

In Situ Process to Form Passivated Tunneling Oxides for Front-Surface Field in Rear-Emitter Silicon Heterojunction Solar Cells

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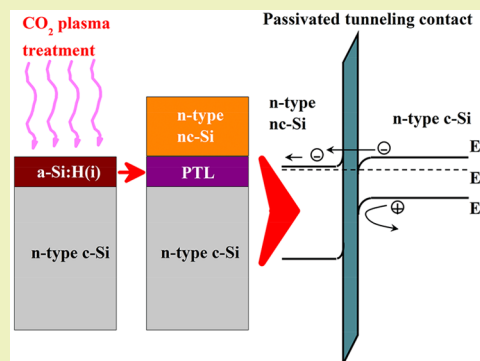
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ABSTRACT: A novel approach involving CO₂ plasma treatment of intrinsic hydrogenated amorphous silicon was developed to form ultrathin silicon oxide (SiO_x) layers, that is, passivated tunneling layers (PTLs), for the fabrication of passivated tunneling contacts. These contacts were formed by depositing the PTL/n-type hydrogenated nanocrystalline layer (nc-Si:H(n))/c-Si(n) stacks. The results indicated that a higher CO₂ plasma treatment pressure was preferred for the formation of oxygen-rich components in the silicon oxide films, with Si²⁺, Si³⁺, and Si⁴⁺ peaks, and a smoother PTL/c-Si heterointerface. The PTLs with higher oxidation states and lower surface roughness exhibited advantages for the c-Si surface passivation, with a maximum implied open-circuit voltage of approximately 743 mV. The lowest contact resistivity of approximately 60 mΩ cm² was obtained using nc-Si:H(n)/PTL/c-Si(n) as the passivated tunneling contact. Most importantly, the *in situ* process can help prevent the contamination of the heterointerface during device fabrication processes.

KEYWORDS: Passivated tunneling layer (PTL), Silicon oxide (SiO_x), Silicon surface passivation, CO₂ plasma treatment



INTRODUCTION

Recently, the highest efficiency achieved for a crystalline silicon solar cell, approximately 26.7%, was reported by Kaneka, Japan.¹ This device structure however had an interdigitated back-contact configuration, which requires a complicated and expensive fabrication process. Cost effectiveness is one of the crucial factors in manufacturing industrial solar cells. Thus, low prices and compatible high performance are the prime requisites for industrial production of solar cells. Hydrogenated amorphous silicon/crystalline silicon heterojunction (a-Si:H/c-Si) technology has the advantage of a simple process and low cost, in addition to highly efficient photovoltaics (PV) manufacturing compared with conventional crystalline silicon solar cells.^{2–6} Additionally, it is the least expensive among the current commercial silicon-based PV technologies.^{7,8}

The a-Si:H/c-Si heterojunction solar cells exhibit a high open-circuit voltage ($V_{oc} > 0.75$ V) owing to the high passivation quality of a-Si:H(i),⁹ and resulting high efficiency. The a-Si:H/c-Si heterojunction can be roughly classified into two groups according to the emitter configuration. These are the front-emitter (FE) configuration and the rear-emitter (RE) configuration. The RE configuration is currently being

researched intensively owing to its potential for a high short-circuit current density (J_{sc}) and higher fill factor (FF).^{9–11} In the FE configuration, the primary requirements for the p-type emitter are (1) thinness and low optical absorption, which minimize the parasitic absorption within the emitter layer, leading to additional light being absorbed into the absorber layer and a higher J_{sc} , and 2) a high conductivity, which reduces the series resistance of the devices and improves the FF. However, these are conflicting requirements for a single p-type layer.^{12,13} The RE configuration can, however, overcome the limitation of the FE configuration. First, in the RE configuration, the p-type emitter thickness can be freely controlled to achieve design of the film conductivity, which, in turn, improves the FF. Changing the thickness has no negative effect on the optical absorption or the J_{sc} . Moreover, the doping capability in the n-layer is higher than that in the p-layer; consequently, the conductivity of the film is higher in the case of the n-layer.¹⁴ This high film conductivity in the n-layer

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provides reinforcement for forming wider finger spacing in the RE configuration, reducing the shadow loss at the front surface and improving the J_{sc} .

Recently, in RE a-Si:H/c-Si heterojunction solar cells, the front-surface-field was configured using an a-Si:H(i) layer and a heavily doped n-type hydrogenated amorphous silicon (a-Si:H(n^+)) layer in a stacked sequence. The stacked a-Si:H layers exhibited a small optical bandgap (~ 1.7 eV). This small bandgap can disturb the front parasitic absorption and, hence, prejudice the J_{sc} . This drawback can be addressed by employing wider bandgap materials, such as μ c-Si:H and silicon tunneling oxide stacks,^{15–17} as alternatives to the conventional a-Si:H stacks.^{18,19} To form the wider bandgap-passivated silicon tunnel oxide, various methods have been investigated, such as wet and thermal oxidation and plasma-enhanced chemical vapor deposition (PECVD). Among these, the wet and thermal oxidation method exhibits disadvantages with respect to thickness control and the large valence-band offset at the heterointerface owing to the exceedingly large optical bandgap (~ 9 eV),^{20,21} in addition to a high processing temperature, which can cause wafer bending and entail high processing expenses. The devices based on the passivated silicon oxide deposited via PECVD suffer from a high series resistance, resulting in a low FF.²² In the present study, to form a passivated silicon oxide (SiO_x) layer (herein termed a passivated tunneling layer (PTL)), a CO_2 plasma treatment of the passivated a-Si:H(i) layer was employed for the first time. One of the advantages of the *in situ* process is that it helps to prevent contamination of the heterointerface due to the vacuum break that occurs when employing other methods.

EXPERIMENTAL SETUP

For the PTL experiments, one-side-polished n-type CZ Si wafers ($1\text{--}10\ \Omega\text{cm}$, $525\ \mu\text{m}$ thick, $\langle 100 \rangle$ oriented) were utilized. Organic residues on the wafer surface were removed via ultrasonic cleaning, followed by the RCA-1 and the RCA-2 cleaning procedures. Before the deposition of a-Si:H(i), the wafers were dipped in a hydrofluoric acid solution (1%) for a few minutes to remove the native oxides. Then, 3 nm-thick a-Si:H(i) layers were deposited on both sides of the wafers, followed by *in situ* CO_2 plasma treatments with pressures ranging from 1600 to 2200 mTorr to form the PTLs. The detailed conditions of the a-Si:H(i) layer deposition and the CO_2 plasma treatment are presented in Table 1.

Table 1. Process Parameters for a-Si:H(i) Layer and CO_2 Plasma Treatment Pressure for PTLs and Relative Intensities of Oxidation States for Different CO_2 Plasma Treatment Pressures

Layer	Gas ratio ($\text{SiH}_4\text{:H}_2\text{:CO}_2$)	Temp. ($^\circ\text{C}$)	Pressure (mTorr)	$I_{\text{Si}^{1+}}/(I_{\text{Si}^{2+}} + I_{\text{Si}^{3+}})$
a-Si:H(i)	1:4:0	200	1400	
PTL		200	1600	3.44
			1800	7.25
			2000	5.78
			2200	2.50

The thickness of the PTLs was determined using spectroscopic ellipsometry (SE, VASE, J. A. Woollam) in the wavelength range of 240–1700 nm at room temperature. The quasi-steady-state photoconductance (QSSPC), a commercial photoconductance setup from Sinton Consulting (WCT-120), was employed to measure the minority carrier lifetime (τ_{eff}). To identify the contact resistivity (ρ_c) at room temperature, silver was deposited via thermal

evaporation, using a shadow mask, onto the nc-Si(n)/PTL/c-Si(n) layer stack in the transfer length method (TLM) patterns.²³ An X-ray photoelectron spectroscopy (XPS) system with Cu $K\alpha$ radiation (1486.6 eV) was employed to investigate the chemical composition of the PTLs. The depth profiles of the SiH, O, SiH₂, etc., at the PTL/c-Si heterointerface were obtained using secondary ion mass spectroscopy (SIMS, CAMECAIMS-7F-magnetic-sector). High-resolution transmission electron microscopy (HR-TEM, JEM-2100F-HR-JEOL) was performed with an operation voltage of 200 kV to examine the cross section of the PTL/c-Si heterointerface.

RESULTS AND DISCUSSION

The objective of the proposed approach was to obtain *in situ* hydrogenated amorphous silicon oxide (a- $\text{SiO}_x\text{:H}$) films via CO_2 plasma treatment of the a-Si:H(i) layer. Hence, the XPS spectra were measured to confirm the composition of the a- $\text{SiO}_x\text{:H}$, as shown in Figure 1a. In addition, the XPS spectrum

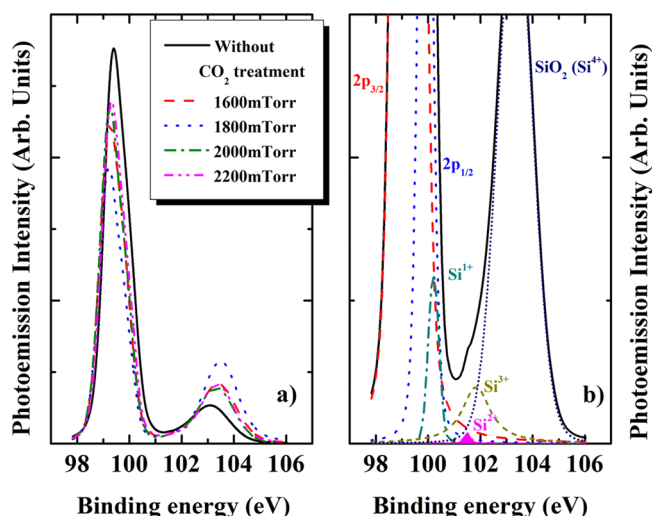


Figure 1. (a) Si ($2p_{3/2}$) core-level XPS raw data for various CO_2 plasma treatment pressures. (b) Exemplary peak fit for a CO_2 plasma treatment pressure of 2200 mTorr, showing the different oxidation states.

of the as-deposited a-Si:H(i) film has been presented for reference. The XPS spectrum indicates that the reference sample consists approximately entirely of hydrogenated amorphous silicon bonds, such as Si–Si, Si–H, and Si–H₂.²⁴ After the CO_2 plasma treatment, the peak energy of approximately 100.2 eV was shifted to a higher binding energy. This shift in the peak position is attributed to a bonding break (Si–Si, Si–H, and Si–H₂), followed by interdiffusion of the free hydrogen atoms. The amounts of Si–O and O–H bonds were, then, increased. These phenomena lead to a reduction in the Si^{0+} peak intensity, while promoting the formation of Si^{1+} , Si^{2+} , Si^{3+} , and Si^{4+} peaks with higher binding energies, as shown in Figure 1b. This improved the silicon oxidation states, which assisted the formation of oxygen-rich components within the a- $\text{SiO}_x\text{:H}$ film.^{25,26}

The distribution of the oxidation states elucidated the structure of the SiO_2/Si interface and the quality of the passivated c-Si surface.^{27,28} The dependence of the oxidation state represented by $I_{\text{Si}^{1+}}/(I_{\text{Si}^{2+}} + I_{\text{Si}^{3+}})$, on the treatment pressure was investigated and is shown in Table 1. Here, $I_{\text{Si}^{1+}}/(I_{\text{Si}^{2+}} + I_{\text{Si}^{3+}})$ was maximized at a treatment pressure of

approximately 1800 mTorr; the oxidation state ratio declined below and above this value. Notably, all oxidation species were detected in all the pressure ranges; however, Si^{1+} was the dominant species. Moreover, at a higher treatment pressure, the high oxidation states, such as Si^{2+} and Si^{3+} , were more pronounced. Himpsel et al. reported that on the Si (100) surface²⁶ the Si^{2+} state is more pronounced than the Si^{1+} and Si^{3+} states, owing to the bond topology of the truncated bulk structure with two broken bonds per atom. In contrast, the presence of all the oxidation states on the Si (100) surface deviates from the ideal SiO_2/Si interface.²⁶ Therefore, the oxidation states appeared to be consistent with the nonideal interface model.

A SIMS depth profile was obtained to investigate the diffusivity and/or the distribution of atoms within the vicinity of the heterointerface for untreated samples (Figure 2a) and

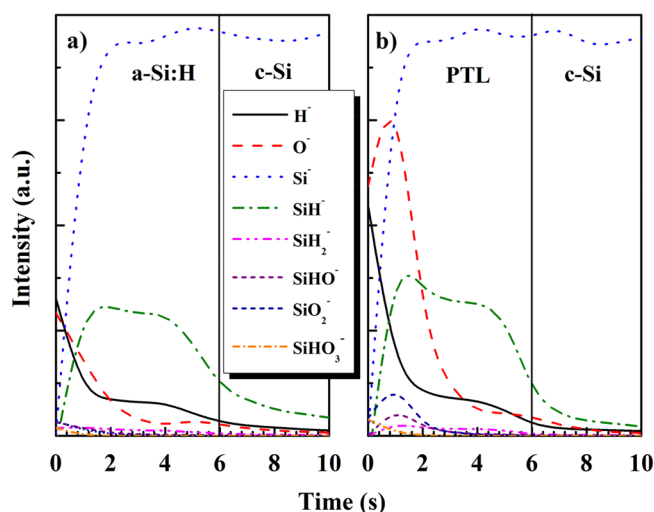


Figure 2. SIMS depth profiles of various ion species of the a) a-Si:H/c-Si and b) PTL/c-Si heterointerfaces; the PTL was formed at the plasma treatment pressure of 2200 mTorr.

for treated samples (Figure 2b). After the treatment, the intensity of all the ion species increased. It was observed that SiO_2^- and SiHO^- developed within the PTL and the PTL/c-Si heterointerface. With the help of plasma energy, all the ion species were redistributed to the preferred locations. Weak Si–Si, Si–H, and Si–H₂ bonds existed naturally in the a-Si:H(i) films. These bonds, particularly the Si–H bonds, may have been broken before interdiffusion, upon the plasma treatment. Thus, the improvement in the intensity of the SiH^- ions, beneficial for defect passivation, is attributed to the plasma energy, as shown in Figure 2b. Moreover, atomic oxygen may have diffused from the surface, where it had a high concentration, into the a-Si:H(i) layer and heterointerface, where it had a low concentration. Consequently, oxygen atoms may have reacted with Si and/or H to form the SiO or the O–H bonds. In addition, the presence of hydrogen atoms may have contributed to the incorporation of substantial amounts of hydrogen at the interface, as reported by Grunthaner et al.²⁵ The results from this study agreed with those of Grunthaner et al., who reported that the oxide layers were formed via high-temperature steam oxidation and wet chemical oxidation.²⁸

One of the disadvantages of the oxide layers is the high barrier between the front surface field and the n-type c-Si heterointerface, as shown in Figure 3a. This high barrier can contribute to a high series resistance (RES_s), owing to the low probability of electrons tunneling through the oxide layer, leading to a low FF and unsatisfactory performance.^{20,22} To evaluate the probability of electrons tunneling through our PTL, the TLM was employed under different CO_2 plasma treatment conditions. The specific contact resistance (ρ_c) derived from the TLM measurements as a function of the CO_2 plasma treatment is presented in Figure 3b. As shown, ρ_c tends to increase with increasing treatment pressure. The ρ_c value before the treatment is also presented for comparison. The lowest ρ_c of 22 m Ω cm² was observed for the before-treatment sample, and the highest ρ_c value was observed for the sample treated at the highest pressure. Importantly, the ρ_c values for all the samples were within the acceptable range for device

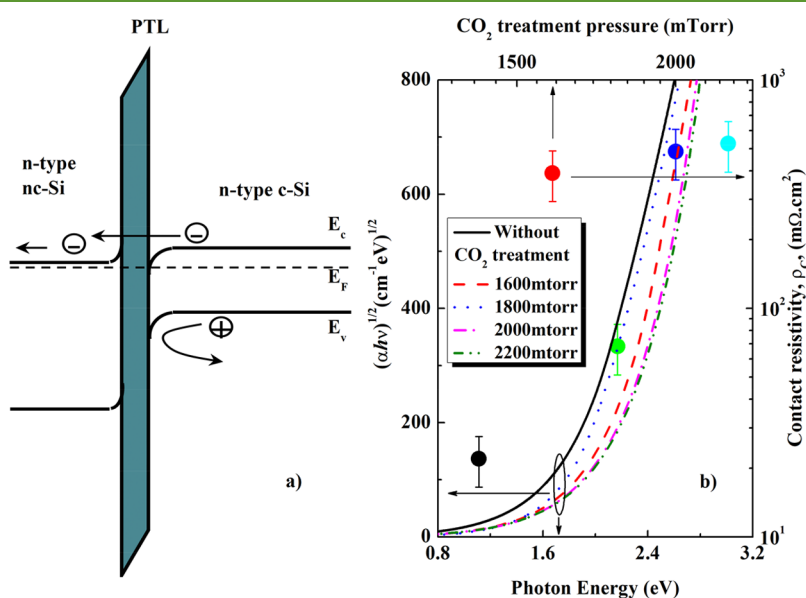


Figure 3. (a) Energy band diagram of nc-Si(n)/PTL/c-Si(n). E_C , E_V , and E_F represent the conduction band, valence band, and Fermi level, respectively. (b) Contact resistivity (ρ_c) derived from TLM measurements with respect to the CO_2 plasma treatment pressure and the optical bandgap of the as-deposited sample and the treated samples plotted as a function of the photon energy.

fabrication.²⁹ The probability of electrons tunneling through PTLs, i.e., the $T(E)$, can be expressed as follows

$$T(E) \propto \exp\left(-d_{\text{ox}}\sqrt{\frac{2m_t}{\hbar^2}\Phi}\right) \quad (1)$$

where d_{ox} represents the PTL thickness; m_t represents the tunnel mass of the particle; Φ represents the height of the potential barrier of the PTL on the c-Si; and $\hbar$ represents the reduced Planck constant.³⁰ Here, the d_{ox} of the PTLs was kept constant. Theoretically, $T(E)$ decreases with an increase in Φ . The optical absorption coefficient of the PTLs with different CO₂ plasma treatment pressures was characterized via SE. Using the optical absorption coefficient, the optical bandgaps were determined and are presented in Figure 3b. With a higher treatment pressure, the PTLs exhibited oxygen-rich components, thus yielding a larger optical bandgap. Consequently, Φ was higher, leading to a lower $T(E)$ and a higher ρ_c .

To evaluate the proposed method, the surface passivation quality of the PTL on a c-Si(n) wafer was investigated. The results of the passivation quality in terms of the minority carrier lifetime (τ_{eff}) ratios, i.e., $\tau_{\text{eff}(n)}/\tau_{\text{eff}(0)}$, with respect to the CO₂ plasma treatment pressure are shown in Figure 4a. Here,

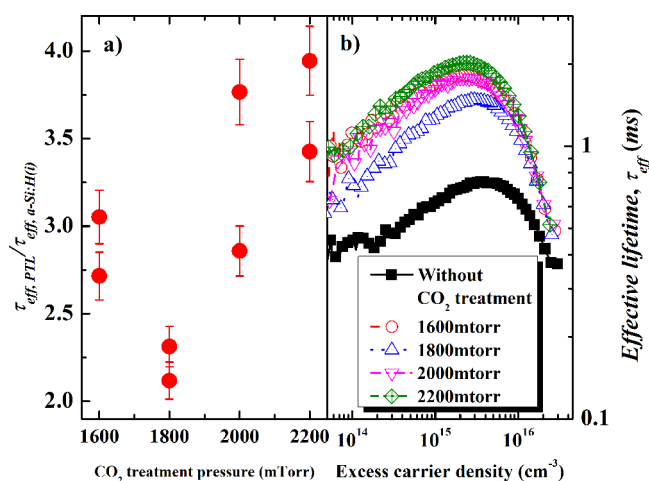


Figure 4. (a) $\tau_{\text{eff, PTL}}/\tau_{\text{eff, a-Si:H(i)}}$ ratios with respect to the CO₂ plasma treatment pressure. (b) Variation of τ_{eff} in the bulk c-Si(n) measured using QSSPC as a function of the treated pressure of the PTL/c-Si(n) configuration.

$\tau_{\text{eff}(n)}$ represents the minority carrier lifetime for the CO₂ plasma treatment pressures of $n = 1600, 1800, 2000$, and 2200 mTorr; $\tau_{\text{eff}(0)}$ represents the τ_{eff} of the a-Si:H(i) deposited on the c-Si surface. After the treatment, the minority carrier lifetime was improved by a factor of more than two, compared with that of the untreated samples. Moreover, a higher treatment pressure yielded a longer minority carrier lifetime. In addition, a plot of τ_{eff} as a function of the injection level of the excess carrier density was obtained to gain insight into the passivation mechanism, as presented in Figure 4b. It can be seen that the τ_{eff} increased from low ($\sim 5 \times 10^{13} \text{ cm}^{-3}$) to high ($\sim 3 \times 10^{16} \text{ cm}^{-3}$) injection levels of the excess carrier density, with an increase in the plasma pressure. Two possible passivation mechanisms, the field-effect passivation and/or the Schottky contact, can explain the improvement in the τ_{eff} in the low level of carrier density injection.¹³ As reported by Strithanrathikhun et al., negative fixed charges are preferred for

the p-type substrate.³¹ However, the present data using the n-type substrate contradicts the argument. Here, it can be observed that the PTL with a larger bandgap created the larger valence band offset (ΔE_v) at the PTL/c-Si heterointerface. This larger ΔE_v may help to push the minority carriers (holes) away from the interface. This will lower the interface recombination, and in turn, a higher τ_{eff} can be seen for a higher plasma treatment pressure. At the high level of excess carrier injection, it is clear that the variation of the τ_{eff} relates to the defects at the PTL/c-Si heterointerface. Thus, the improvement in τ_{eff} at the high level of injection could be correlated to the diffusivity and/or the distribution of atoms, such as hydrogen and oxygen, within the vicinity of the heterointerface, as observed in Figure 4b. Finally, the improved τ_{eff} in the entire range of level injection could be attributed to both the Schottky barrier height (field effect passivation) and suppressed defect density at the PTL/c-Si heterointerface.

To understand the improvement in τ_{eff} with the treatment pressure more clearly, SE characterization was performed. The spectra of the imaginary part of the effective dielectric function (ϵ_{im}) on the oxygen-rich samples after the plasma treatment under various conditions are shown in Figure 5a. The (ϵ_{im}) for

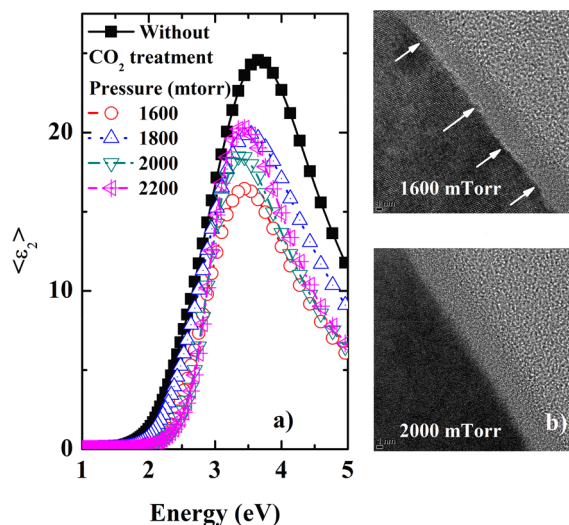


Figure 5. (a) Effect of the CO₂ plasma treatment pressure on the imaginary part of the pseudodielectric function for PTLs deposited on c-Si surfaces. (b) Cross-sectional HR-TEM images of the PTL/c-Si heterointerface for CO₂ plasma treatment pressures of 1600 and 2200 mTorr.

all the samples exhibited a single, smooth peak at approximately 3.4 eV, indicating a completely amorphous phase. In addition, it was observed that all treated samples showed a lower amplitude value of ($\epsilon_{\text{im, max}}$) compared with the as-deposited sample of a-Si:H(i). The behavior of ($\epsilon_{\text{im, max}}$) could be due to the incorporation of foreign atoms, such as hydrogen and oxygen.³² Moreover, it was reported that the films having higher microscopic roughness demonstrated lower amplitude values of ($\epsilon_{\text{im, max}}$). Here, the samples treated with a lower pressure showed lower ($\epsilon_{\text{im, max}}$) values and a higher surface roughness.^{27,33} The HR-TEM images of the two selected samples, treated at 1600 and 2000 mTorr, were employed to characterize the surface roughness of the PTL/c-Si heterointerface and are depicted in Figure 5b.²⁷ The HR-TEM images indicated that the PTL/c-Si heterointerface of the sample at a lower treatment pressure of 1600 mTorr had a

higher surface roughness, as shown in Figure 5b and marked with white arrows. Kim et al. reported that a higher surface roughness can be preferable for defect formation near the PTL and the c-Si heterointerface as it leads to a lower τ_{eff} .¹³ This result is similar to that of Bian et al.,²⁷ which contradicts the ones from Himpsel et al.,²⁶ who reported that very rough or defective surfaces produced a higher density of the oxidation states.

To determine the optimal PTL composition for a high open-circuit voltage, the correlation between iV_{oc} and the $I_{\text{Si}}^{1+}/(I_{\text{Si}}^{2+} + I_{\text{Si}}^{3+})$ ratio was investigated, as shown in Figure 6a. The highest

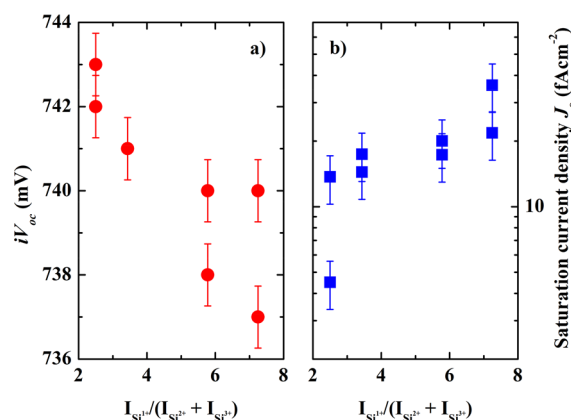


Figure 6. (a) iV_{oc} and (b) J_0 obtained via QSSPC measurements with respect to the $I_{\text{Si}}^{1+}/(I_{\text{Si}}^{2+} + I_{\text{Si}}^{3+})$ ratio.

iV_{oc} of 743 mV was obtained for the lowest $I_{\text{Si}}^{1+}/(I_{\text{Si}}^{2+} + I_{\text{Si}}^{3+})$ ratio of 2.5. The passivation of the c-Si surface with the PTL yielded an iV_{oc} of 743 mV, the highest iV_{oc} value reported to date among all c-Si surfaces passivated by PTLs. The improvement in the iV_{oc} with the reduction of $I_{\text{Si}}^{1+}/(I_{\text{Si}}^{2+} + I_{\text{Si}}^{3+})$ can be explained by the increase in the high oxidation states, which agrees well with the results obtained by Bian et al.²⁷ Furthermore, as discussed in the previous section, the higher oxidation states led to a remarkable increase in the optical bandgap. Thus, this higher optical bandgap can create a higher ΔE_{v} at the PTL/c-Si heterointerface which may assist in turning the minority carriers (holes) back and lowering the leakage current J_0 , as confirmed from Figure 6b. Additionally, the improvement in the intensity of the peak corresponding to the SiH^- and SiO^- ions, as proved by the SIMS depth profile, may have helped to passivate the PTL/c-Si heterointerface. Consequently, the passivated surface was smooth, as validated by the TEM images, and exhibited a high iV_{oc} and a lower J_0 , as well.

CONCLUSIONS

In summary, a new approach for obtaining PTLs via CO_2 plasma treatment of an ultrathin a-Si:H(i) layer was proposed. When the treatment pressure was increased, the PTLs tended to form oxygen-rich components and exhibited a smoother PTL/c-Si heterointerface. The passivated tunneling contacts constructed via the deposition of a PTL/nc-Si:H(n)/c-Si stack, exhibited a very high iV_{oc} of 743 mV and a very low contact resistivity of around $60 \text{ m}\Omega \text{ cm}^2$. Owing to the high passivation quality, the high tunneling probability, and the *in situ* process,

the proposed method is suitable for forming PTLs in the RE heterojunction solar-cell configuration.

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Notes

The authors declare no competing financial interest.

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