si:H films, promoting structural relaxation, and ultimately improving the stability of the film;[11−14] that is, hydrogen is important in improving the a-Si/c-Si interface and a-Si bulk quality,[6,15−17] which is key in obtaining high efficiency SHJ solar cells.[1,2] Obviously, increasing the hydrogen dilution ratio in the production of a-Si:H films leads to a high concentration of hydrogen, which should benefit passivation as described above. Unfortunately, the high concentration of hydrogen also induces serious etching and at the same time reduces the deposition rate.[12] In fact, hydrogen plasma may produce severe microstructural damage of the c-Si surface due to this etching effect, especially when the deposition rate is low.[18−20] The presence of surface damage leads to a high dangling bond density which is hard to eliminate.[20,21] Additionally, the condition of high hydrogen dilution also encourages epitaxial growth of silicon films on c-Si substrates. As is known, the epitaxial Si layers have a detrimental effect on passivation.[22] That is, hydrogen diluted silane plasma has the potential of achieving excellent passivation, but highly diluted silane plasma does not, in fact, often offers good passivation due to the plasma damage on c-Si surface and the characteristics in promoting crystallization.[23−25] Therefore, how to avoid this plasma damage and epitaxial growth effectively is an essential role to play in the potential advantage of hydrogen diluted silane plasma achieving excellent passivation quality, and it is worth being studied.

In this study, hydrogen diluted silane plasma (HDSP, gas flow ratio (H_2/SiH_4) = 10:1) was used to prepare passivation layers. High depletion pure silane plasma (PSP) was used as a reference, since it has been demonstrated to potentially ensure quality passivation.[1,6,26] Similar to the investigations mentioned above, a single-step HDSP does not exhibit good passivation compared with high depletion PSP. Based on this, we propose a two-step method to prepare a-Si:H passivation layers in SHJ solar cells by inserting a PSP deposited buffer layer in front of the HDSP process to produce an excellent passivation effect. The highest effective minority carrier lifetime ($\tau_{\rm eff}$) exceeds 4500 µs, which is a value much larger

*Supported by the National Natural Science Foundation of China under Grant Nos 61574009, 11274028, 11574014, 51302081 and 61575010, and the Science and Technology Commission of Beijing Municipality under Grant Nos Z151100003315018 and Z151100003515004.
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than that of single HDSP and PSP processes. The insertion of the PSP buffer layer effectively inhibits plasma damage and epitaxial growth, insuring a sharp a-Si/c-Si interface. The following HDSP process insures sufficient hydrogen diffusion to a-Si/c-Si which further saturates residual dangling bonds. Finally, an SHJ solar cell with an efficiency of 22.4% was fabricated through the optimization of the buffer layer thickness, yielding $V_{\rm OC}$ up to 735 mV.

In our work, the SHJ solar cells were fabricated on commercial solar grade Czochralski-grown (Cz) silicon wafers (n-type, 3–5 Ω·cm, 200 µm thick, (100) oriented). The wafer surface was chemically textured to generate a pyramid structure, and then was cleaned by the RCA process. Very high frequency plasma enhanced chemical vapor deposition equipment (VHF-PECVD, 40 MHz) was used to prepare amorphous silicon layers at 220°. The indium tin oxide (ITO) layers were prepared by the magnetron sputtering method. Finally we used the screen printing method to form the front and back silver electrodes. Just before a-Si:H layer deposition, the native oxide on the wafer surfaces was removed in a hydrofluoric acid solution. After deposition, effective minority carrier lifetimes ($\tau_{\rm eff}$) were measured with a Sinton consulting WCT-120 quasi-steady-state photo-conductance system. In addition, a-Si:H films were also characterized by the Fourier transform infrared spectroscopy (FTIR) spectroscopy. To confirm whether there was epitaxial Si presenting at the interface, high resolution transmission electron microscopy (HR-TEM, FEI Tecnai G2 F30) images were taken. Details about the structure and fabrication process of complete heterojunction solar cells are described elsewhere.[27]

For passivation studies, intrinsic a-Si:H layers with a thickness of about 7 nm were deposited on both sides of textured Cz wafers using PECVD. Three deposition sequences were tested using a single-step HDSP process, a single-step high depletion PSP process, and by a two-step method, consisting of an HDSP process following a high depletion PSP process. Layers deposited through high depletion PSP and HDSP are 3 nm and 4 nm, respectively. Table 1 lists $\tau_{\rm eff}$ of c-Si wafers passivated through the three deposition schemes, which are given at a minority carrier density of 5×10^{15} cm^{-3}. The two-step method shows the best passivation quality, followed by the PSP process. Here $\tau_{\rm eff}$'s are 2808 µs and 1300 µs, respectively. The HDSP process shows the worst passivation, and $\tau_{\rm eff}$ is only 306 µs. The advantage of the two-step method in passivation originates from the following three aspects.

Table 1. Detailed deposition parameters and the corresponding effective minority carrier lifetimes of the three schemes.

Recipe	Hydrogen dilution ratio	Power density (mW/cm^2)	Self-bias voltage (V)	$R_{\rm d}$ (Å/s)	$\tau_{\rm eff}$ (µs)
HDSP	10	32	180	0.8	306
PSP	0	30	90	7.9	1345
Two-step method					2808

Firstly, the adoption of the buffer layer deposited through high depletion PSP, as mentioned above, greatly decreases the risk of plasma damage and serious epitaxial growth. The detailed deposition parameters of high depletion PSP and HDSP are listed in Table 1. It can be seen that the input power densities of the two recipes are almost the same, 30 mW/cm^2 and 32 mW/cm^2, respectively. However, the self-bias voltage and deposition rate show very large difference. The deposition rate ($R_{\rm d}$) of HDSP is extremely low (less than 1 Å/s), while the self-bias voltage is 180 V. As a comparison, the self-bias voltage of high depletion PSP with a $R_{\rm d}$ of nearly 8 Å/s is only 90 V. Therefore, high depletion PSP with a high $R_{\rm d}$, low hydrogen content and low self-bias voltage greatly reduces the plasma damage to c-Si surface.[8,20] Additionally, the use of PSP could also effectively avoid the risk of epitaxial growth at the a-Si/c-Si interface.[1,28,29] The a-Si/c-Si interface of the sample prepared through the two-step method was measured by HR-TEM, as shown in Fig. 1(a). Figure 1(a) presents an atomically abrupt interface, which obviously means that the epitaxial growth does not occur.

Secondly, the following HDSP process could ensure sufficient hydrogen content at the a-Si/c-Si interface which effectively passivates dangling bonds. According to the work of An *et al.*,[30] hydrogen supplied to the surface of a-Si:H penetrated up to 20 nm deep, thus atomic hydrogen can easily penetrate through the a-Si:H buffer layer to a-Si/c-Si interface and can combine with c-Si surface dangling bonds,[4,6] as shown in Fig. 1(b). Therefore, the HDSP process may lead to higher hydrogen content at the a-Si/c-Si interface compared with the PSP process. The hydrogen content at the a-Si/c-Si interface is hard to measure, but this could be evaluated through the hydrogen content of thin a-Si:H layers. In this study, the FTIR spectra of 42-nm-thick intrinsic a-Si:H films deposited on polished high resistance c-Si wafers (>5000 Ω·cm) are measured. Figures 2(a) and 2(b) represent the FTIR spectra of a-Si:H layers deposited through the two-step method (6 cycles, film a), and the PSP process (film b). In an FTIR spectral region, peaks from monohydride (SiH) bonds (2000 cm^{-1}) and higher hydrides (SiH_2) bonds (2100 cm^{-1}) are present. Hydrogen content ($C_{\rm H}$) was calculated through the measured FTIR spectra, and it is presented in Table 2. As is expected, the hydrogen content of film a is larger than that of film b, which will lead to a low interface defect state density.

Thirdly, the quality of a-Si:H layers deposited through the HDSP process is usually better than that of PSP.[12,31] FTIR spectra show that the ratio of the SiH_2 peak area to the SiH peak area in Fig. 2(a) is much smaller than that in Fig. 2(b). The calculated microstructure factor R is smaller than that of film b, as listed in Table 2. This means that the deposited a-Si:H matrix through HDSP is more ordered, containing fewer voids and defect states,[4,6,15,22] indicating that film a is more in line with the requirement of device grade solar cells.

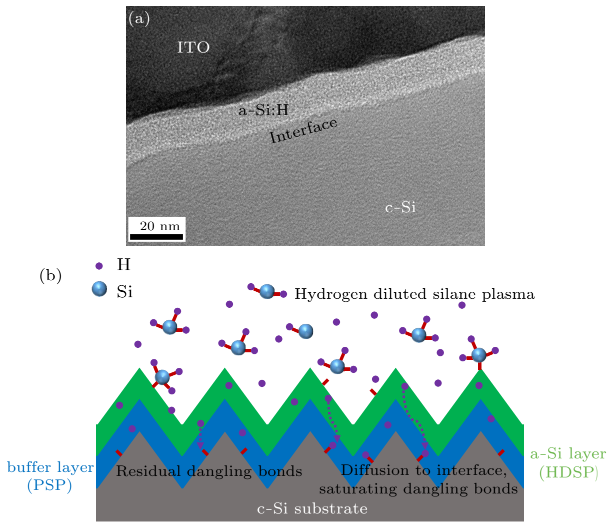

Fig. 1. (a) HR-TEM micrograph of the interface between c-Si substrate and a-Si:H layer deposited through the two-step method. (b) Schematic diagram of the hydrogen passivation mechanism of the two-step method.

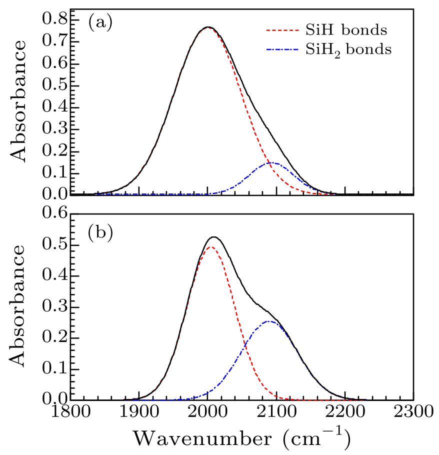

Fig. 2. Measured FTIR absorbance spectra of 42-nm-thick as-deposited a-Si:H layers deposited on (100) c-Si wafers, (a) the two-step method and (b) pure silane plasma.

Table 2. Detailed information of the as-deposited a-Si:H layers.

Layer properties	R	$C_{\rm H}$
Film a	11.36%	18.24%
Film b	20.29%	15.45%

Compared with the single HDSP process or the single high depletion PSP process, the two-step method combines the advantages of the two processes, leading to the significant passivation improvement of the a-Si/c-Si system on Cz solar grade silicon wafers.

Next, to further improve the passivation quality, the buffer layer thickness is optimized. The thickness of the buffer layer prepared through high depletion PSP changed from 0 nm to 7 nm, and a-Si:H layer deposited through HDSP changed from 7 to 0 nm, maintaining the total a-Si:H film thickness to 7 nm. The result is presented in Fig. 3(a). From Fig. 3(a), the curve peaks at around 2 nm, where a lifetime of 4190 µs is observed, when the buffer layer exceeds 2 nm, $\tau_{\rm eff}$ gradually decreases. When the buffer layer is less than 2 nm, the increase of $\tau_{\rm eff}$ is attributed to the gradually improved interface quality (less c-Si surface plasma damage and less possibility of film epitaxial growth). With the continuing increase of the buffer layer thickness, the passivation quality becomes continually worse. The increase of the buffer layer thickness will weaken the ability of hydrogen diffusion to interface,[32] and thus the possibility of hydrogen combining with interface dangling bonds decreases,[33,34] leading to the degradation of passivation.

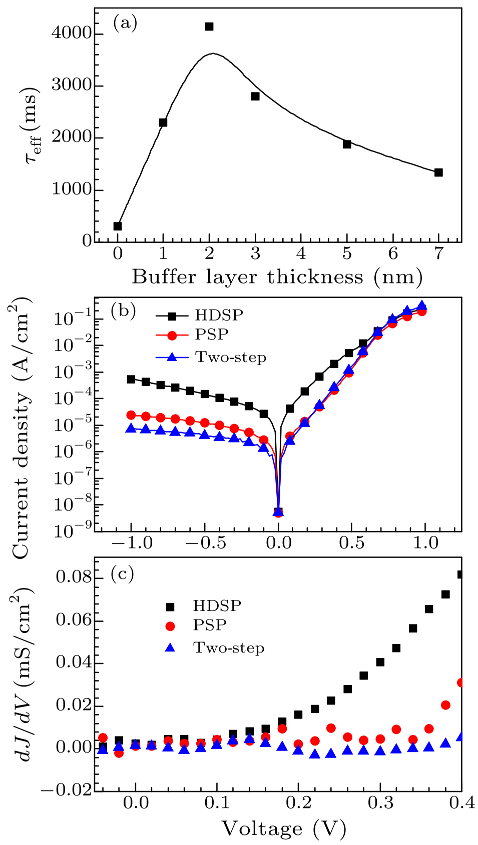

Fig. 3. (a) Effective minority carrier lifetime as a function of the buffer layer thickness. (b) Dark J–V curves and (c) illuminated shunt conductance of SHJ solar cells with different passivation layers.

Based on the results presented above, the PSP buffer layer was finally determined to be 2 nm in this study, and the highest $\tau_{\rm eff}$ exceeds 4500 µs. SHJ solar cells were completed by conventional processes including magnetron sputtering and screen-printing. On solar cell precursors (textured wafers passivated with as-deposited 13 nm i/n and 20 nm i/p layer stacks), $\tau_{\rm eff}$ up to 3500 µs was measured. The performance of SHJ solar cells with different passivation layers are listed in Table 3. As can be seen from Table 3, the short-circuit current density ($J_{\rm SC}$) and fill factor (FF) of the SHJ solar cells with different intrinsic a-Si:H passivation layers do not show a significant difference. However, the open-circuit voltage (V_{OC}) exhibits a similar dependence on the passivation layer as τ_{eff}. The value of V_{OC} of solar cells passivated through the two-step method reaches up to 735 mV. The generation rate and recombination rate of carriers in the space charge region are equal when the p–n junction is in thermal equilibrium. However, if the p–n junction is reverse-biased, the thermal excitation carriers generated through recombination center are driven away by the electric field before recombination. That is, the reverse current density increases with the interface defect density. Figure 3(b) shows the measured dark current density versus voltage (J–V) curves of SHJ solar cells, the reverse current density of the solar cell passivated through the two-step method is the lowest. This means that the interface defect density at the a-Si/c-Si interface is lowest. A plot of the derivative $G(V) = dJ/dV$ against V near J_{SC} represents the shunt conductance. From Fig. 3(c), it could also be found that the two-step method exhibits the lowest illuminated shunt conductance which reveals the best passivation quality. Thanks to the excellent passivation obtained by the two-step method, heterojunction solar cells with an area of 239 cm^2 have been prepared, yielding to open-circuit voltage up to 735 mV and total-area efficiency up to 22.4%.

Table 3. The performance of SHJ solar cells with different passivation layers.

	Cell area (cm^2)	E_{ff} (%)	V_{OC} (mV)	J_{SC} (mA/cm^2)	FF (%)
PSP		17.55	580	38.98	77.61
HDSP	238.95	21.64	710	38.97	78.24
Two-step method		22.43	735	39.04	78.18

In summary, a two-step method of preparing amorphous silicon passivation is proposed, showing excellent passivation quality in preparing the SHJ solar cell. The introduction of a buffer layer deposited through high depletion PSP avoids the risk of serious plasma damage and epitaxial growth during the HDSP process, which fully plays the advantage of HDSP in affording hydrogen to a-Si/c-Si interface. Based on this method, a large area (239 cm^2) solar cell with total-area efficiency up to 22.4% is achieved. Thanks to excellent passivation quality, open-circuit voltage up to 735 mV is yielded. The two-step method has a rather wide process window; and quite good passivation quality can be obtained when the buffer layer thickness varies from 2 nm to 5 nm, showing great potential in industrialization.

We appreciate Mr. Mingfang Dai, Doctors Yuanmin Li and Hui Zhao, Mr. James Huang, Ms. Lan Chen at Hanergy Thin Film Solar Group, R & D Center, for great support and helpful discussions.

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