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Dopant-grading proposal for polysilicon passivating contact in crystalline silicon solar cells

Duy Phong Pham, Junsin Yi^{*}

Department of Electrical and Computer Engineering, Sungkyunkwan University, Suwon, 16419, Republic of Korea

HIGHLIGHTS

- Doping grading technique for high-quality poly-Si/c-Si passivating contact.
- Suppressing c-Si into massive dopant diffusion and defects inside poly-Si.
- A simple and efficient technique for high-efficiency device manufacturing.

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ABSTRACT

Polycrystalline silicon/crystalline silicon (poly-Si/c-Si) passivating contacts are an attractive option for improving the efficiency of c-Si-based solar cells. The heavy doping required for a poly-Si layer to ensure high-quality passivation of the contact can cause substantial dopant diffusion into the c-Si during the high thermal annealing process, as well as internal defects; this reduces the passivation quality. We propose a simple dopant grading of the poly-Si layer to suppress dopant diffusion and defects. The grading is implemented by varying the dopant concentration through poly-Si preparation. Accordingly, a high dopant concentration is distributed far from the c-Si interface, whereas a low one is an inverse. The grading improves passivation quality significantly, allowing for a high implied open-circuit voltage (iV_{oc}) of 730 mV and a low recombination current density (J_0) of 5.1 fA/cm². Owing to the grading, the solar cell devices exhibit enhancements of 10 mV, 0.5%, and 0.6% in the open-circuit voltage, fill factor, and efficiency, respectively. A silicon heterojunction solar cell using a back-side-graded poly-Si layer achieves a conversion efficiency of 22%. The proposed grading technique exhibits considerable potential as a simple and efficient technology for c-Si solar cells.

1. Introduction

Efficient conversion of solar energy into electricity is necessary to partly satisfy the increasing global demand for electrical energy. Hence, the development of photovoltaic (PV) technologies is being promoted to circumvent the use of traditional non-renewable energy sources. This mainly involves manufacturing low-cost, high-performance, stable, and environmentally friendly PV devices. Accordingly, state-of-the-art PV generators, such as perovskites [1,2], quantum dots [3,4], and dye-sensitized [5–7] and organic solar cells [8], are potential materials for low-cost and simple manufacturing of PV devices. However, the stability, performance, and commercial-scale production of such devices remain uncertain, which necessitates significantly higher market competition. Currently, crystalline silicon (c-Si)-based photovoltaic (PV)

devices represent a viable alternative for the PV industry and market [9, 10]. The importance of cost reduction for PV systems has prompted further improvements in c-Si cell performance [11]. These improvements are essential because of continuing technological progress. In addition to the progress in production technology and engineering, recent efforts have been devoted to innovative passivating technologies [12–14] and/or new passivating concepts [15] to widen the applicability of c-Si cell devices. Passivating-contact technologies have been devoted to reducing surface defects, enhancing carrier collection, and thus improving device performance [15,16].

Passivating contacts using polycrystalline silicon (poly-Si) formed on the thin silicon oxide (SiO_x) surface of c-Si, referred to briefly as poly Si/c-Si contacts, represent a state-of-the-art passivating technology for c-Si solar cells [17–19]. This technology considerably restricts the

^{*} Corresponding author. .

E-mail addresses: pdphong@skku.edu (D.P. Pham), junsin@skku.edu (J. Yi).

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recombination losses due to the direct contact between the c-Si/metal of traditional cell structures, such as passivated emitters, rear totally diffused cells [20], and/or rear contact [21] cells. In addition, this technique can sustain high-temperature industrial photovoltaic (PV) manufacturing steps, such as high-temperature metallization firing; this process makes solar cells more thermally stable than traditional silicon heterojunction (SHJ) solar cells, which specifically require low-temperature manufacturing steps [17,20]. The poly-Si/c-Si passivating mechanism is attributed to the excellent interface chemical passivation of the interfacial SiO_x film (normally 1.4–1.5 nm) and the additional field-effect passivation (AFP) of heavily doped poly-Si layers [22]. Poly Si/c-Si contacts can be prepared by depositing a doped silicon layer on the oxidized c-Si surface using plasma-enhanced chemical vapor deposition (PECVD), followed by a high thermal annealing step (generally at a temperature over 800 °C) with a dwell time of several tens of minutes to crystallize the doped Si layer (solid-phase crystallization) into a doped poly-Si layer [23]. During the annealing process, dopants from poly-Si layers can diffuse extensively into the c-Si absorber and compromise the passivation quality. To suppress dopant diffusion, a “fast” thermal annealing process with a “short” dwell time has been suggested [24]. Furthermore, a quantum well structure between c-Si and poly-Si has recently been proposed to limit this diffusion [25]. However, confining dopants within poly-Si for efficient AFP while suppressing the dopant diffusion during the annealing process remains a challenge; further innovations in manufacturing technologies for poly Si/c-Si contacts are therefore required. Simple and low-cost techniques are preferred in industrial manufacturing.

To widen the applicability of c-Si solar cells, as mentioned earlier, we developed a simple technique for dopant grading inside the poly-Si layer to enhance the device performance. The grading was implemented during PECVD of phosphorus-doped hydrogenated amorphous silicon (n-a-Si:H). The grading idea was derived from the dopant diffusion mechanism, considering the significant difference in dopant concentration between the poly-Si layer and the c-Si absorber [26,27]. This

difference created an inevitable diffusion gradient from the poly-Si into the c-Si absorber under high temperature [26–28]. A high dopant concentration inside the poly-Si, distributed near the poly-Si/c-Si interface, facilitates rapid dopant diffusion into c-Si during thermal annealing. Consequently, a higher concentration should exist far from the interface, and a lower concentration should be observed near the interface. The dopant distribution inside the poly-Si layer was finely optimized in this study and is discussed herein.

2. Experimental details

2.1. Preparation of poly- SiO_x layers

First, 30-nm-thick n-a-Si:H layers were deposited on both sides of planar commercial Czochralski (CZ) n-type monocrystalline wafers (orientation of (100), resistivity of 1–2 Ω cm, and thickness of 200 μm) using PECVD. Silane (SiH_4), hydrogen (H_2), and phosphine (PH_3) precursor gases were employed during the PECVD, along with deposition parameters such as a working pressure of 200 mTorr, a plasma source power density of 208 mW/cm^2 , and a substrate temperature of 220 °C. Before the n-a-Si:H deposition, the wafers underwent standard surface cleaning using the Radio Corporation of America (RCA) procedure, including RCA-1 and RCA-2, followed by surface oxidation to form a 1.5-nm thick SiO_x layer using a thermal tube furnace system at an activated temperature of 700 °C and a dwell time of 15 min in an oxygen-rich environment. After a high-temperature annealing step at 900 °C for 30 min in a nitrogen-rich environment, the n-a-Si:H/ SiO_x /c-Si samples were transformed into n^+ -poly-Si/ SiO_x /c-Si samples, as illustrated in Fig. 1. The experimental procedure selected for the poly-Si layer has been optimized in a previous study [25]. As seen in Fig. 1a and b, for sample A1, without doping grading of the poly-Si layer, the $P_{\text{GR}} = [\text{PH}_3]/([\text{SiH}_4] + [\text{PH}_3])$ gas ratio was maintained during the PECVD of the initial n-a-Si:H layers; by contrast, in sample A2, with doping grading, the P_{GR} gas ratio varied during the PECVD. The gas ratio

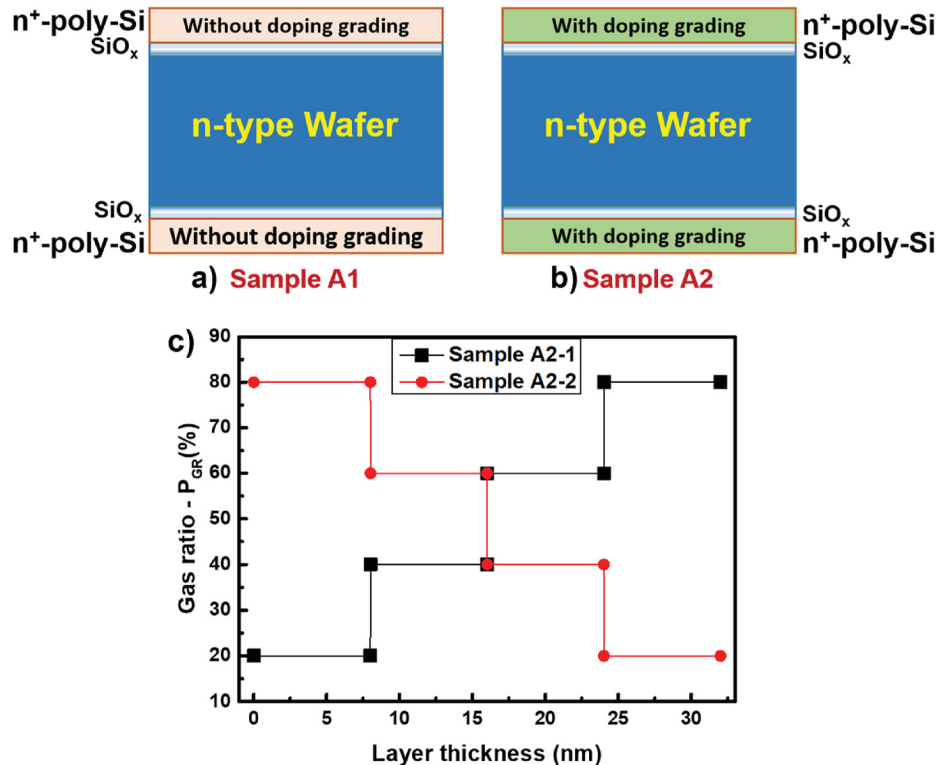


Fig. 1. Symmetric structural diagrams of poly-Si/c-Si contacts: a) sample A1, without doping grading; b) sample A2, with doping grading of poly-Si layers. c) Two doping profiles through poly-Si thickness of sample A2, named A2-1 and A2-2.

variations during the PECVD through the n-a-Si:H thickness are shown in Fig. 1c, corresponding to samples A2-1 and A2-2. For sample A2-2, a higher gas ratio was observed near the c-Si/SiO_x interface, and a lower gas ratio was found farther from this interface. The gas ratio of sample A2-1 was inversely distributed with respect to that of sample A2-2, as shown in Fig. 1c.

2.2. Device fabrication

SHJ solar cell devices were fabricated on both-side-textured, 170- μm -thick CZ monocrystalline wafers. Before the thermal 1.5-nm SiO_x growth, the wafers underwent RCA-1 and RCA-2 cleaning followed by being dipped in dilute hydrofluoric acid (HF, 10%) to remove the native oxide layer. After the n-a-Si:H (30 nm) PECVD only at the rear, the samples underwent a high-temperature annealing step to form the n-poly Si contact. Thereafter, the samples were dipped in HF again to remove the front SiO_x layer. Subsequently, stacks of an intrinsic hydrogenated amorphous silicon (i-a-Si:H) (5 nm)/p-type hydrogenated nanocrystalline silicon (nc-Si:H) (30 nm) were prepared at the front. Layers of indium doped in oxide (ITO) were then deposited on a rectangular-shaped mask with a calibrated area of 10.24 cm² on both sides using a sputtering system. The electrodes were screen-printed with an Ag grid on the front side and an Ag full cover on the back side. The cell efficiency was characterized using a solar simulator system under standard one-sun illumination (AM1.5, 100 mW/cm², 25 °C).

2.3. Material characterization

A cross-section high-resolution transmission electron microscopy (CS-HRTEM) system (JEM 2100F) was used to determine the thickness and crystallinity of the samples. Before capturing the CS-HRTEM images, the samples were subjected to a focused ion beam (FIB) preparation technique to support high-quality cross-sectional images. Raman measurements (Dongwoo Optron – Ramboss 500i system) were used to estimate the crystallinity of the poly-Si layers prepared on quartz substrates. The system included a laser source (Ar⁺ ion) with an excitation wavelength of 514 nm. The samples were measured in a backscattering configuration. The dark conductivity of the poly-Si layers was measured at room temperature on evaporated coplanar aluminum electrodes using a semiconductor analyzer (EL420C). A photoconductance lifetime tester (Sinton WCT-120) was used to measure the minority carrier lifetime and implied open-circuit voltage (iV_{oc}). The recombination current density (J₀) was determined using a Sinton WCT-120 by measuring the transient photoconductance decay mode and using the Kane-Swanson calculation [29]. Secondary ion mass spectroscopy (SIMS) was employed to estimate the dopant profiles of the samples. The transfer length measurement (TLM) was used to estimate the contact resistivity of the contacts. The parasitic current for the TLM was limited by removing the poly-Si area not covered by the Ag-grid electrodes, using a plasma etching system.

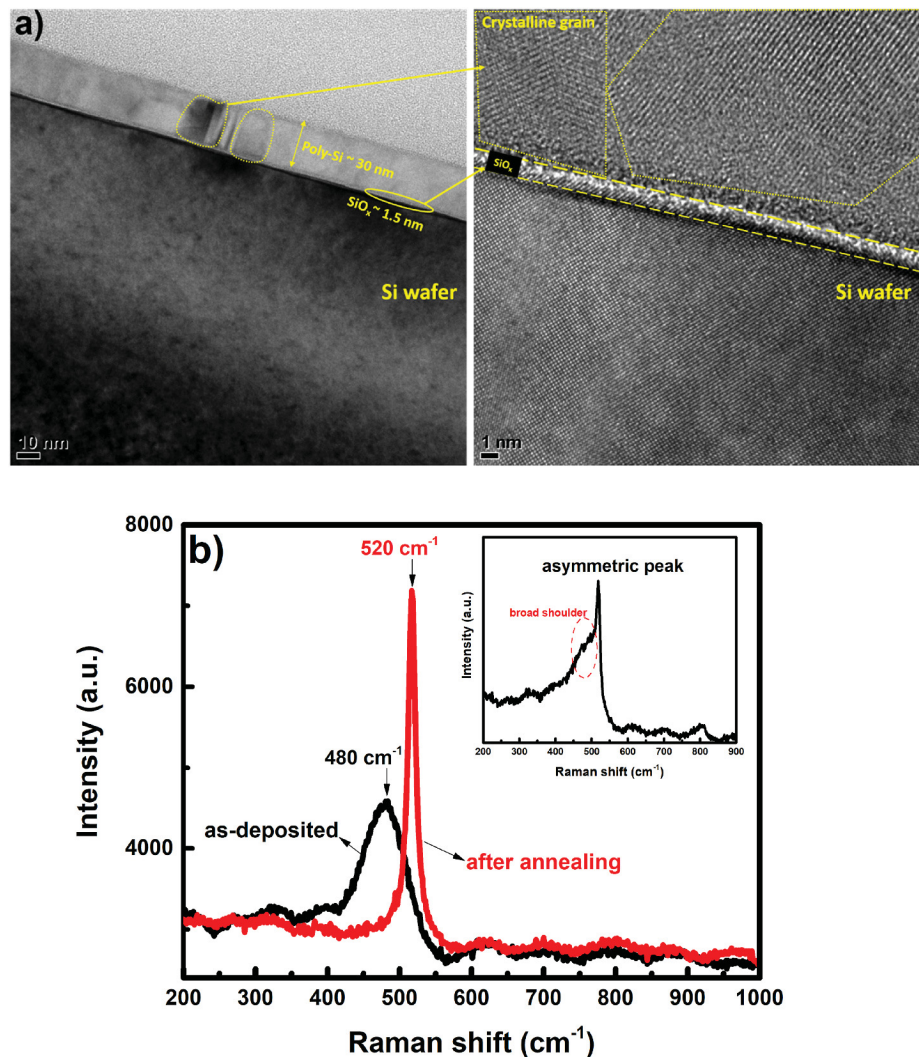


Fig. 2. a) Cross-sectional high-resolution TEM image, and b) Raman spectra of a typical sample A1.

3. Results and discussion

Fig. 2 shows the CS-HRTEM image of sample A1 after high thermal annealing. The main target of the annealing step was to ensure solid-phase crystallization of the as-deposited a-Si:H layer, dopant activation, and poly-Si/c-Si contact formation. The aforementioned figure confirms the formation of a polycrystalline phase, denoted by large crystalline grains (columns) separated by the grain boundaries. Additionally, the Raman spectra of the as-deposited and post-annealed sample A1 in Fig. 2b demonstrate a transition from an amorphous phase of the as-deposited film—characterized by a broad peak centered at 480 cm^{-1} —to the solid crystalline phase—characterized by a sharp peak at 520 cm^{-1} after the annealing step. Generally, incomplete (or partial) crystallization of a silicon film is characterized by a “broad shoulder” on the left side of the 520-cm^{-1} -peak, as illustrated in the inset of Fig. 2b. This shoulder is due to the large amount of amorphous phase in the film structure [30–32]. Consequently, the sharply symmetric peak at 520 cm^{-1} in Fig. 2b, compared with that in the inset, indicates perfect crystallization of the poly-Si film, which considerably limited the amorphous phase. Perfect crystallization can reduce defect densities, activate dopants, and enhance conductivity through the poly-Si layer. Apart from the 30-nm thick poly-Si layer, Fig. 2a shows the formation of a thin 1.5 nm SiO_x layer that was formed after the oxidation of the c-Si surface. SiO_x can provide surface chemical passivation of c-Si, whereas the poly-Si layer is generally prepared with heavy doping to form a high band-bending level with the c-Si absorber and thus a carrier-selective contact; this is known as AFP.

The doping level in poly-Si was examined to find an optimized point. The doping level in the poly-Si was varied by changing P_{GR} for the as-deposited a-Si:H layers. Fig. 3a shows the iV_{oc} and J_0 values of samples A1 and A2 as functions of P_{GR} . In addition, Fig. 3b shows the σ_d and ρ_c values of sample A1 as a function of P_{GR} . The iV_{oc} value increased with P_{GR} from 20% to 50% and then decreased considerably at a higher P_{GR} . The J_0 value showed a trend opposite to that of iV_{oc} . High-quality passivation of the poly Si/c-Si contact generally requires both high iV_{oc} and low J_0 values [18,25]. As shown in Fig. 3a, the passivation quality of the contact was great at $P_{\text{GR}} = 50\%$ with a high iV_{oc} (720 mV) and low J_0 (9.2 fA/cm^2). The enhancement in the passivation quality (higher iV_{oc} and lower J_0) when P_{GR} increased from 20% to 50% can be explained based on the AFP mechanism. The band diagrams in Fig. 4 illustrate the AFP mechanism of the passivating contact. With a low doping level for the poly-Si layer (Fig. 4a), the Fermi level (E_f) is far from its conduction band level (E_c), which causes a slight downward band-bending of the c-Si absorber toward the surface. Hence, minority carriers (holes) can be transported through contact, thereby causing significant recombination at the contact interface, which lowers the passivation quality. In contrast, a higher doping level for the poly-Si layer (Fig. 4b) can move its Fermi level (E_f) closer to the conduction band level (E_c). This results in greater downward band-bending of the c-Si, which prevents minority carrier (hole) transport and promotes majority carrier (electron) transport. Effective hole-reflection results in a significant reduction in recombination at the interface, thus enhancing the passivation quality. The higher doping level due to the increase in P_{GR} from 20% to 50% is reflected in the σ_d and ρ_c variations shown in Fig. 3b. The σ_d value increased rapidly from $P_{\text{GR}} = 20\%$ –50% and then tended to stabilize, whereas ρ_c decreased steadily with increasing P_{GR} . It is deduced that activating further dopant concentration into the poly-Si layer caused a significant increase in σ_d , elevating the E_f and thus probably enhancing the passivation quality. However, when $P_{\text{GR}} > 50\%$, a considerable deterioration in the passivation quality (lower iV_{oc} and higher J_0) was observed, as shown in Fig. 3a; this cannot be explained based on the AFP mechanism, which probably relies the intensive dopant diffusion into the c-Si. As shown in Fig. 3b, the conductivity of the poly-Si layers seemed to level off at $P_{\text{GR}} > 50\%$. This means that large amounts of residual dopants, inactivated into poly-Si, can diffuse deeply into the c-Si during high thermal annealing, thus reducing passivation

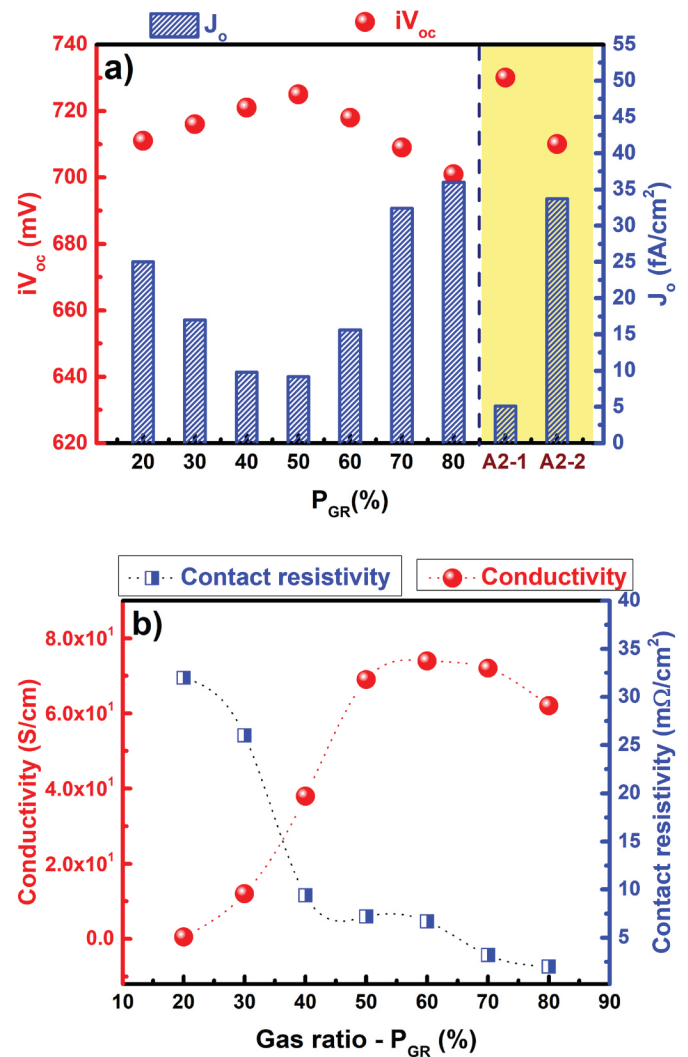


Fig. 3. a) iV_{oc} and J_0 for samples A1 and A2 and b) conductivity and contact resistivity of sample A1 as a function of the P_{GR} gas ratios.

quality.

Furthermore, the steady decrease in ρ_c for $P_{\text{GR}} > 50\%$ suggests deep dopant diffusion into the c-Si interface. Generally, ρ_c is inversely related to the transport of both majority (electron) and minority (hole) carriers, whereas J_0 is directly related to the transport of minority carriers; this is a reason for the recombination at the interface. Deep dopant diffusion can support majority carrier transport and enhance minority carrier diffusion through the contact due to the reduced barrier/band-bending at the c-Si interface. This leads to low ρ_c values but high J_0 values for $P_{\text{GR}} > 50\%$, as shown in Fig. 3a and b. To highlight the substantial dopant diffusion, Fig. 5 shows the depth profiles of the phosphorus element into the c-Si interface at three typical percentages of P_{GR} —20%, 50%, and 80%—for sample A1. At $P_{\text{GR}} = 80\%$, large amounts of dopant diffused deeply into the c-Si, approximately over 10^{19} atom/cm^3 at 100 nm from the c-Si interface. The dopant diffusion was reduced significantly as P_{GR} decreased to 20%. For example, only approximately 10^{17} atom/cm^3 was detected at 100 nm from the c-Si interface. The detrimental effects of dopant diffusion on the passivation quality have been observed experimentally by different research groups; however, the key physicochemical mechanisms behind the deterioration remain unclear [33–35]. Accordingly, suppressing the dopant diffusion is desirable for minimizing both ρ_c and J_0 and thus enhancing passivation quality.

The deterioration at $P_{\text{GR}} > 50\%$ can also be attributed to the reduction in the crystallinity due to the high dopant level. Fig. 6a shows

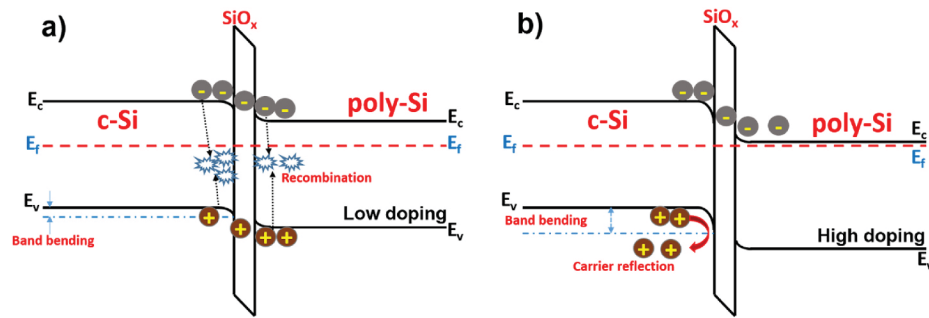


Fig. 4. Modeling band diagrams of poly-Si/c-Si contacts with low and high doping of poly-Si layers.

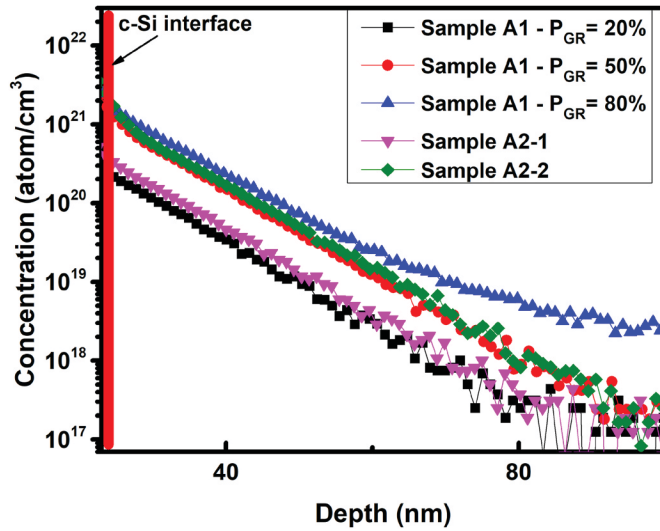


Fig. 5. Depth profiles of dopants inside the c-Si absorber with different dopant variations of poly-Si layers.

the Raman spectra of the poly-Si layers as a function of P_{GR} . Compared with the sharply symmetric peaks at $P_{GR} = 20\%$ and 40% , the peaks at the high doping levels ($P_{GR} = 60\%$ and 80%) appeared as an “amorphous shoulder.” Fig. 6b shows the deconvolution of the peak at $P_{GR} = 80\%$ using the Gaussian fitting model. The result indicates that the “amorphous shoulder” can be deconvoluted by a peak at approximately 485 cm^{-1} , representing the amorphous phase [30]. The heavy doping can partly cause lattice defects, such as lattice mismatching, dislocations, interstitial atoms, and vacancies, in the silicon host crystal lattice [36], resulting in an amorphous phase. The lattice defects can act as carrier traps [37] and are therefore likely to reduce passivation quality, as shown in Fig. 3a. For excellent passivation quality, it is critical to maintain a highly doped poly-Si layer and fewer defects while constraining the dopant diffusion into the c-Si host. Accordingly, we examined the dopant-grading processes of the poly-Si layer, as shown in Fig. 1c (samples A2-1 and A2-2). As shown in Fig. 3a, the passivation quality of sample A2-1 (including high iV_{oc} of 730 mV and low J_0 of 5.1 fA/cm^2) was improved more than that of the reference sample A1 at $P_{GR} = 50\%$, whereas that of sample A2-2 deteriorated compared with that of sample A2-1. Fig. 5 indicates that in sample A2-1, the deep dopant diffusion into the c-Si absorber was considerably reduced compared with that in sample A1 at high doping levels ($P_{GR} \geq 50\%$). By contrast, in sample A2-2, heavy dopant diffusion was observed in the vicinity of the c-Si interface, as in sample A1 at $P_{GR} = 80\%$; however, the dopant diffusion decreased with depth. In the physical mechanism, dopant diffusion seems to be inevitable during the high thermal annealing process because dopants tend to diffuse from a region of higher concentration, such as the poly-Si layer, to that of lower concentration, such

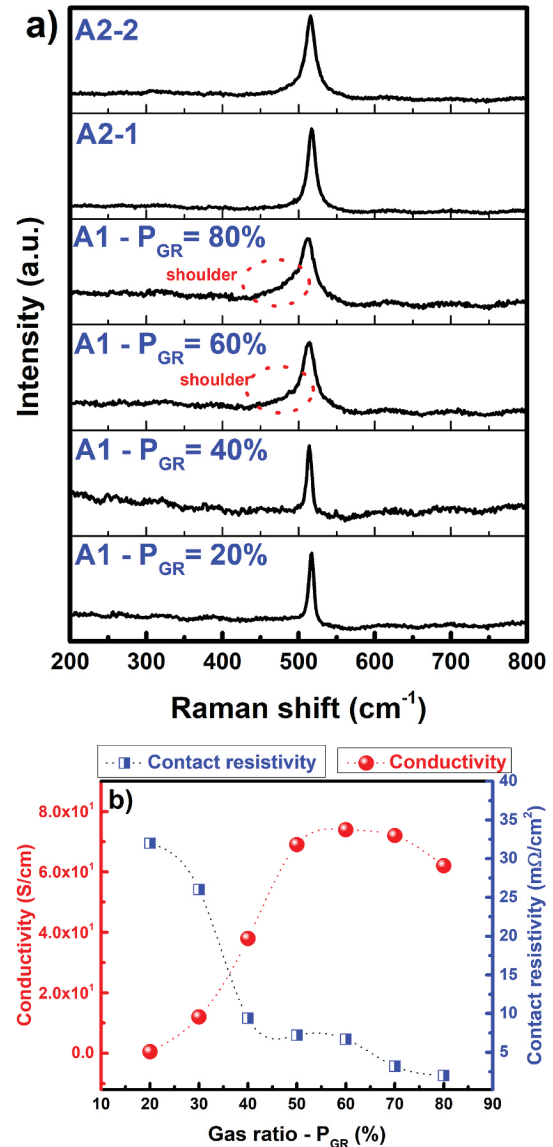


Fig. 6. a) Raman spectra of poly-Si layers deposited on quartz substrates, and b) the peak deconvolution using Gaussian fitting of the sample A1 at $P_{GR} = 80\%$.

as the c-Si absorber. The concentration and depth of the diffusion into c-Si depend essentially on the thermal annealing process and the dopant concentration provided from the poly-Si layers. In this study, for sample A2-1, layers with high concentration were distributed far from the c-Si interface (Fig. 1c). This considerably limited the extensive diffusion into

the c-Si interface (Fig. 5) and thus improved the passivation quality (Fig. 3a). However, in sample A2-2, the highly doped layers were located near the interface; as a result, the high dopant concentration facilitated diffusion into the interface and thus reduced the passivation quality.

In other respects, the Raman spectra of sample A2-1 (Fig. 6a) showed a significant reduction in the “amorphous shoulder” compared with that of sample A1 at $P_{GR} = 60\%$ and 80% . This indicates that the grading processes reduced the crystalline defects due to the high dopant concentration, as mentioned previously. In conclusion, the dopant grading in sample A2-1 efficiently suppressed dopant diffusion and lattice defects, thus enhancing the passivation quality further.

The SHJ solar cell devices were examined using the flowchart shown in Fig. 7a and the cell structure in Fig. 7b. The devices were fabricated with different rear-side n-type poly-Si layer preparations, including sample A1 at $P_{GR} = 50\%$ and 80% and samples A2-1 and A2-2. Fig. 7c shows a photograph of a typical real device at the front surface. Fig. 7d shows the J–V curves of the devices under one-sun illumination. The cell parameters, including open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill factor (FF), and efficiency (E_{ff}), are listed in Table 1. The parameters of cell A1 at $P_{GR} = 50\%$ (A1 – $P_{GR} = 50\%$) were used as a reference for comparison. For cell A1, at $P_{GR} = 80\%$ (A1 – $P_{GR} = 80\%$), V_{oc} and FF were reduced compared with those of the reference; this was possibly due to the deep dopant diffusion and considerable lattice

Table 1

Cell parameters of the typical devices.

Sample	V_{oc} (mV)	J_{sc} (mA/cm ²)	FF (%)	E_{ff} (%)
A1 – $P_{GR} = 50\%$	700	39.0	78.5	21.4
A1 – $P_{GR} = 80\%$	680	38.6	74.0	19.4
A2-1	710	39.3	79.0	22.0
A2-2	690	38.7	75.5	20.1

defects, as mentioned previously.

With the back-side grading process, cell A2-1 showed a considerable increase of 10 mV in V_{oc} and a slight enhancement of 0.5% in FF, compared with the reference, while maintaining nearly the same J_{sc} values; this resulted in an improvement of 0.6% in E_{ff} . Due to the high dopant diffusion, V_{oc} and FF were reduced in cell A2-2. These results demonstrate that dopant diffusion was the main reason for the reduction in passivation quality and thus in V_{oc} and FF. Furthermore, they clearly demonstrate that the grading technique used for cell A2-1 can further improve V_{oc} and FF by suppressing dopant diffusion and reducing lattice defects. With the A2-1 grading technique, an SHJ solar cell can achieve a potential efficiency of 22%.

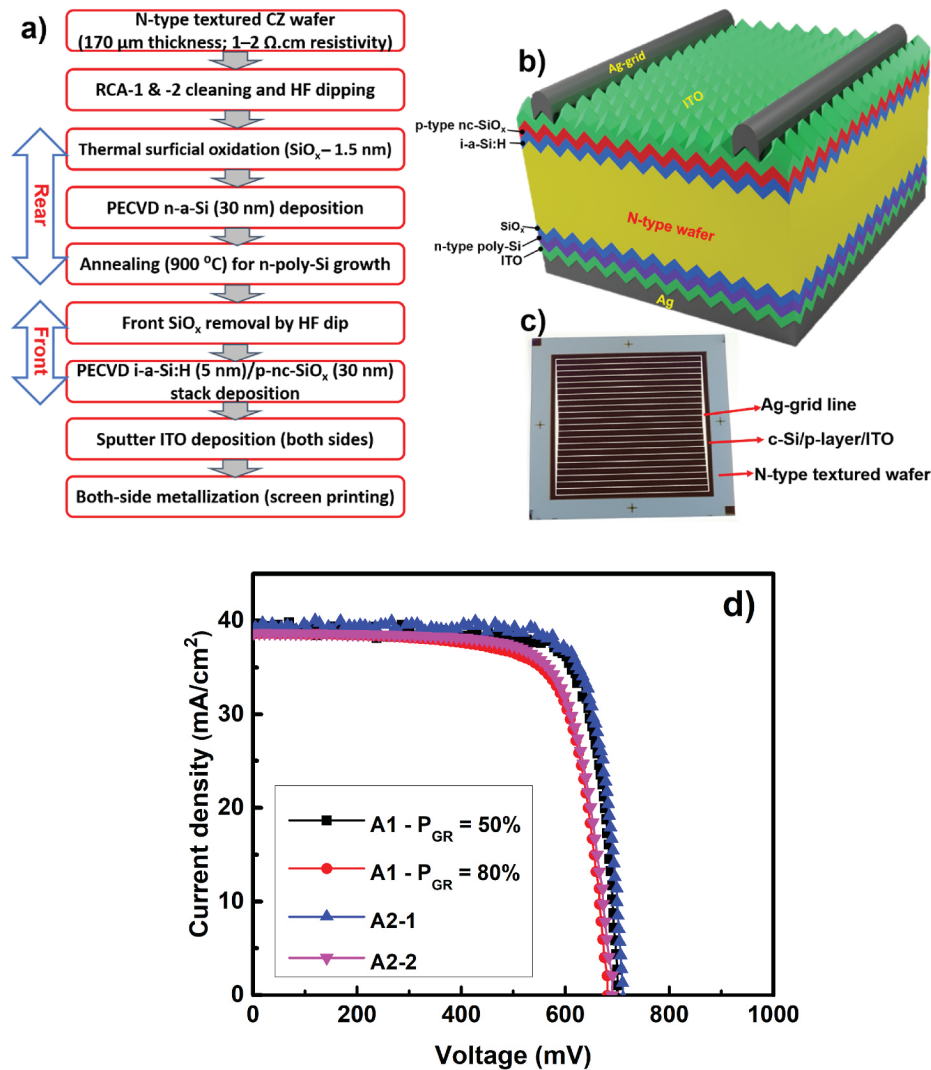


Fig. 7. a) Flowchart of the device procedure; b) schematic of device structure; c) practical photograph of the device at the front; and d) J–V curves of devices under standard one-sun illumination.

4. Conclusion

Dopant grading of the poly-Si layer was suggested to enhance the passivation quality and thus the cell performance. After the high thermal annealing process, the poly-Si showed perfect solid-phase crystallization with a large grain size, which can reduce internal defects and offer a high conductivity for the AFP mechanism. Doping and doping grading in poly-Si was controlled by varying P_{GR} during the PECVD. As P_{GR} increased from 20% to 50%, the passivation quality was improved due to further AFP. At $P_{GR} > 50\%$ (high doping), the passivation quality was reduced due to the substantial dopant diffusion into the c-Si interface. Grading with a high dopant concentration distributed far from the c-Si interface significantly reduced the deep dopant diffusion into c-Si and thus possibly improved the passivation quality. Inverse grading increased the dopant diffusion and thus reduced the passivation quality. Furthermore, the grading reduced lattice defects, such as the amorphous phase, owing to the heavy doping inside the poly Si phase. Accordingly, an SHJ cell device with dopant grading showed a considerable improvement of 10 mV in V_{oc} by and 0.5% in FF compared with the reference device. The dopant-grading technique is expected to simplify industrial manufacturing of high-quality poly-Si/c-Si passivating contacts for c-Si solar cells.

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CRedit authorship contribution statement

Duy Phong Pham: Investigation, Methodology, Conceptualization, Data curation, Software, Writing – original draft. **Junsin Yi:** Validation, Project administration, Funding acquisition, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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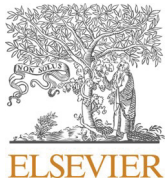
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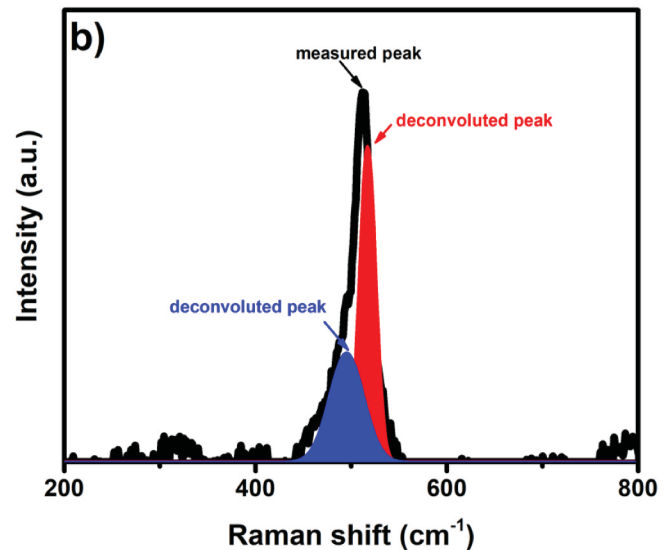
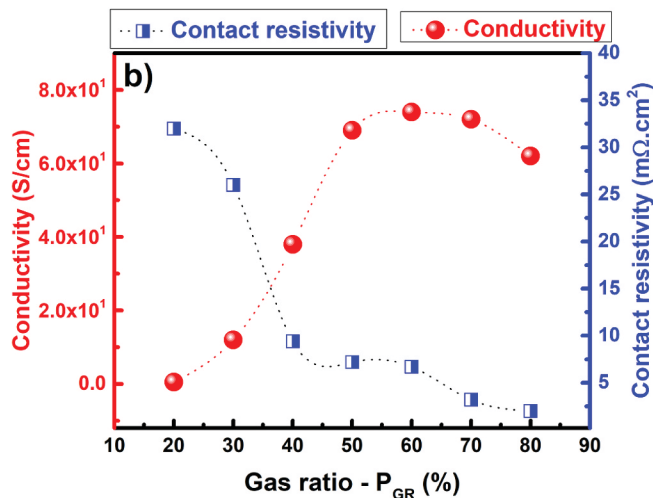
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Department of Electrical and Computer Engineering, Sungkyunkwan University, Suwon, 16419, Republic of Korea

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