Mechanism of silver/glass interaction in the metallization of crystalline silicon solar cells

Xinjie Sun1, Shanshan Yao1, Juanjuan Xing1,2, Jiefeng Zhang1, Yunxia Yang1, Hongbo Li1, Hua Tong1,3 and Xiao Yuan1

1 Key Laboratory for Ultrafine Materials of Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai, 200237, People’s Republic of China
2 School of Materials Science and Engineering, Shanghai University, Shanghai, 200444, People’s Republic of China
3 Authors to whom any correspondence should be addressed.

E-mail: xingjuanjuan@shu.edu.cn and tonghua@ecust.edu.cn

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Abstract

In order to reveal the interaction between solid substances (Ag powder and glass frit) during the metallization of crystalline silicon solar cells, the effect of glass frit on the Ag powder sintering and the mechanism of Ag colloid formation in glass phase were investigated. The results show that the Ag powder could grow into larger grains as mixed with a certain amount of glass frit, because the corrosion of Ag by glass melt enabled early start of Ag sintering. This makes the internal grain size and electric resistivity of sintered Ag lines to be closely related to the glass content in the silver paste. Subsequently, it was found that the formation of Ag colloid in glass phase is a physical process rather than a chemical transformation process. Taking Pb-B–Zn-Al composite oxide glasses for exemplification, a feasible strategy of raising the solubility of Ag in glass melt is proposed.

1. Introduction

To date the screen-printed silver (Ag) paste metallization has been dedicated to significant application in the manufacture of almost all the commercial crystalline silicon (c-Si) solar cells. Ag paste is a complex system of hybridized multiphase mainly consisting of Ag powder, glass frit and organic carrier. In firing, these components perform their specific functions: the Ag powder is sintered to be conductive lines, the glass frit is converted into interface medium to bond Ag lines onto Si surface, and the organic carrier works for paste printing [1, 2]. The important impact that Ag paste metallization imposes on cell efficiency is reflected in Ag line resistivity and Ag/Si contact resistivity [3, 4]. Even for the presently leading mono-crystalline Si cells with conversion efficiency over 20%, there is still a space of at least 20% increment in efficiency that can be achieved by improving Ag paste metallization [5].

In order to reduce the damage to cells, the peak firing temperatures of Ag paste metallization are usually set at 750–850 degrees Celsius below the melting point of bulk Ag, which makes the sintering activity of Ag powder affected significantly by various internal and external factors. Aiming to improve the conductivity of sintered Ag lines, the control over the morphology, size and surface modification of Ag powder has been studied [6–8]. Additionally, quite a few attempts of employing some additives such as Ag nanoparticles [9, 10], silver iodide (AgI) [11], silver acetate (CH3COOAg) [12] and so on, were tried to enhance the sintering activity of Ag powder. For the Ag/Si contact, the glass phase medium formed at the interface controls Ohmic conduction property of this contact [13]. In the glass phase, the embedding of Ag colloids was found to be a key factor for the formation of Ag/Si Ohmic contact [14]. Based on this physical model, several explanations such as tunneling [15] and percolation [16, 17] mechanisms have been put forward for electron transport across this contact. Moreover, in the practical powder generation application, the long-term running reliability of the photovoltaic modules...
assembled from a series of solar cells by soldering strongly depends on the adhesion of Ag contact to Si wafers, which shall be at least greater than 1 N mm$^{-1}$ [18].

The Ag paste metallization proceeds along with a variety of reactions occurring sequentially or simultaneously in a short time, causing a few important issues related to the interaction between Ag powder and glass frit. Well understanding this interaction is of absolute importance due to the urgent need for better guidance in material design and metallization processing modulation. The sintering of Ag powder in paste should be especially different from that of single-phase Ag powder alone because of the presence of glass frit. Until now there has not been a clear clarification on this effect. Quite a few of researchers thought the Ag colloids as the product from the interfacial reaction associated with glass phase and SiNx passivation layer, as described by the below formula 1–2 [19, 20].

\[
PbO(\text{glassphase}) + \text{SiN}_x \rightarrow \text{Pb} \tag{1}
\]
\[
Pb + \text{Ag}_2\text{O} \rightarrow \text{Ag} \tag{2}
\]

However, this explanation is unconvincing, because not only there was lack of reliable evidence, but also in fact Ag colloids may appear in glass phase at other sites besides the interface. And also, there is still lack of study about how to control the size and number of Ag colloids in glass phase.

With regard to the above issues, we launched two independent investigations in separated systems, of which one was focused on the effect of glass on Ag powder sintering and another one was concentrated to the mechanism of Ag colloid formation in glass phase. By relating the new achieved findings to the actual Ag paste metallization for c-Si solar cells, we intend to give a clear illustration on the interaction between Ag powder and glass frit in Ag paste metallization.

2. Experimental section

2.1. Materials

All chemical reagents were used as received without further purification. The Ag powders in spherical shape and with average diameter size of 1.22 μm were purchased from Suzhou Smart Surface Material Company. The Ag foils in thickness of 200 nm were purchased from Qinghe Pure Silver Material Company. Glass frit was prepared using melt-quenching method. Typically, a mixture of oxide reagents in specified cation molar ratios (Pb : B : Zn : Al = 40 : 50 : 5 : 5) was grinded in an agate mortar and melted at 1050 °C for 1 h. The glass melt was quenched in deionized wafer at room temperature, and then the glass bulks were collected and grinded into glass frit with average diameter size of around 2.6 μm. The Ag paste was prepared on a three-roller machine. Detailed prescription of Ag paste is listed in table 1.

| Component         | Ag powder | Glass frit$^*$ | Organic carrier$^*$ |
|-------------------|-----------|---------------|---------------------|
| Mass proportion (wt%) | 87.5 ~ 90 | 0 ~ 2.5       | 7.5 ~ 10            |

$^*$ in order to investigate the effect of glass frit on the Ag sintering activity, diverse Ag pastes were prepared in which the content of glass frit was adjusted from 0% to 2.5% and the content of Ag powder and organic carrier varied correspondingly.

$^*$ the organic carrier was mixture of solvent (e.g. terpenol), thickener (e.g. ethocel), plasticizer (e.g. phthalate), surfactant (e.g. caprylic acid), thixotropic agent (e.g. hydrogenated castor oil) and other additives.

For the test of Ag line resistivity, Ag pastes were screen-printed into S shaped pattern with width of 4 mm, height of 18–20 μm and total length of 50 cm on monocrystalline Si wafers. The printed wafers were dried at 250 °C for 3 min and then fired in an open infrared furnace by three step heating processes: first, the temperature was increased to 550 °C in 60 s; second, the temperature was rapidly increased to 800 °C in 8 s; third, the temperature was maintained at 800 °C for 8 s.

For the test of Ag/Si contact resistivity by transmission line method (TLM), Ag pastes were screen-printed into five uniformly long and spaced lines with width of 0.1 mm, height of 18–20 μm, length of 10 mm and inter-line space of 1 mm on monocrystalline Si wafers. The printed wafers were treated and fired by same procedure for the test of Ag line resistivity.
In the application of Ag paste metallization for solar cells, 156 mm × 156 mm monocrystalline Si wafers were adopted. In sequence, the Si wafers first went through cleaning by deionized wafer, texturing by NaOH aqueous solution, diffusion by using POCl3 source, edge etching and SiNx antireflection coating by PECVD. Then Ag pastes were deposited on the Si wafers by using screen printing machine (Baccini, Italy), which were equipped with 360–16 screen for printing 45 μm-width finger lines and ran with 1300 mm snap-off distance, 82 N pressure and 230 mm s⁻¹ printing speed. For all the Si wafers, the same commercial Al rear paste and Ag rear paste were deposited on the back surface by screen printing to from alloyed Al back surface field and Ag back electrode. Finally, the Si wafers were fired in a nine-temperature-region belt furnace (Despatch, America) at a set peak temperature of 910 °C and belt speed of 230 inch min⁻¹.

2.3. Sintering of Ag foils
Two sets of Ag foils with a thickness of about 200 nm were employed, of which one was coated with glass frit and another one was untreated. The foils were fired in an open electric furnace at diverse temperatures from 200 °C to 800 °C for 60 s.

2.4. Dissolution of Ag in glass phase
A mixture of Ag powder and glass frit in mass ratio of 1:99 was placed into a corundum crucible and heated at 200 °C for 1 min. Then, the glass melt was poured onto a steel plate at room temperature. Same treatment was carried out for a mixture of silver nitrate (AgNO₃) and glass frit, in which the mass ratio of Ag and glass was set to 1:99.

2.5. Measurement and characterization
Field-emission scanning electron microscope (FE-SEM, Hitachi S-4800 and Zeiss Supra55) was employed to observe the morphology of samples. A digital micro-ohmmeter was operated for the measurement of Ag line electric resistivity and Ag/Si contact resistivity by TLM. UV and visible spectrophotometry was used for the study of optical absorption of glass samples. X-ray photoelectron spectrometer (XPS) was applied for the identification of elemental valence states in glass phase. The electrical parameters of solar cells were measured on photovoltaic I-V test system under AM1.5 spectrum at the temperature of 25 °C.

3. Results and discussion
In the currently exemplified Ag pastes for front-side metallization of c-Si solar cells, the Ag powder accounts for nearly 90% of the total mass, while the content of glass frit is less than 3%. During a rapid firing process, the glass frit was found to make significant impact on the Ag powder sintering activity. Figure 1 presents the top view SEM images and internal grain size distribution charts of three sintered Ag lines corresponding to 0 wt%, 0.8 wt% and 1.2 wt% of glass frit contained in the Ag pastes, respectively. It can be clearly observed that there was remarkable difference in the internal grain size between the three Ag lines. With the absence of glass frit, the sintered Ag powder showed an aggregation state (figure 1(a1)), and the average size of Ag grains was around 1.25 μm (figure 1(a2)), having a negligible growth compared to the original size (1.22 μm) of Ag powder. In contrast, the Ag powder was sintered much more densely to exhibit clear grain boundary outline (figures 1(b1) and (c1)) and grew into bigger grains as the glass frit was added into the paste (figures 1(b2) and (c2)), implying that the Ag powder sintering was advanced at an elevated temperature. In addition, the Ag grain size increased with the increasing of glass frit content. The average sizes of Ag grains were 2.12 μm (figure 1(b2)) and 2.91 μm (figure 1(c2)) for 0.8 wt% and 1.2 wt% of glass frit contained in the pastes, respectively.

The electrical conductivity of Ag lines, an important index for Ag paste metallization quality, is closely related to the Ag powder sintering. When the content of glass frit in Ag paste changes, the conductivity of sintered Ag lines will vary due to the variation of sintering compactness and internal grain size. In the current study, the phase resistance (Rₚ) is used to evaluate the conductive ability of Ag lines. According to equation (3),

\[ R_p = R_{line} \times M_{line} = \rho_{l} \times m \times \frac{l}{I^2} \]  \hspace{1cm} (3)

where \( R_{line} \) represents the measured line resistance, \( M_{line} \) the mass of Ag lines, \( \rho_{l} \) the line resistivity, \( m \) the mass density and \( l \) the length of lines, the \( R_p \) is determined by two uncertain variables, the \( \rho_{l} \) and \( m \) as the \( I \) is fixed same for all the measured samples. In the case of small content (<3%) of glass frit, the \( m \) of the sintered Ag lines varies little. Consequently, the change of \( R_p \) should be entirely caused by the change of \( \rho_{l} \).

As shown in figure 2, compared to the case of excluding glass frit in the Ag paste, the adding of glass frit with content less than 0.6 wt% led to smaller \( R_p \) values, and the \( R_p \) reached a minimum value as the glass frit content was around 0.4 wt%. When the glass frit content was increased from 0.4 wt% to 0.8 wt%, the \( R_p \) rose rapidly. Then it remained a slow growing rate as the glass frit content continued to increase. This change resulted from
two effects. On the one hand, the presence of glass frit made the Ag powder sintered more compactly and grow into larger grains (figures 1(b1) and (1c1)), which was apt to decrease the $\rho_r$ of Ag lines. On the other hand, a part of glass substance entered the Ag grain boundary to impede electron transport between the grains, increasing the $\rho_r$. When the glass frit content was little (e.g. $< 0.4$ wt% in the current samples), the former effect should be dominant, leading to reduction in the $R_p$. With further increasing of the glass frit content, the latter effect became more notable to increase the $R_p$. But when the glass substance saturated in the Ag grain boundary, the $R_p$ of the sintered Ag lines turned to be less sensitive to the increasing of the glass frit content.
Eberstein et al [21] studied the sintering shrinkage of Ag powder to show the effect of glass frit on the Ag paste sintering, and found that the glass containing Ag compacts show an accelerated shrinkage compared to the glass free Ag compact at an earlier shrinkage state, which can lead to a remarkable shift of the sinter curve towards lower temperatures. However, in this study the relevant mechanism did not be discussed. In order to reveal the mechanism of glass frit affecting Ag sintering activity, we did an experiment to observe the morphology evolution of Ag foils experiencing a 60 s heating treatment at diverse temperatures from 200 °C to 800 °C. For comparison, two sets of Ag foils with a thickness of about 200 nm were employed, of which one was coated with glass frit and another one was untreated. The SEM observation (figure 3) shows that the glass frit coated Ag foils could gain earlier sintering. This evolution became marked as the temperatures was greater than 500 °C, at which the glass frit was softened and spread over the foil surface (figure 3(a1)). Due to the heat-induced shrinkage effect and the corrosion effect from glass melt, large cracks were formed in the foil. As the temperature rose up to 600 °C, the foil gradually decomposed into many small islands (figure 3(a2)). This is because of the corrosion of Ag by glass melt, which resulted in liquefaction of Ag surface and shrink the Ag into dispersed particles under surface tension. These Ag particles showed active sintering feature and the dense bonding between them lead to formation of clear grain boundary (figures 3(a3) and (a4)) as the temperature was greater than 700 °C. By high-resolution SEM, the corrosion of Ag surface by glass melt can be traced. As shown in figure 3(a5), a large amount of Ag colloids was precipitated on the Ag surface after cooling. In contrast, without glass frit coating the Ag foil remained fairly stable at 500 °C (figure 3(b1)); and it slowly split into Ag particles when the temperature rose from 600 °C to 700 °C (figures 3(b2), (b3)). Even at the temperature of 800 °C, the sintering activity of Ag particles was poor in view of no grain boundary formed between them (figure 3(b4)). And also, no Ag colloids were found on the surface after cooling (figure 3(b5)).

Although the practical peak firing temperatures (750 °C–850 °C) of Ag paste metallization are lower than the melting point (960 °C) of Ag metal, a few of researchers suggested that it should be a liquid sintering process of Ag powder [8]. But in the previous literatures, the evidence and mechanism explanation were absent. Our above observation verifies that it is the corrosion of Ag by glass melt that results in liquefaction of Ag surface (figure 3), which facilitates liquid phase sintering of Ag powder during Ag paste metallization. This effect not only benefits Ag sintering at relatively low temperature, but also plays an important role in the formation of Ag colloids in glass phase.

For Ag/Si contact via a glass medium, the presence of Ag colloids in glass phase enables Ohmic conduction across the contact [15]. If it is not so, the direct Ag/Si contact will result in a Schottky barrier [22]. The kinetics of contact formation during the sintering of Ag paste includes two independent but strongly interacting single kinetic phenomena, the reaction kinetics at the wafer surface and the phase transport kinetics of the Ag paste [21]. At the wafer surface, three important single reactions take place, including Ag solution and precipitation in the amorphous interface layer, interface layer growth, and silicon etching [21]. With regard to the dissolution of Ag in glass melt and the subsequent formation of Ag colloids in cooled glass phase, the mechanism has not been clearly clarified yet, because the reactions occurring in the actual Ag paste metallization for c-Si solar cells are likely to involve the change in valence of Ag and some other elements, such as Pb, Bi and so on [19]. Accordingly, the primary interaction between Ag powder and glass frit in a firing process may be veiled against tracing and extracting. Therefore, we investigated the firing of a compound of only glass frit and Ag powder. Simultaneously, a mixture of glass frit and silver nitrate (AgNO3) was fired for comparison.

After firing at 800 °C for 60 s, both the Ag powder and the AgNO3 were all completely incorporated into the glass phase. In the case of Ag powder, the cooled glass block showed red color (left inset in figure 4(a)), implying

![Figure 3. SEM observation of two sets of Ag foils experiencing a 60 s heating treatment at diverse temperatures. Samples shown in (a1)–(a5) were coated with glass frit, and samples shown in (b1)–(b5) were raw foils. (a5) and (b5) show high-magnification SEM images of foil surfaces after heating at 800 °C. The inset in (a4) shows an amplified image of grain boundary.](image-url)
that it contained massive nano-sized Ag colloids in view of the emergence of plasma resonance absorption in the UV–visible absorption spectrum (figure 4) [23, 24]. According to the SEM observation (figure 4(b)), these Ag colloids ranged from several to tens nanometers in diameter. Differently, the cooled glass block with AgNO$_3$ dissolution showed slightly yellow color (right inset in figure 4(a)) as same as the pure glass. The inexistence of plasma resonance absorption in the UV visible absorption spectrum (figure 4(a)) implies that no Ag colloids were formed in the glass phase. This could be also confirmed by the SEM observation (figure 4(c)).

Further measurement on the valence states of Ag element in the glass phase was carried out by using x-ray photoelectron spectrometer (XPS). As shown in figure 5(a), the Ag element from Ag powder was verified to be zero-valent, for the Ag3d5/2 and Ag3d3/2 peaks located at 374.1 eV and 368.2 eV, respectively [25]. In contrast, the Ag element from AgNO$_3$ was monovalent according to the Ag3d5/2 and Ag3d3/2 peaks at 373.7 eV and 367.8 eV, respectively [24, 26]. Such results indicate that the incorporation of Ag element into glass phase was not accompanied with the change of its valence states, but different valence states of Ag element would lead to diverse combination styles in the light of optical absorption characteristics (figure 4(a)). It is inferred that in a firing process the zero-valent Ag element entered the glass melt like network-modifier, and in the cooling process it was then separated from the glass network and aggregated into colloids due to sudden drop in the solubility (figure 4(b)). Consequently, the glass network structure remained as same as the initial. Except for the appearance of plasma resonance absorption of Ag colloidal particles, there was no other change in the absorption spectra (figure 4(a)). Differently, the monovalent Ag element (cations) was incorporated into the glass phase as network former in the form of Ag$_2$O. As a result, no Ag colloids were formed in the glass phase (figure 4(c)), but the glass network structure changed, inducing a red-shift in the absorption edge (figure 4(a)).

Figure 4. (a) UV-vis absorption spectrum of glass blocks. The insets show digital photographs of two glass blocks, which were formed from the reactions of glass frit with Ag powder (left) and AgNO$_3$ (right), respectively. (b), (c) High-resolution SEM images recorded on two glass blocks, which were formed from the reactions of glass frit with Ag powder (b) and AgNO$_3$ (c), respectively.
It should be mentioned that a few of researchers, e.g. Eberstein et al [21], suggested that during sintering some Ag is solved as silver oxide in the amorphous interface layer, transported to the Si surface, and reduced to metallic Ag particles as described by Formula 2 [20]. In our study, however, it has been experimentally proved that the Ag colloidal particles in the glass phase were formed from recrystallization of metallic Ag, and the Ag colloids may grow in glass phase at other sites besides the interface (see figure S1 is available online at stacks.iop.org/MRX/7/016315/mmedia in Supporting Information). These two different views may be attributed to the different nature of the glass used on both sides. In addition, we have not found that the Pb element contained in the glass phase could contribute to the formation of Ag colloidal particles. In the above discussed samples, the zero valence of Pb element was not detected. There were only bivalence and tetravalence states for the Pb element (figure 5(b)), which corresponded to two different coordination structures in the glass network [27].

The size and amount of finally formed Ag colloids are related to the amount of elemental Ag dissolved in glass melt. From the point of view of the crystal nucleation theory, the higher the solubility of elemental Ag in glass melt, the smaller the critical nuclear size and the greater the number of nuclei [28]. Zhou et al found that the glass with low glass transition (Tg) temperature can dissolve more Ag in heating and produce more Ag precipitation in cooling [8]. This means that the formation of Ag colloids in glass phase is most likely a physical process relying on the dissolution of metallic Ag in glass melt. In our study, it is further found that the solubility of Ag in glass melt depends on the proportion of network modifier in glass phase. To take Pb-B-Zn-Al composite oxide glass for exemplification, we prepared two Ag pastes using different glass frit respectively labelled as G1 (40Pb-50B-5Zn-5Al) and G2 (40Pb-40B-15Zn-5Al), of which the former one contained relatively less ZnO network modifier. Taking into account the adhesion of Ag contact to Si wafers, the content of glass frit added in the Ag paste was selected to be 2.0 wt%, which can produce a peeling force of more than 2 N/mm for the Ag contact (figure S2). Through a standard screen-printed Ag paste metallization for c-Si solar cells, the Ag/Si

![Figure 5. XPS spectrum. (a) Ag 3d3/2 and 3d5/2 peaks of two glass blocks, which were formed from the reactions of glass frit with Ag powder (1) and AgNO3 (2), respectively. (b) Pb 4f7/2 peak of the glass block formed from the reaction of glass frit with Ag powder.](image-url)
contact via a glass phase medium in thickness of tens to hundreds nanometers was formed, as typically shown in figure 6(a). For the two Ag pastes, the dimension and structure of Ag/Si contact was basically the same. It was observed by high-resolution SEM that a large number of Ag colloids in diameter size of several nanometers were distributed in the G1 glass phase at the Ag/Si contact interface (figure 6(b)); while very fewer and bigger (50–100 nm in diameter) Ag colloids were contained in the G2 glass phase (figure 6(c)). This indicates that the

Figure 6. (a) Typical cross-sectional SEM image of Ag/Si contact of a c-Si cell. (b), (c) High-resolution images of Ag/Si contact by G1 glass phase and G2 glass phase, respectively.
The solubility of elemental Ag was higher in G1 glass melt than in G2 glass melt. Because of containing less ZnO network modifier, the G1 glass melt could have more additional capability to accommodate Ag.

According to the tunneling mechanism proposed for Ag paste metallization contact \cite{14–16}, the efficiency of electron transport via Ag/Si contact depends significantly on the size and amount of Ag colloids in interface glass phase. This deduction is well consistent with the results from our current study. By transmission line method (TLM), the Ag/Si contact resistivity was tested, as shown in figure 7. When G1 glass frit was used, the contact resistivity was 0.03 \( \Omega \cdot \text{cm}^2 \), which was smaller than half of the value (0.08 \( \Omega \cdot \text{cm}^2 \)) in the case of employing G2 glass frit. Consistent difference was also reflected in the output performance of the cells. Table 2 presents the I-V cell characterization results. In comparison, the two cells had small difference in open circuit voltage (\( V_{oc} \)) and short circuit current (\( I_{sc} \)) but large difference in fill factor (FF). It is clear that the greater FF gained with G1 glass frit was attributed to the lower series resistance (\( R_s \)), which was 31% less than that as G2 glass frit was used. As a result, the cell efficiency with G1 glass frit had 0.27 percentage point increase compared to what was achieved with G2 glass frit.

In addition, the glass itself may cause leakage and recombination at Ag/Si contact interface to induce substantial electrical loss of solar cells, for which the growth of lead particles in the glass layer attached to Si was considered to be the main cause \cite{29}. Lead particles were not formed in our glass, which can be confirmed by the XPS characterization (figure 5(b)). This difference in the observations of both sides may be due to the different composition and properties of the glass. The open-circuit voltage and shunt resistance (\( R_{sh} \)) of the cells are sensitive to leakage and recombination. In our study, both the open-circuit voltage and shunt resistance of G1 glass cell was only slightly higher that of G2 glass cell. This implies that in our case the series resistance (or Ag/Si contact resistance) should be the key factor of cell electrical loss.

### 4. Conclusion

In summary, we elucidate the mechanism and influence of the interaction between Ag powder and glass frit in the Ag paste metallization for c-Si cells. The results from our study show that the corrosion of Ag by glass melt enables early start of Ag sintering at an elevated temperature. Because the presence of glass substance in Ag grain boundary would impede electron transport between the grains, the amount of glass frit added in Ag paste needs to be carefully optimized in order to obtain desirably high conductivity for the sintered Ag lines. The formation of Ag colloids in glass phase has been verified to be a physical process relying on the dissolution of elemental Ag in glass melt. Moreover, we present a feasible strategy of raising the solubility of Ag in glass melt by decreasing the

| Glass frit | \( V_{oc} \) (mV) | \( I_{sc} \) (A) | \( R_s \) (mΩ) | \( R_{sh} \) (Ω) | FF (%) | Efficiency (%) |
|-----------|----------------|---------------|----------------|----------------|--------|---------------|
| G1        | 638.7          | 9.626         | 2.52           | 121.63         | 78.53  | 19.92         |
| G2        | 637.6          | 9.613         | 3.66           | 118.79         | 77.98  | 19.65         |

![Figure 7. TLM results of Ag/Si contact via G1 glass phase and G2 glass phase, respectively.](image)
proportion of network modifier in the glass phase. This strategy should be very valuable for greatly improving the metallization technology for high-efficiency silicon solar cells.

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Notes

The authors declare no competing financial interest.

ORCID iDs

Xinjie Sun https://orcid.org/0000-0002-1528-5876

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