

Metal-Complex Inks for Lower Cost and Improved Passivation for Silicon Photovoltaic Metallization

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Abstract. This contribution introduces the silicon PV community to screen-printable metal-complex inks that potentially will reduce Ag usage in Si PV metallization to one-quarter and costs to one-third that of traditional particle-based pastes while also improving passivation. Metal-complex inks are formulated using a Tollen's reaction to produce inks with a high percentage of diamminesilver (I) cations (22 wt %) in a solution of acetate and formate anions. When printed and dried, labile ammonia ligands evaporate, leaving behind silver cations which, when reduced by formate anions and acetic acid, plate out silver and silver acetate. When annealed to just 300 °C a dense metallic silver film forms with excellent conductivity, and adhesion to silicon. When compared to traditional particle-based screen-printing pastes, the metal-complex inks are much denser, have higher conductivity, use less Ag, and are a fraction of the cost. Importantly, the inks anneal from 90 – 450 °C allowing for improved passivation schemes compared with fired SiNx. This contribution highlights first experiments on the improved passivation of metallized poly-Si/SiO₂ passivated contacts using metal-complex Ag inks.

Keywords: Poly-Si Contacts, Passivation, Metallization, Metal-Complex Inks

1. Background

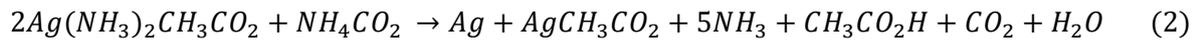
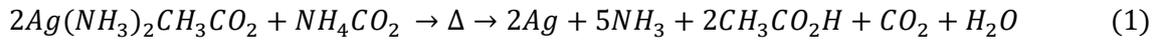
PERC cells require about 70 mg of Ag per M6 wafer, but higher-efficiency cells like TOPCon and HIT require 130 and 160 mg of Ag per M6 wafer, respectively.[1] Currently about 20 tons of Ag is consumed per GW of PV production (2019). Given the global annual PV production in 2020 was 135 GWp with a learning curve of nearly 24%, Ag consumption for PV will continue to rise. Without a change in Ag consumption levels, Si PV production will consume all of the annual global Ag production by 2028, when PV production levels are expected to be nearly 1 TW per year.[2] Other estimates are lower, but have similar consequences for the cost of Ag in PV cells.[3] This rather dire picture clearly outlines the need to reduce the current Ag consumption rates per cell, but more importantly to remove Ag from PV production altogether.

This contribution explores the use of a new type of non-particle-based, screen-printable Ag paste for PV metallization called metal-complex inks that can reduce costs and the amount of Ag per cell and ultimately provide a chemical pathway to transition to Cu metallization.

Metal-complex inks were introduced into the market a few years ago for low-cost, lower-temperature metallization of consumer electronics but have not been thoroughly tested for silicon PV applications. The fundamental concept of this class of inks is that they “precipitate” Ag films onto substrates at relatively low temperatures from a Ag-containing compound, rather

than binding and sintering Ag particles at high annealing temperatures. One can think of it as a nano-scale plating process where metal atoms nucleate from a solution to form a film.

In the simplest case for Ag, the inks have a high percentage of diamminesilver (I) cations (22 wt%), as well as acetate and formate anions.[4] When the ink is printed and dried, the labile ammonia ligands evaporate, leaving behind silver cations. These are then reduced by formate anions and acetic acid, leaving silver and silver acetate following these equations:



When the printed solution is annealed at 90 °C, the ammonia ligands and other reactants boil away, leaving only a dense metallic silver film (Fig. 1c-f). Because the inks are particle-free, they can be inkjet printed at high speeds without clogging the nozzles or formulated to be screen-printed using standard PV equipment. Cu containing inks can also be formulated.

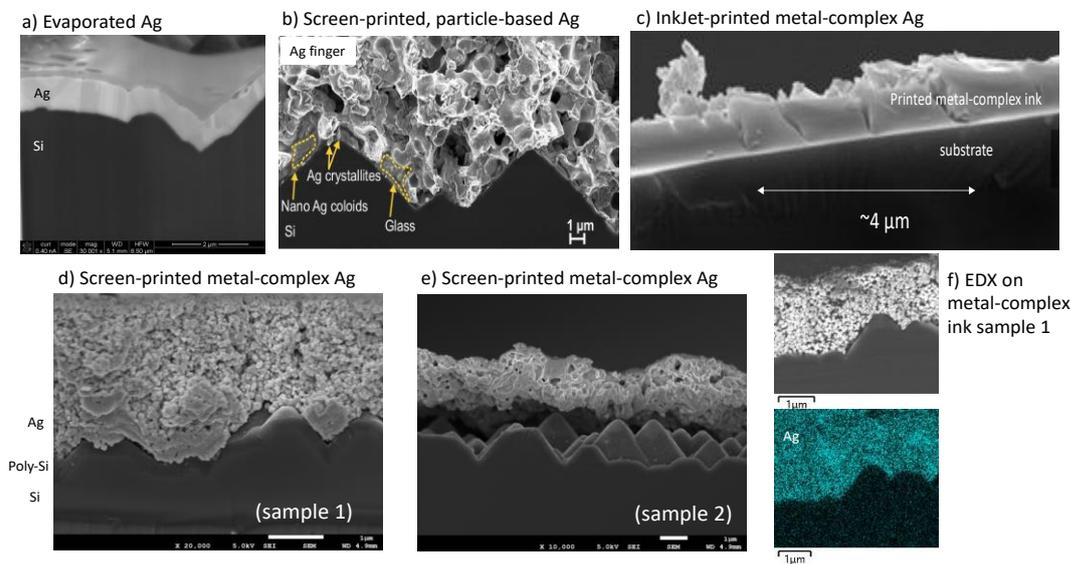


Figure 1. Cross-sectional SEM images of printed metals. a) evaporated Ag, b) screen printed Ag, c) ink-jet printed Ag metal-complex ink, d), e), f) Screen printed Ag metal-complex ink (this work)

Figure 1 shows SEM cross-sectional images of Ag deposited on silicon using different deposition methods and pastes (inks). Fig. 1a is an evaporated Ag film on a textured poly-Si/SiO₂ passivated contact showing a dense, conformal film. This relatively gentle and low temperature metallization process basically preserves the passivation of the contact. Fig. 1b shows a screen-printed Ag film on a texture Si surface. The film is porous and a heterogenous mixture of sintered Ag particles and glass frits which requires a thick layer (20-30 μm) to overcome the high resistivity, compared to bulk Ag. Fig. 1c shows the new Ag metal-complex ink, inkjet-printed onto a smooth substrate. Note the much higher density of the film (~93% of bulk Ag [5] compared with the particle-based metal line (Fig. 1b) (~40% of bulk Ag). [5] The metal-complex film is much closer in density and morphology to the evaporated film of Fig. 1a. This is a key distinguishing characteristic of metal-complex inks that allows much thinner films (and less Ag) to match line resistances of screen-printed films. The greater density and lack of frit filler allows conductivity values 80 - 90% to that of bulk Ag compared to 30 - 40% for particle-based pastes.[6] Unoptimized screen-printed metal-complex Ag inks are shown in Figs 1d-f. The nucleation of the Ag ions is more random in these examples producing highly dense, but still porous films compared to evaporated films.

In this contribution we explore a Ag metal-complex ink on two relevant surfaces for PV applications. The first is a highly doped Poly-Si/SiO₂ passivating contact as used on the back contact of a TOPCon device and the second is an ITO layer found on silicon heterojunction devices (SHJ).

2. Experiment

Double-side textured, RCA cleaned n-Cz wafers were annealed in a tube furnace to grow a 1.5 nm SiO₂ tunnelling oxide followed by 200 nm of LPCVD-grown poly-Si. P dopant atoms were added via a thin layer of PECVD a-Si:P. The samples were annealed at 850 °C for 30 mins followed by 15 nm of Al₂O₃ deposited by atomic layer deposition which were annealed at 450 °C for 30 mins in forming gas. Photoconductive Decay (PCD) and Photoluminescence (PL) measurements were taken in the as-deposited state giving iV_{oc} values of ~730 mV for n-type samples. The samples were then etched in a ~3% HF solution to remove the Al₂O₃ before screen printing with the metal-complex inks. Additional samples were produced on glass substrates consisting of approximately 80 nm of tin doped indium oxide (ITO). Finally, samples were prepared with an ITO layer over the previously mentioned poly-Si/SiO₂ passivated contact layers. The Ag metal-complex inks were supplied by ElectronInks Inc with a product number of EI909. The inks were screen printed onto the samples and annealed in a box furnace under clean, dry air from 60 °C to 160 °C using a ramp rate of 10 °C/min and held at 160 °C for 20 mins. Next, using a ramp rate of 30 °C/min, the samples were taken to 300 °C and held for 30 mins.

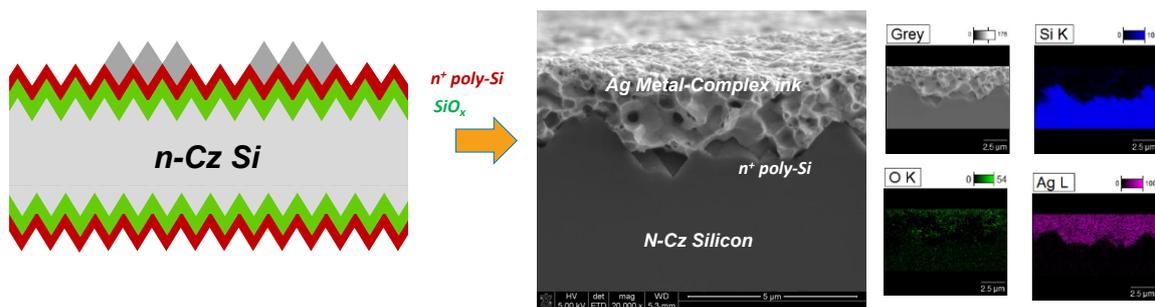


Figure 2. (Left) Schematic of symmetric poly-Si/SiO₂ passivated contact sample with metal-complex ink screen printed on the top surface. (center) Cross-sectional SEM image of the Ag metal-complex ink screen printed over a textured surface. (right) EELS images of the SEM cross-sectional view showing Si, O, and Ag relative concentration maps.

Figure 2 shows the Ag metal-complex ink deposited on the poly-Si/SiO₂ passivating contact structure. Note the porous, dense honey-comb-like structure of the annealed ink. The passivation under the metal was nearly equal to the field (non-metal regions), but the contact resistivity was very high. We performed cross-sectional SEM and Electron Energy Loss Spectroscopy (EELS) on the samples looking for a dielectric blocking layer between the metal and poly-Si but did not observe such a film at the resolutions shown in figure 2. Understanding why the metal does not contact poly-Si is under investigation. Next, we characterized the metal films on the ITO layer (Figure 3) and found very low contact resistivity. Combining our results, we printed the Ag metal-complex ink on a poly-Si contact coated with a very thin layer of ITO (~10 nm) to improve the contact resistivity. As shown in Figure 4, The current vs voltage data between printed transfer

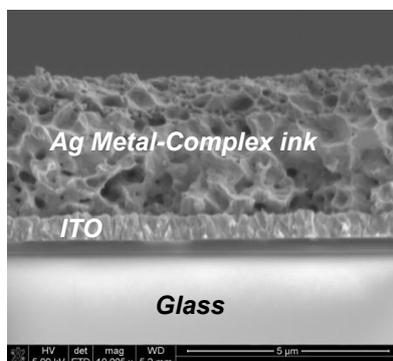


Figure 3. Cross-sectional SEM view of Ag metal-complex ink on ITO on glass.

length measurement (TLM) pads were Ohmic and the TLM analysis showed a contact resistivity between the metal ink and the ITO/poly-Si contact to be $\rho_c = 0.1 \text{ m}\Omega\text{-cm}^2$. This is a

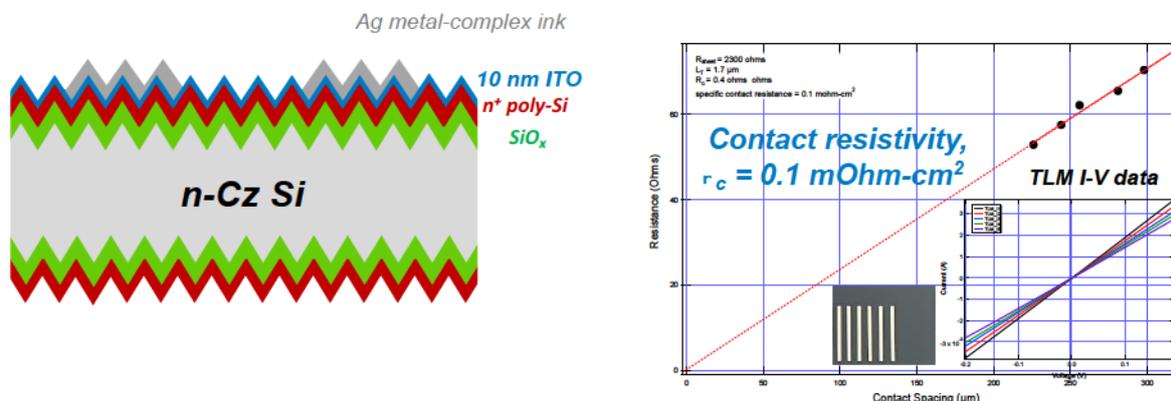


Figure 4 (left) Symmetric poly-Si/SiO₂ passivated contact sample with 10 nm of ITO deposited on the top poly-Si surface and Ag metal-complex ink screen printed over the ITO layer. (right) TLM data showing Ohmic contact (inset graph) between the TLM pads (image of contact pad pattern) and analyzed data showing a contact resistivity between the Ag metal-complex ink and ITO/poly-Si to be 0.1 mΩ-cm².

very promising result for contact to transparent conductive oxides. Ideally, this same value could be obtained directly to poly-Si with further development.

Figure 5 is a PL image of the sample from Figure 4 looking through the wafer at the back of the metallized regions. The image shows that under the metal the passivation is nearly as good as in non-metallized regions. This indicates that the metal-complex inks, with their lower processing temperatures, not only does not significantly increase the recombination at the metal/ITO/poly-Si interface, but also does not lower the passivation in the field region. Using calibrated PL, the sample in Figure 5 indicates an iV_{oc} under the screen-printed metal of 720 mV. The field, non-metallized regions, indicate an iV_{oc} of 730 mV. This low recombination under the metal is one of the most intriguing features of the metal-complex ink approach to solar cell metallization as passivation is nearly preserved under the contacts. The low temperature annealing protocol allows other passivation schemes to be considered in solar cell processes such as Al₂O₃ plus a forming gas anneal instead of a high-temperature firing anneal of SiNx. This intriguing aspect of the metal-complex inks is currently under investigation.

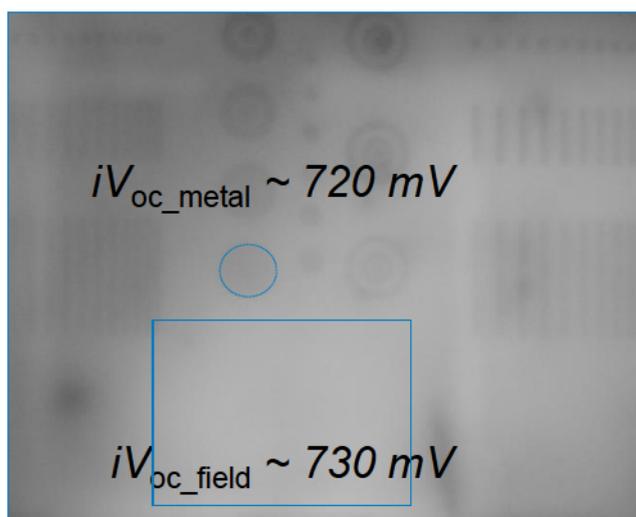


Figure 5. PL image of a screen printed ITO/poly-Si/SiO₂/c-Si sample (see schematic in Figure 4) looking through the sample to the back of the metal regions. Under the metal the iV_{oc} is 720 mV and in the field region the iV_{oc} is 730 mV.

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Data availability statement

All data mentioned in this paper is either in the figures or can be accessed via the first author.

Author contributions

D.Y.: Conceptualization, Investigation, Data Curation, Formal Analysis, Project Administration, Writing – original

draft; W.N.: Investigation; M.P.: Investigation; M. K.: Investigation; H. G.: Investigation; S.T. : Investigation, Visualization, Formal Analysis; M. L.: Conceptualization, Resources

Competing interests

The authors declare no competing interests.

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