Origin of Screen-printed Metal Contact Losses in Crystalline Silicon Solar Cells

Myeong Sang Jeong  
Korea Institute of Energy Research

Sang Hee Lee  
Korea Institute of Energy Research

Sungjin Choi  
Korea Institute of Energy Research

Kwan Hong Min  
Korea Institute of Energy Research

Jong Hoon Lee  
Ulsan National Institute of Science and Technology

Min Gu Kang  
Korea Institute of Energy Research

Kyung Taek Jeong  
Korea Institute of Energy Research

Sang Kyu Kwak  
Ulsan National Institute of Science and Technology  https://orcid.org/0000-0002-0332-1534

Hee-eun Song  
Korea Institute of Energy Research

Tae Kyung Lee (✉ tklee8865@gnu.ac.kr)  
Gyeongsang National University  https://orcid.org/0000-0003-0238-2420

Sungeun Park  
Korea Institute of Energy Research

Article

Keywords:

Posted Date: August 3rd, 2022

DOI: https://doi.org/10.21203/rs.3.rs-1918210/v1

License: ☇ This work is licensed under a Creative Commons Attribution 4.0 International License. 
Read Full License
Origin of Screen-printed Metal Contact Losses in Crystalline Silicon Solar Cells

Authors

Myeong Sang Jeong¹,¹, Sang Hee Lee¹,¹, Sungjin Choi¹, Kwan Hong Min¹, Jong Hoon Lee²,
Min Gu Kang¹, Kyung Taek Jeong¹, Sang Kyu Kwak³, Hee-eun Song¹*, Tae Kyung Lee¹,⁴*,
and Sungeun Park¹*

Affiliations

¹Photovoltaics Research Department, Korea Institute of Energy Research (KIER), 152 Gajeong-ro, Yuseong-gu, Daejeon 34129, Republic of Korea
²Ulsan National Institute of Science and Technology (UNIST) Central Research Facilities (UCRF), UNIST, Ulsan 44919, Republic of Korea
³School of Energy and Chemical Engineering, UNIST, Ulsan 44919, Republic of Korea
⁴School of Materials Science and Engineering, Gyeongsang National University (GNU), Jinju 52828, Republic of Korea

⁵These authors contributed equally

*Corresponding authors

E-mail: hsong@kier.re.kr; tklee8865@gnu.ac.kr; separk@kier.re.kr
Abstract

Crystalline silicon solar cells are considered mainstream products in the photovoltaic market. To further improve their performance, it is important to maintain good contact between metal electrodes and the Si surface because the state of the metal–Si interface affects the saturation current density $J_{0,\text{metal}}$ and open-circuit voltage. Moreover, the large saturation current density strongly attributes to the performance degradation of solar cells. Therefore, the interfacial structure formed by the metal electrodes and Si surface must be examined to minimize the $J_{0,\text{metal}}$ value. In this study, we investigated the formation mechanism of Ag crystallites on the surface of Si emitter layer in screen-printed Ag paste. Interestingly, $J_{0,\text{metal}}$ was minimized by Ag epitaxial growth, which was verified using an atomic-scale approach. Furthermore, the effect of P doping on the Ag–Si interfacial structure reduced $J_{0,\text{metal}}$. Our study can provide new insights into the origin of $J_{0,\text{metal}}$ for realizing high-performance solar cells.
Crystalline silicon (c-Si) solar cells currently dominate the industrial photovoltaic market, and the passivated contact technology is widely used for improving their performance. By applying this technology, various types of solar cell structures have been developed, such as passivated emitter and rear cell (PERC), tunnel oxide passivated contact (TOPCon), poly-Si on oxide (POLO), rear poly-Si (PERPoly), and monoPoly^TM^1–6. These structures improved the performance of solar cells by enhancing their passivation characteristics and the quality of silicon wafers. However, the efficiency of this approach was limited without enhancing the contact characteristics of metal electrodes. Since the screen printing of metal electrodes is the final step of the solar cell fabrication process, the solar cell performance strongly depends on the metal electrode configuration. For example, the saturation current density in the PERC structure (i.e., most widely utilized in industrial photovoltaic systems) was significantly influenced by the metal electrode parameters^7,8. Hence, to enhance the performance of c-Si solar cells, it is necessary to minimize the saturation current density of their metal electrodes ($J_{0,\text{metal}}$).

For this purpose, the formation mechanism of the metal electrode on the Si surface and Ag–Si interfacial structure must be explicitly examined. The contact between the c-Si surface and metal electrodes generally represents a non-ideal metal–insulator–semiconductor structure, which is made from the metal electrode, glass frit, and Si atoms^9–11. Accordingly, it is necessary to consider not only the carrier recombination on the Si surface, but also the recombination process occurring in the Ag–Si contact region, which can be characterized by a double-diode model including two different types of the saturation current density ($J_{01}$ and $J_{02}$)^12,13. Here, $J_{01}$ is related to the carrier recombination in the quasi-neutral and surface regions, and $J_{02}$ reflects the Shockley–Read–Hall recombination in the space charge region (SCR)^14,15. In this study, the variations in $J_{0,\text{metal}}$ (i.e., included in $J_{01}$) and $J_{02}$ were investigated with respect to temperature during the firing process. In particular, the $J_{0,\text{metal}}$ value decreased at a certain firing
temperature due to the epitaxial growth of Ag crystallites on the Si emitter surface. Subsequently, we proposed a plausible Ag electrode formation mechanism in the c-Si solar cell and Ag–Si interfacial structure on the atomic scale based on the results of transmission electron microscopy (TEM) observations (Fig. 1a). In addition, we theoretically examined the origin of $J_{0,metal}$ at the Ag–Si interface by conducting density functional theory (DFT) calculations. It was found that Ag epitaxial growth was the key process affecting the $J_{0,metal}$ value because of the elimination of Si dangling bonds. Moreover, the doping of the n-type Si emitter layer with P atoms decreased the $J_{0,metal}$ due to the lower number of metal-induced gap states (MIGS).

**Saturation current density in c-Si solar cells**

During the firing process, the carrier recombination on the metal electrode surface increased due to the etching of the passivated layer, and the SCR was damaged by the electrode growth in the depth direction. Because both processes were strongly related to $J_{0,metal}$ and $J_{02}$, we investigated the influence of firing temperature on these saturation current densities by measuring the Suns open-circuit voltage ($Suns-V_{oc}$) (details of the PERC solar cell fabrication process and analysis of the saturation current density are provided in Methods). According to Fig. 1b, $J_{02}$ increased from 0.1 to 5.7 nA/cm² after increasing the firing temperature from 750 to 950 °C due to the SCR degradation caused by the increase in the size and distribution of inverted pyramid pits on the Si surface at high temperatures. Interestingly, $J_{0,metal}$ decreased from 95 to 31 fA/cm² when the firing temperature increased from 750 to 850 °C. Furthermore, after the firing temperature increased from 850 to 950 °C, $J_{0,metal}$ slightly increased from 31 to 52 fA/cm², indicating that unlike $J_{02}$, $J_{0,metal}$ could be minimized at a certain temperature corresponding to the maximum pseudo efficiency ($pEfficiency$) value. Notably, other solar cell parameters, $V_{oc}$ and pseudo fill factor ($pFF$), were mainly influenced by $J_{0,metal}$ and $J_{02}$.
respectively (Supplementary Fig. 1). Next, we examined the variations in $V_{oc}$, $pFF$, and $pEfficiency$ with $J_{0,metal}$ and $J_{02}$ using the double-diode model. As indicated by the red dashed lines in Fig. 1c, $J_{0,metal}$ and $J_{02}$ were the main parameters affecting the $V_{oc}$ and $pFF$ values, respectively, which was consistent with the experimental data presented in Supplementary Fig. 1. These results indicate that the two saturation current densities strongly influenced the $pEfficiency$ of c-Si solar cells. However, owing to the relatively small effect of $J_{02}$ in the range of firing temperatures of our interest, $pEfficiency$ was mainly determined by $J_{0,metal}$. Thus, establishing the origin of $J_{0,metal}$ is critical for improving the performance of solar cells. It is well known that $J_{0,metal}$ is caused by the diffusion of metal atoms into the Si surface$^{16–18}$. Consequently, achieving a better understanding of the Ag–Si contact structure is important for decreasing the $J_{0,metal}$ value.

Mechanism of Ag crystallite formation

Because the minimization of $J_{0,metal}$ at the certain firing temperature could be mainly affected by the Ag–Si contact structure, we investigated the mechanism of Ag crystallite formation on the surface of the Si emitter layer (see details in Methods). Generally, Ag crystallites are formed after etching the SiN$_x$ and Si layers via the redox reactions with PbO, which are conducted in the glass frit. Owing to the increase in the firing temperature, Ag ions are dissolved in the glass frit to form a Ag–Pb alloy. After that, solid Ag is deposited onto the Si surface through redox reactions with Si atoms$^{19–21}$, which increases the saturation current density of c-Si solar cells. For this reason, the crystal structure of the Ag–Si interface was studied to identify the origin of recombination processes occurring at this interface$^{20,22–29}$. However, the relationship between Ag metallization and the saturation current density remained unclear. Hence, we investigated the formation mechanism of Ag crystallites on the
Si surface and Ag–Si interfacial structures. Fig. 2 shows the morphology of the Si surface observed in the temperature range from 600 °C (the starting temperature of glass melting) to 950 °C by scanning electron microscopy (SEM). Between 600 and 700 °C, the area of the Si surface exposed by etching the SiNₓ layer and the size and distribution of Ag precipitates increased. These precipitates were formed by the deposition of Ag ions on the Si surface during the firing process. After firing at 750 °C, inverted pyramid pits were detected on the Si surface as reported by Schubert et al. The size and distribution of Ag crystallites increased due to the increase in the number of inverted pyramid pits at firing temperatures above 750 °C, which increased the $J_{01}$ value (including $J_{0,metal}$). Moreover, $J_{02}$ can be increased by damaging the Si emitter layer. We also determined the roles of the glass frit and Ag atoms in the Ag paste by studying the glass frit/SiNₓ/Si and Ag/SiNₓ/Si structures. The glass frit/SiNₓ/Si structure contained inverted pyramid pits, which indicated that the Si surface was etched by PbO species in the glass frit (Supplementary Fig. 2). In the Ag/SiNₓ/Si structure, the Si surface was etched by the redox reaction between Ag and Si (Supplementary Fig. 3). However, this reaction was observed only in certain regions, which could be explained by the occurrence of endothermic reactions between Ag and O according to the Ellingham diagram. Although the Si surface was locally etched by the reaction with Ag atoms, its lifetime decreased due to surface recombination (Supplementary Fig. 4). Overall, we found that the glass frit and Ag etched the SiNₓ passivation and Si emitter layers and that the PbO of the glass frit was the main component participating in the redox reactions with SiNₓ and Si.

After etching the SiNₓ passivation and Si emitter layers, Ag crystallites were formed epitaxially on the Si emitter layer. Fields et al. reported that Ag crystallites were formed through the direct reaction of Ag atoms with the Si surface. Moreover, Ballif et al. and Jeong et al. observed the epitaxial growth of Ag crystallites on the Si surface and formation of a superlattice structure at the Ag–Si interface, respectively. To confirm the epitaxial growth of
the Ag layer, we investigated the Ag–Si interfacial structure on the atomic scale by high-angle annular dark field scanning transmission electron microscopy (HAADF–STEM). Fig. 3a and Supplementary Fig. 5 describe the epitaxial formation of Ag crystallites along the Si(111) surface. Generally, conventional epitaxial growth easily occurs at similar lattice constants of the substrate and the growing film; however, it is very difficult to realize at a lattice mismatch of 7–8%. The lattice constants of the Ag and Si structures were 4.090 and 5.431 Å, respectively, which corresponded to a lattice mismatch of 24.7%. Therefore, it was difficult to grow an Ag film epitaxially on the Si surface. However, according to the domain matching epitaxy concept\textsuperscript{32–34}, Ag can grow epitaxially on the Si surface due to the 3\textsubscript{Si}-to-4\textsubscript{Ag} lattice matching\textsuperscript{31,34–38}. We also found that the Ag–Si interfacial structure was constructed by the 3\textsubscript{Si}-to-4\textsubscript{Ag} matching on the atomic scale (the right side of Fig. 3a), indicating the absence of recombination processes caused by defects, dislocations, or Si dangling bonds. The obtained results also demonstrated the presence of Pb atoms in the produced crystallites (Figs. 3b and c, and Supplementary Fig. 6), and relative contents of Ag and Pb elements were 97.54 and 2.46 wt.%, respectively (Supplementary Fig. 7). Furthermore, we investigated the crystallinity of Pb species by high-resolution transmission electron microscopy (HRTEM) (Figs. 3d and e). The obtained images revealed that Pb crystals were located on the top sides of Ag crystallites, while the observed fast Fourier transform (FFT) pattern corresponded to the Pb pattern with an interatomic distance of 1.75 Å in the (220) direction. The growth mechanism of Ag crystallites on the Si surface during the screen printing process is summarized in Fig. 4. In the firing process, inverted pyramid pits were generated by etching the SiN\textsubscript{x} passivation and Si emitter layers through the redox reaction between PbO and Si species. Furthermore, the Ag–Pb alloy was formed by the dissolution of Ag ions in the glass frit. During the cooling process that occurred after the peak temperature, Ag crystallites were formed epitaxially on the inverted pyramid pits of the Si surface by the separated Ag ions in the Ag–Pb alloy. After the epitaxial
growth of Ag crystallites on the Si surface, Pb crystallites were produced on their top sides. Therefore, the minimization of $J_{0,\text{metal}}$ at a certain temperature in Fig. 1b was likely induced by reducing the number of defects at the Ag–Si interface (Si dangling bonds) due to the epitaxial growth of the Ag layer on the Si surface. Furthermore, the glass frit (especially its PbO component) plays a critical role in the further decrease in $J_{0,\text{metal}}$ and performance enhancement of c-Si solar cells because it determines the size and distribution of the inverted pyramid pits produced by etching the SiNx passivation and Si emitter layers.

Interfacial properties of Ag–Si contact

To find a way to minimize the $J_{0,\text{metal}}$ value in the Ag–Si interface at a certain firing temperature (Fig. 1b), DFT calculations were performed (see details in Methods and Supplementary Figs. 8-10). In the previous sections, we experimentally observed that Ag crystallites were formed epitaxially on the Si surface due to the $3_{\text{Si}}$-to-$4_{\text{Ag}}$ lattice matching (Fig. 5a). First, we investigated the epitaxial growth of Ag on the Si surface thermodynamically by comparing the total energies of the non-epitaxial (disordered) and epitaxial Ag systems grown on various Si surfaces. The obtained results indicated that the epitaxial growth of Ag was thermodynamically favorable on the Si(111) surface regardless of P doping (Fig. 5b). In particular, the epitaxial growth of Ag on the P-doped Si surface was significantly more favorable than that of the disordered system, while the Si(110) surface was thermodynamically unfavorable for the epitaxial growth of Ag species. Although the Si(100) surface was unfavorable for the pristine system (see the inset in Fig. 5b), P doping turned it into a thermodynamically favorable substrate for the epitaxial growth of the Ag layer. Hence, the (111) and (100) surfaces were the preferred Si structures for the epitaxial growth of Ag crystallites on the P-doped (n-type) Si emitter layer from the thermodynamic point of view.
Next, we calculated the formation energies of these two systems to determine the most suitable surface for Ag epitaxial growth (Fig. 5c). The formation energy of the (111) surface was thermodynamically more favorable than that of the (100) surface. Moreover, P doping slightly decreased the formation energy, and its type II (P doping near the Ag–Si interface) was the most beneficial process. Therefore, the epitaxial growth of Ag preferably occurs on the Si(111) surface, and P doping further increases its feasibility.

Finally, we investigated the MIGS in the Ag–Si interfacial structure. In general, MIGS are induced at metal–semiconductor interfaces due to the Fermi level pinning effect, which increases the Schottky barrier height and promotes the recombination of free charge carriers. For these reasons, we estimated the number of MIGS by calculating the local density of states (LDOS) of each Si layer in the Ag–Si interfacial structure. It was found that regardless of the Si surface and P doping types, the first Si layer was the dominant layer strongly affected by MIGS because of its direct contact with Ag (Supplementary Fig. 11). Based on the LDOS data, we integrated the MIGS region of each system. As shown in Fig. 5d, the integrated MIGS region of the Si(111) surface was lower than that of the Si(100) surface. In particular, when P atoms were introduced near the Ag–Si interface (P doping type II), the number of MIGS decreased. We also examined the dangling bond states (DBS) of Si by calculating the LDOS of Si systems containing dangling bonds to compare the effects of MIGS and DBS (Supplementary Fig. 12). The density of DBS obtained for the Si(111) surface was much larger than the density of MIGS (Fig. 5e), and this difference was further increased by P doping due to the significant increase in the DBS density. In contrast, the Si(100) surface exhibited a marginal difference between the MIGS and DBS densities (Supplementary Fig. 13); nevertheless, the decrease in MIGS density due to P doping was also observed. These results indicate that for the Si(111) surface, the epitaxially grown Ag contact represents a key factor suppressing the DBS carrier recombination, which can be further inhibited by P doping. We
also confirmed the effects of various P doping configurations on the numbers MIGS and DBS (Supplementary Fig. 14 and Supplementary Note 1). In particular, P doping near the Ag–Si interface decreased the number of MIGS as compared with that of the pristine system. Moreover, the MIGS and DBS of the (111) surface were significantly affected by the different P doping types compared to the (100) surface. To this end, it was found that in the epitaxially grown Ag crystallites on the P-doped Si emitter layer, both the epitaxial Ag contacts, and P doping effects strongly inhibited the carrier recombination process due to the significant decrease in the number of DBS on the Si(111) surface, which was the dominant surface of the textured Si substrate (Fig. 5f). Therefore, the findings of this work confirm the positive effects of the epitaxially formed Ag crystals and P doping on the $J_{0,\text{metal}}$ minimization process.

In conclusion, we identified the origin of recombination losses by screen-printed metal electrodes in c-Si solar cells. For this purpose, we investigated the mechanism of Ag crystallite formation on the Si surface during the firing process. Owing to the etching of the SiNx passivation and Si emitter layers by the PbO component of the glass frit, inverted pyramid pits were generated, and Ag ions were metallized on the surface of the Si emitter layer. Furthermore, we directly observed that the epitaxial growth of Ag crystallites occurred on the Si surface due to the $3\text{Si}$-to-$4\text{Ag}$ lattice matching. We also theoretically examined the interfacial properties of the Ag–Si contact structure and found that the minimization of $J_{0,\text{metal}}$ at a certain temperature was induced by the Ag epitaxial growth, which decreased the number of Si dangling bonds in the Si emitter layer etched by the glass frit. Moreover, P doping further inhibited the carrier recombination process by decreasing the number of MIGS. Therefore, our study can provide new insights to achieve a better understanding of the recombination losses by metal electrodes and enhance the performance of c-Si solar cells.
Methods

Fabrication of PERC solar cells. The silicon substrate consisted of a boron-doped p-type c-Si wafer with a size of six inches, thickness of 170 μm, and resistivity of 1–3 Ω·cm. The c-Si wafer was textured using an alkaline solution and then doped in a tube furnace using a POCl₃ source. P-doped emitter layers with a sheet resistance of ~80 Ω/sq were formed on both sides of the c-Si wafer. A wet isolation process was performed to etch one side of the P-doped emitter. After the formation of the \(pn^+\) structure, phosphosilicate glass was removed using a 10% HF solution. Thermal SiO₂ and SiNₓ layers with thicknesses of 2 and 80 nm were deposited onto the front layer using a tube furnace and plasma-enhanced chemical vapor deposition (PECVD) method, respectively. Al₂O₃ layer and SiNₓ capping layer with thicknesses of 5 and 150 nm were deposited onto the rear layer by atomic layer deposition and PECVD, respectively. The Ag and Al electrodes were screen-printed on the front and rear sides using Ag and Al pastes, respectively. Subsequently, a firing process was conducted in a belt furnace at various temperatures (600–950 °C).

Analysis of the saturation current density. Three different steps were performed to predict the solar cell parameters depending on \(J_{0,\text{metal}}\) and \(J_{02}\). First, the saturation current density of the passivated emitter surface (\(J_{0,\text{pass}}\)) was estimated by measuring the quasi-steady-state photocurrent (Sinton WCT-120). The samples utilized for this purpose had P-doped emitters passivated by hydrogenated SiNₓ with symmetrical structures on both sides. The second step involved the determination of \(J_{0,\text{metal}}\) using special grid patterns, which contained mini-cells with areas of 4 cm² and different metal fractions. This method has been originally proposed by Fellmeth et al. and is widely used for the determination of \(J_{0,\text{metal}}\). The third step included the estimations of \(J_{01}\) and \(J_{02}\) in metallized PERC solar cells by conducting Suns-\(V_{oc}\) measurements.
(Sinton). The $J_{01}$ value is composed of the front surface ($J_{0e}$) and base region ($J_{0b}$) components, as shown in equation (1). The $J_{0b}$ value reflects the carrier recombination processes occurring in both the bulk and rear surface regions.

$$J_{01} = J_{0e} + J_{0b} \quad (1)$$

The $J_{0e}$ value is composed of $J_{0\,\text{pass}}$ and $J_{0\,\text{metal}}$ components, as shown in equation (2).

$$J_{0e} = J_{0\,\text{pass}}(1 - F_m) + J_{0\,\text{metal}}F_m \quad (2)$$

Here, $F_m$ is the metal fraction. In this study, the $F_m$ and $J_{0b}$ values equal to 0.04 and 64.838 fA/cm², respectively, were obtained experimentally. The magnitudes of $J_{0\,\text{metal}}$ (Fig. 1b) were determined by the above-mentioned method at various firing temperatures. Moreover, $J_{0\,\text{metal}}$ was strongly related to the weighted metallization area. Other parameters ($J_{02}$, $V_{oc}$, $pFF$, and $p\text{Efficiency}$) depending on the firing temperature were obtained by performing Suns-$V_{oc}$ measurements. The solar cell parameters depending on both $J_{0\,\text{metal}}$ and $J_{02}$ ($V_{oc}$, $pFF$, and $p\text{Efficiency}$) (Fig. 1c) were calculated by varying the $J_{01}$ and $J_{02}$ values of the double-diode model in equation (3).

$$j = j_{\text{ph}} - J_{01}\left\{\exp \left[\frac{qV}{nkT}\right] - 1\right\} - J_{02}\left\{\exp \left[\frac{qV}{mkT}\right] - 1\right\} - \frac{V}{R_{sh}} \quad (3)$$

where $j_{\text{ph}}$, $k$, $R_{sh}$, $n$, and $m$ are the photo-generated current density, Boltzmann’s constant, shunt resistance, ideality factor of diode 1, and ideality factor of diode 2, respectively. In this formula, the series resistance was ignored to consider only the solar cell parameter changes caused by carrier recombination. To calculate $J_{01}$ as a function of $J_{0\,\text{metal}}$, $J_{0b}$, $J_{0\,\text{pass}}$, and $F_m$ were fixed at 64.838 fA/cm², 102.24 fA/cm², and 0.04, respectively (these values were obtained for the experimentally fabricated PERC solar cell). Moreover, $j_{\text{ph}}$, $R_{sh}$, $n$, and $m$ were set to 40 mA/cm², 10000 Ω·cm², 1, and 2, respectively.
Elucidation of the growth mechanism of Ag crystallites. To investigate the Ag crystallites grown on the Si surface and the Si surface morphology by SEM (Hitachi-4800), the sample obtained after the firing process was immersed into a 68 wt.% HNO$_3$ solution for 15 min to remove the Ag bulk region and then into a 5 wt.% HF solution for 30 s to remove the glass frit.

TEM analyses of Ag crystallites and the Ag–Si interface. To investigate the Ag–Si interfacial structure and Pb species by TEM, two types of samples were fabricated via the procedure previously established to produce samples for SEM analysis. The first sample for investigating the Pb structures formed on the surfaces of Ag crystallites was fabricated by a focused ion beam (FIB). The second sample was cut along the Si(111) surface by FIB to observe the resulting cross-section. A JEM-2100F/CS (JEOL Co. Ltd.) TEM instrument, HAADF detector, and energy-dispersive X-ray spectroscopy (EDS) module were used for this purpose.

Computational procedure

DFT calculations. $J_{\text{0,metal}}$ losses at the Ag–Si interface were estimated by performing DFT calculations using the DMol$^3$ program$^{42,43}$. The generalized gradient approximation with the Perdew–Burke–Ernzerhof functional was utilized to calculate the exchange–correlation energy$^{44}$. Spin-polarized calculations were performed, and the Tkatchenko–Scheffler method was applied to obtain van der Waals corrections$^{45}$. DFT semi-core pseudopotentials and the double numerical plus polarization basis set (version 4.4) were used for modeling the core electrons and atomic orbitals, respectively. The convergence criteria for geometry optimizations were $1.0 \times 10^{-5}$ Ha for energy, 0.002 Ha/Å for force, and 0.005 Å for displacement.
The self-consistent field converged at $1.0 \times 10^{-6}$ Ha. The orbital cut-off was set to 4.6 Å. The gamma $k$-point was used with a Monkhorst–Pack grid\textsuperscript{46}. The formation energy of the Ag–Si interfacial structure was calculated using the following equation (4):

$$\text{Formation E} = E_{\text{total system}} - \frac{a}{8} E_{\text{Si bulk}} - \frac{b}{4} E_{\text{Ag bulk}} - \frac{c}{8} E_{\text{P bulk}} - \frac{d}{2} E_{\text{H}_2} \tag{4}$$

where $E_{\text{total system}}$, $E_{\text{Si bulk}}$, $E_{\text{Ag bulk}}$, $E_{\text{P bulk}}$, and $E_{\text{H}_2}$ are the energies of the total system, Si bulk unit cell, Ag bulk unit cell, P bulk unit cell, and H\textsubscript{2}, respectively. The unit cell of bulk P is that of black phosphorus. $a$, $b$, $c$, and $d$ indicate the numbers of Si, Ag, P, and H atoms in the entire system, respectively. The factors 8, 4, 8, and 2 indicate the numbers of Si, Ag, P, and H atoms in the unit cells of bulk Si, bulk Ag, bulk P, and H\textsubscript{2} molecule, respectively. To calculate the LDOS of the (111), (110), and (100) surfaces, the $k$-points were set to $4 \times 4 \times 1$, $3 \times 4 \times 1$, and $4 \times 4 \times 1$, respectively.

**DFT model systems.** To construct the Ag–Si interfacial structure, Si and Ag surface structures were modeled first using their cell-optimized bulk structures. Note that the differences between the lattice constants of the Si and Ag bulk structures and the corresponding reference values (Si\textsubscript{ref}: 5.431 Å and Ag\textsubscript{ref}: 4.090 Å) were 0.295% and −0.056%, respectively. In this study, three different types of Si surfaces ((111), (110), and (100)) were considered. Before obtaining the Ag–Si interfacial structure, the geometries of all surface structures were optimized (Supplementary Fig. 8). For this purpose, their top and bottom sides were terminated with hydrogen atoms. After optimization, the hydrogen atoms were removed from the top surfaces. Moreover, P-doped structures were simulated as well (the doping concentration of P atoms determined experimentally was approximately 2%). By using the geometrically optimized surface systems, interfacial structures were constructed (Supplementary Fig. 9). Owing to the lattice mismatch between the Ag and Si crystal structures, the Ag lattice was compressed to
match the lattice of the Si substrate. We also constructed a non-epitaxial (disordered) Ag structure to investigate the possibility of Ag epitaxial growth on the Si surface from the thermodynamic point of view (Supplementary Fig. 10).


10. Aberle, A. G., Glunz, S. W. & Warta, W. Impact of illumination level and oxide


University of Konstanz (2009).


424  42. Delley, B. An all-electron numerical method for solving the local density functional for
7764 (2000).
426  44. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized Gradient Approximation Made
427  45. Tkatchenko, A. & Scheffler, M. Accurate Molecular Van Der Waals Interactions from
429

**Acknowledgements**

This work was conducted under the framework of the Research and Development of the Korea
Institute of Energy Research (C2-2402), the New & Renewable Energy of the Korea Institute
of Energy Technology Evaluation and Planning (KETEP) granted financial resource from the
Ministry of Trade, Industry & Energy, Republic of Korea (No.20193010014530), and the
National Foundation of Korea (NRF) grant funded by the Korea government
(2022R1F1A1073384). The computational resources were provided by UNIST–HPC and
KISTI (KSC-2020-CRE-0337).
Author contributions

M. S. J. and S. H. L. contributed equally to this study. M. S. J. and S. H. L. conducted majority of experiments, interpreted the results, and wrote the manuscript. K. H. M., M. G. K., and K. T. J. contributed to the analysis of results. J. H. L. performed the TEM measurement and contributed to the TEM analysis. S. K. K. and T. K. L. performed the DFT calculations. H. S., T. K. L., and S. P. conceived the project, interpreted the results, wrote the manuscript, and supervised the study. All authors reviewed and approved the manuscript.

Competing financial interests

The authors declare no competing financial interests.

Additional information

Supplementary information is available in the online version of the paper.

Correspondence and requests for materials should be addressed to H. S., T. K. L., or S. P.

Reprint and permission information is available online at www.nature.com/reprints.
**Fig. 1 | Saturation current densities and c-Si solar cell parameters.**

**a,** Illustration of the growth mechanism of the metal electrode and origin of \( J_{0\text{.metal}} \) in the metal contact structure. **b,** Saturation current densities (\( J_{02} \) and \( J_{0\text{.metal}} \)) and \( p\text{-Efficiency} \) values obtained at different firing temperatures. The red dashed lines indicate the average \( J_{02} \), weighted area \( J_{0\text{.metal}} \times F_m; \)

\( F_m \) (metal fraction) = 0.04, and \( p\text{-Efficiency} \) values. **c,** c-Si solar cell parameters (\( V_{oc}, pFF \), and \( p\text{-Efficiency} \), denoted by the red dashed lines) obtained by varying \( J_{02} \) and \( J_{0\text{.metal}} \) values.
Fig. 2 | Morphological changes in the screen-printed Ag paste/SiNₓ/Si structures after the firing process. SEM images of the Ag precipitates and etch pits formed on the Si surface in the screen-printed Ag paste/SiNₓ/Si structures after firing at 600, 650, 700, 750, 800, 850, 900, and 950 °C. The insets (yellow-colored boxes) indicate the etch pit structures. The yellow dashed circles denote the Ag precipitates. Note that the Ag precipitates and glass frit were removed using HNO₃ and HF solutions.
Fig. 3 | Analysis of the Ag–Si interfacial structure. a, HAADF–STEM image of the Ag–Si interfacial structure (zone axis (Z.A.) = [110]) constructed by the 3 (Si) to 4 (Ag) lattice matching. The scale bar of the inset figure is 60 nm. The firing temperature is 850 °C. b,c, TEM image of the Ag crystallite (b) and TEM–EDS mapping image of Pb atoms (top view) (c). The scale bar of the inset figure in b is 200 nm. d,e, Filtered Pb crystal phase (d) and FFT pattern (e) obtained for the Ag crystallite by HRTEM (Z.A. = [001]).
Fig. 4 | Schematic illustration of the growth mechanism of Ag crystallites on the Si emitter layer surface.
Fig. 5 | Theoretical investigation of the formation of the Ag–Si interfacial structure and its saturation current density. a, Epitaxially grown Ag layer on the Si(111) surface (atomic
Relative energies of the epitaxially grown Ag layers on the Si(111), Si(110), and Si(100) surfaces compared to the energies of the non-epitaxially grown Ag systems. c, Formation energies of the epitaxially grown Ag layers on the Si(111) and Si(100) surfaces. d, MIGS obtained for the (111) and (100) surfaces of the Ag–Si interfacial systems. e, MIGS and DBS obtained for the (111) surface of the Ag–Si interface and Si surface containing dangling bonds, respectively. f, Schematic illustration of the decrease in the saturation current density in the epitaxially grown Ag layer on the Si surface.
Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- SupplementaryInformation.pdf