

## SIMPLE YET EFFICIENT CHEMICALLY DEPOSITED AG REAR SIDE METALLIZATION ON ITO FOR HIGH-EFFICIENCY C-SI SOLAR CELLS

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**ABSTRACT:** A simple process for preparation of full-area Ag rear side contacts on indium tin oxide (ITO) coated heterojunction technology (HJT) Si solar cells was developed. It employs the well known Tollen's reagent to chemically deposit Ag. Investigations of the microstructure revealed that dense Ag layers without pores are formed. Compared with evaporated Ag the optical and electrical performance of HJT solar cells is practically the same if edge shunts can be avoided by thorough application of a polymer ink all around the edge before chemical Ag deposition. Hence, expensive high-vacuum deposition systems can be replaced. The process is well suited for lab R & D and could also find application in production when combined with smart wire connection technology.

**Keywords:** metallization, back contact, ITO

### 1 INTRODUCTION

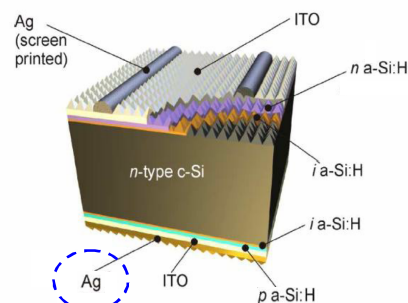
There is growing interest in solar cells featuring heterojunction or passivated contacts because they are the leaders when it comes to high energy conversion efficiency [1]. For both sides contacted cells a transparent conducting oxide (TCO) is applied to the front and rear. TCOs provide low ohmic contact resistance on a-Si:H or polycrystalline Si and act as an efficient antireflection or reflection coating, respectively. Indium tin oxide (ITO) features high electrical conductivity and low light absorption and hence is a widespread TCO. On high efficiency level the benchmark for rear side metallization on ITO for cell optimization in the lab is full area physical vapor deposited (PVD) Ag. Ag forms a very efficient rear side reflector and simultaneously provides high lateral conductivity as well as low contact resistance to ITO. However, huge high-vacuum systems are needed in order to deposit Ag on a large quantity of industrial size solar cells. As a simple to use alternative we investigated the performance of chemically deposited Ag as a full area rear side metallization on silicon heterojunction solar cells. The same chemical process is utilized for industrial mirror production if high optical reflectance is aimed at. For this application the liquids are sprayed on large area glass panes in horizontal inline process machines, see Fig. 1. After silvering the surface is sealed with varnish in order to avoid yellowing. Note that if lower reflectance is sufficient, sputtered aluminum is used for industrial mirror making.



**Fig 1:** Photo of industrial Ag mirror production by spray deposition [2].

### 2 EXPERIMENTAL

6 inch *n*-type CZ Si solar cells featuring a rear side hetero-emitter were investigated. A schematic cross-sectional view is depicted in Fig. 2. The cells were alkaline textured and coated with ITO on both sides. On the front side Ag paste was screen printed in a 5 busbars layout and cured at 200 °C for 20 min. On the rear side we chemically deposited Ag using well known Tollen's reagent [3]. It is an aqueous solution of diaminesilver(I) complex ( $[Ag(NH_3)_2]^+$ ). Deposition starts as soon as it is mixed with a reducing agent.

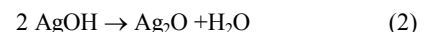


**Fig. 2:** Schematic representation of a Si heterojunction-technology (HJT) solar cell.

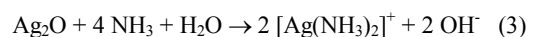
The chemical reactions are as follows [4]: Aqueous solutions of silver nitrate and sodium hydroxide are combined:



Silver hydroxide precipitates and forms the more stable and also only slightly water soluble silver(I) oxide:



Adding ammonia the solution becomes transparent due to the formation of easily water soluble diaminesilver(I) complex:



This is Tollen's reagent. Note that the diaminesilver(I) complex breaks down to silver nitride ( $Ag_3N$ ) within about 1 h at room temperature if the storage container is

not perfectly sealed. Silver nitride is highly explosive leading to surprise detonations. At low mechanical pressure and elevated temperature it decomposes to metallic silver and nitrogen gas. Hence, for safety reasons promptly mix Tollen's reagent after preparation with reducing agent as described in the next paragraph. This way handling is perfectly safe. For industrial applications diaminesilver(I) complex is stabilized by additives and very long shelf life is obtained. Commercial solutions containing diaminesilver(I) complex are declared as stable.

As a reducing agent we chose an aqueous solution of glucose. It is readily available and not toxic. Glucose is not as effective as e. g. formaldehyde because in water it predominantly exists in closed ring forms [5], see Fig. 3, which don't act as a reducing agent. Nevertheless, in equilibrium 0.25 % of the glucose is in the desirable open-chain aldehyde form shown in Fig. 4.

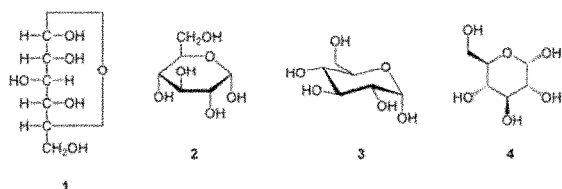


Fig. 3: Closed ring forms of glucose dissolved in water.

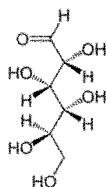
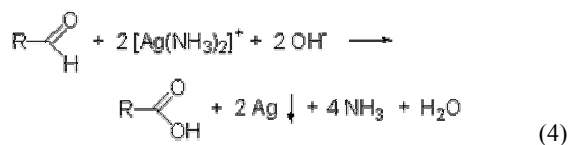


Fig. 4: Open-chain aldehyde form of glucose in water. It is a reducing agent for the diaminesilver(I) complex in Tollen's reagent.

Combining aqueous solution of glucose and Tollen's reagent the following reaction takes place in which the diaminesilver(I) complex is reduced by the aldehyde form of glucose. The aldehyde group oxidizes, gluconic acid is formed and the silver ions are reduced to metallic silver:



In order to speed up reaction rate the temperature can be increased to e. g. 55 °C so that a solid Ag layer is formed within about 2 min. See [3] and the hands-on instruction in reference [6] for more details.

As mentioned in the introduction, in industrial mirror manufacturing the liquids are sprayed on the glass panes. In contrast, in this work we simply placed the solar cells bottom up on a horizontally levelled plastic base and poured aqueous solution of glucose and Tollen's reagent simultaneously onto, see Fig. 5. It is important to note that we applied polymer varnish to the circumferential edge of the cell before silvering in order to minimize edge shunting. After silvering residual chemicals were rinsed with DI water and the cells were dried in N<sub>2</sub>.

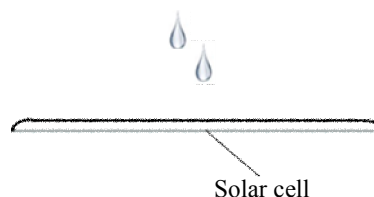


Fig. 5: Schematic representation of the process for silvering the rear side of HJT cells.

As a reference, full area rear side metallization was applied on the same type of cells by vacuum evaporation of Ag. All the cells were characterized by illuminated *IV*, dark *IV*, *suns-V<sub>oc</sub>* and light reflection measurements.

Additionally, with the same process we chemically deposited Ag on *p*-type alkaline textured CZ Si wafers which were not coated with ITO before. The sheet resistance of the Ag layer was mapped by four point probe measurements and its microstructure was investigated by secondary electron microscopy (SEM).

### 3 RESULTS AND DISCUSSION

#### 3.1 Thickness uniformity

Fig. 6 is a photo of a 6 inch Si wafer after full-area chemical silver deposition. No holes or cracks are visible in the Ag layer on a macroscopic scale. Because polymer varnish was not applied to the edge of this cell, Ag deposition extends up to the rim.



Fig. 6: Photo of a 6 inch alkaline textured CZ Si wafer (without ITO on the Si and without polymer ink at the edge) chemically coated with Ag.

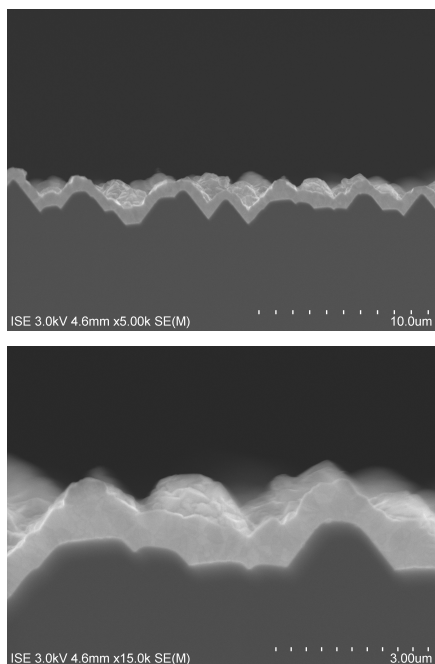
Fig. 7 depicts the sheet resistance of the Ag layer measured on 9 spots on a 6 inch Si wafer. Note that the effect of the Si substrate on the measured values is negligible because its sheet resistance is high (about 50 Ω/sq). In a preceding experiment we found that within the measurement error the electrical conductivity of chemically deposited Ag and bulk Ag are equal. Using this value we calculated the thickness of the Ag layer from the measured sheet resistance considering the surface area of alkaline textured cells which is a factor of 1.7 larger compared to flat surfaces. The result is shown on the right hand side of Fig. 7. The average Ag thickness is 654 nm and the thickness variation is ± 13 %. Hence, reasonable thickness uniformity was obtained by the simple chemical deposition process investigated in this work.



**Fig. 7:** **Left:** Photo of a 6 inch CZ Si wafer (without ITO in this case) chemically coated with Ag showing the measured sheet resistance of the deposited Ag in  $m\Omega/sq$ . **Right:** The same photo showing the thickness map of the Ag layer in nm calculated from the measured sheet resistance.

### 3.2 Microstructure and adhesion of the Ag layer

Fig. 8 shows SEM pictures of an ion polished cross section of a chemically deposited Ag layer on an alkaline textured Si wafer. The Ag layer is formed by small grains that are densely packed. No gaps between Ag grains or between Ag and Si were found. The thin Ag layer very closely follows the lines of the underlying alkaline textured Si surface. On a microscopic scale the Ag layer thickness variation is quite low.



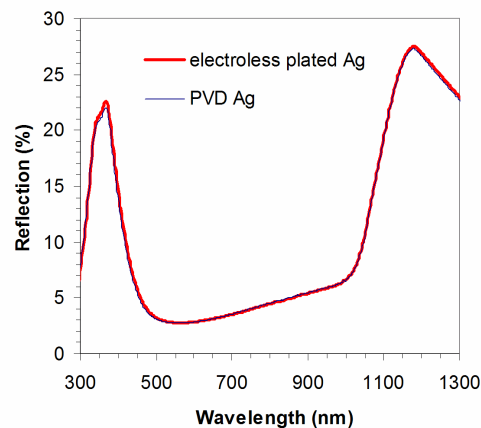
**Fig. 8:** Secondary electron microscope pictures taken of a cross section of electroless plated Ag on alkaline textured CZ Si (without ITO in this case).

To check adhesion of chemically deposited Ag on HJT cells we performed tape tests. They were passed. However, when it comes to soldering of tinned Cu connector ribbons onto the rear contact, Ag completely alloys with the Sn on the ribbons leading to low adherence. Hence, for this application another metal layer could be deposited on the Ag.

### 3.3 Optical performance

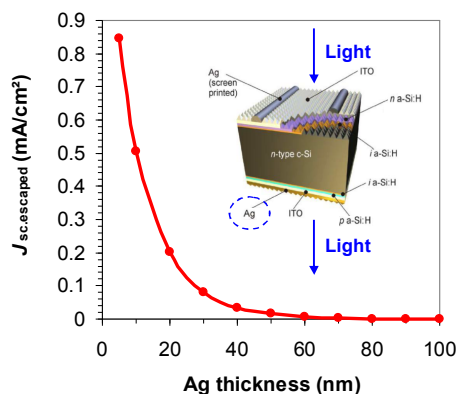
By means of an integrating sphere we measured the front side global reflection of Si HJT cells featuring full area chemically deposited Ag and thermally evaporated

Ag on the rear, respectively. The Ag layer thickness was about  $1 \mu m$  on both samples. Fig. 9 shows that the measured curves overlay exactly. Considering this result for wavelengths exceeding  $1000 \text{ nm}$ , which refers to reflection of infrared light from the rear of the cells, we conclude that the optical performance of chemically deposited Ag and PVD Ag is the same.



**Fig. 9:** Measured front side global reflection of Si HJT cells featuring about  $1 \mu m$  thick full area chemically deposited Ag and thermally evaporated Ag on the rear, respectively.

For cost reasons it is desirable to reduce the Ag layer thickness as much as possible. However, very thin Ag films are optically transparent. To find out the minimum Ag thickness needed for high infrared light reflection we calculated the short circuit current density loss due to transmitted light ( $J_{sc,escaped}$ ) as a function of Ag thickness for a  $150 \mu m$  thick HJT cell. We used the ray tracing app 'SunSolve' [7] without change of the preset optical constants. It can be seen from Fig. 10, that  $J_{sc,escaped}$  is negligible for Ag layers being thicker than  $60 \text{ nm}$ . Note that this thickness corresponds to  $26 \text{ mg}$  of Ag if the surface area enhancement factor of alkaline textured Si (1.7) is taken into account.

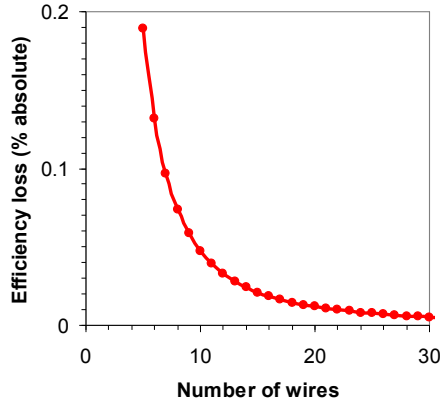


**Fig. 10:** Calculated short circuit current density loss owing to infrared light that escapes to the rear of a HJT cell as a function of the Ag rear contact's thickness.

### 3.4 Resistive power loss

With respect to minimum Ag thickness it is also important to investigate the lateral resistive power loss in the full-area Ag contact. As a meaningful example we assumed a  $100 \text{ nm}$  thick Ag layer on a  $22 \%$  efficient HJT solar cell. Fig. 11 shows the calculated absolute

efficiency loss caused by the lateral electrical resistance of the Ag as a function of the number of equally spaced contacting wires. The efficiency loss is less than 0.02 % absolute for 16 wires which is the number often used in smart-wire interconnection technology. Hence, in combination with the results of the optical assessment in paragraph 3.3 we conclude that thin full area Ag rear contacts are suitable as an efficient rear contact.



**Fig. 11:** Calculated efficiency loss of a 22 % efficient 6 inch Si cell caused by lateral electrical resistance of the Ag rear contact.

### 3.5 Solar cell results

A comparison of the measured electrical performance parameters of 6 inch HJT cells featuring chemical deposited and vacuum evaporated Ag rear contacts, respectively, is presented in Table 1. The thickness of the Ag layer was about 1  $\mu\text{m}$  in both cases. The short circuit current densities ( $J_{sc}$ ) as well as the open circuit voltages ( $V_{oc}$ ) of the cells are practically equal. However, the fill factor ( $FF$ ) of the cell featuring chemically deposited Ag is 0.7 % absolute lower compared to the cell featuring evaporated Ag. The pseudo fill factor ( $pFF$ ) is 0.9 % absolute lower. Theoretically the reductions in  $FF$  and  $pFF$  should be the same because the series resistances are about the same. We attribute the small difference to the measurement errors of the illuminated  $IV$  and suns- $V_{oc}$  curves.

The shunt resistance is reduced from 363 to 3  $\text{k}\Omega \text{cm}^2$  in case of chemically deposited Ag compared with PVD Ag. Calculations reveal that this accounts for 0.4 % absolute fill factor reduction. Analysis of the measured dark  $IV$  curves showed that the remaining  $FF$  decrease of about 0.4 % absolute is caused by an increased second diode recombination current density ( $J_{02}$ ) in the cell featuring chemically deposited Ag rear contact. However, we don't attribute this to Ag deposition but to variations in the cell batch. This hypothesis is supported by the fact that during chemical Ag deposition no mechanical force is applied which could cause an increase of  $J_{02}$ . A larger number of cells have to be manufactured in order to verify this and improve the statistics.

It is interesting to consider again the series resistances of the cells which are virtually identical. Because vacuum evaporated Ag is known to provide very low contact resistance on ITO, it can be concluded that the contact resistance of chemically deposited Ag on ITO is very low, too.

## 4 SUMMARY AND CONCLUSION

Dense Ag layers without pores are formed by Tollen's reagent combined with aqueous solution of glucose. No gaps between Ag layers and cells were found. This explains why the measured optical and electrical performance of the chemically deposited Ag is the same as that of vacuum evaporated Ag. We even found that the contact resistance of chemically deposited Ag on ITO is as low as that of vacuum evaporated Ag.

For HJT cells featuring full area chemically deposited Ag on the rear side, there is the danger of shorting front and back side across the cells' edges. Hence, extra measure has to be taken by thorough application of a polymer ink around the edge. All things considered, the chemically deposited Ag rear contact yielded 21.4 % efficiency compared with 21.6 % for the evaporated Ag.

When it comes to potential industrial applications, simulations showed that an Ag layer thickness of 100 nm is sufficient to reduce the efficiency loss caused by the full area rear contact's electrical resistance to 0.02 % absolute if 16 wires are used for cell contacting. In this case the Ag material costs are 1.7 euro cent per cell provided that the residual Ag in the aqueous solution after chemical deposition is recycled. In comparison, the standard metallization of Si heterojunction cells in industry is low-curing-temperature Ag paste. The price of 39 mg of this paste is approximately the same. However, due to its higher bulk resistivity it provides only about 1/3 to 1/2 of the electrical conductivity of a 100 nm thick pure Ag layer.

## 5 REFERENCES

- [1] <https://www.nrel.gov/pv/assets/pdfs/pv-efficiencies-07-17-2018.pdf>.
- [2] [www.youtube.com/watch?v=OtUof0EH3-E](http://www.youtube.com/watch?v=OtUof0EH3-E).
- [3] C. Heber, Publications of the Astronomical Society of the Pacific 23 (1911) p. 15–19.
- [4] B. Tollens, Berichte der Deutschen Chemischen Gesellschaft 15 (1882) p. 1635–1639 (in German).
- [5] P. C. Heinrich, M. Müller and L. Graeve, Biochemie und Pathobiochemie (2014) p. 27 (in German).
- [6] [www.wikihow.com/Make-Mirrors-by-Silvering-Glass](http://www.wikihow.com/Make-Mirrors-by-Silvering-Glass).
- [7] [www.pvlighthouse.com.au](http://www.pvlighthouse.com.au).

**Tab. 1:** Comparison of the measured electrical performance parameters of 6 inch heterojunction CZ Si solar cells featuring chemically deposited and thermally evaporated full area Ag rear contacts, respectively.

	$J_{sc}$ ( $\text{mA}/\text{cm}^2$ )	$V_{oc}$ ( $\text{mV}$ )	$FF$ (%)	$pFF$ (%)	$R_{ser}$ ( $\Omega \text{cm}^2$ )	$R_{shunt}$ ( $\text{k}\Omega \text{cm}^2$ )	Efficiency (%)
Evaporated Ag	37.8	728	78.5	83.0	0.94	363	21.6
Chemically deposited Ag	37.8	727	77.8	82.1	0.93	3	21.4