

Direct-Write Contacts: Metallization and Contact Formation

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M.F.A.M. van Hest, C.J. Curtis, A. Miedaner,
R.M. Pasquarelli, T. Kaydanova, P. Hersh,
and D.S. Ginley
National Renewable Energy Laboratory

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DIRECT-WRITE CONTACTS: METALLIZATION AND CONTACT FORMATION

Maikel F.A.M. van Hest, Calvin J. Curtis, Alex Miedaner, Robert M. Pasquarelli, Tanya Kaydanova,
Peter Hersh, and David S. Ginley
National Renewable Energy Laboratory, 1617 Cole Blvd., Golden, CO 80401 USA

ABSTRACT

Using direct-write approaches in photovoltaics for metallization and contact formation can significantly reduce the cost per watt of producing photovoltaic devices. Inks have been developed for various materials, such as Ag, Cu, Ni and Al, which can be used to inkjet print metallizations for various kinds of photovoltaic devices. Use of these inks results in metallization with resistivities close to those of bulk materials. By means of inkjet printing a metallization grid can be printed with better resolution, i.e. smaller lines, than screen-printing. Also inks have been developed to deposit transparent conductive oxide films by means of ultrasonic spraying.

INTRODUCTION

In an effort to reduce the cost and improve efficiency of photovoltaics, alternatives to conventional processing techniques are becoming a necessity. One of the most attractive alternative approaches is the application of direct-write approaches for depositing contact metallization. Using inkjet printing as the direct-write technique has multiple benefits over the currently used screen-printing or photolithographic techniques. The first benefit is that inkjet printing is a non-contact technique. As wafer and ribbon Si cells get thinner this is especially attractive allowing higher process yield. This is also potentially useful for textured or thin films on plastics where conformal coating is difficult by contact methods. The second benefit of using inkjet printing is that the resolution of the contact grid lines can be improved compared to screen-printing. Where typical line widths for screen printing are around 100 μm , line widths using inkjet printing can be reduced to less than 50 μm , which significantly reduces the shadow losses by the contact grid and therefore increasing the overall cell efficiency.

APPROACH

Multiple inks have been developed that can be used to inkjet print metal grids. Silver, copper, nickel, and aluminum metal organic decomposition (MOD) inks have been developed that will form pure metal at low temperature (<200°C) with near bulk conductivity [1,2]. A modified Fujifilm-Dimatix material printer (see fig. 1) has been used to deposit line patterns. For initial testing of ink an ultrasonic spray system is used to print uniform films (see fig. 1).

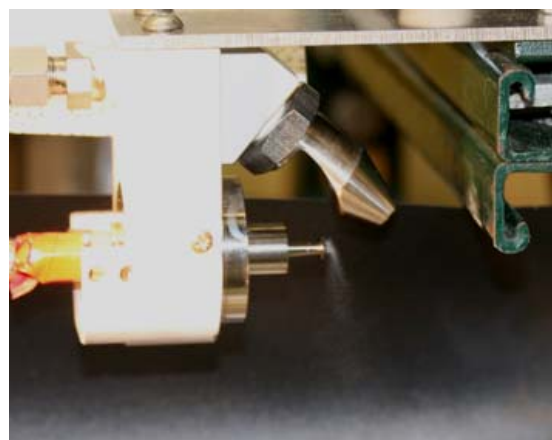


Fig. 1: Fujifilm-Dimatix Materials Printer (top), inkjet head and ink cartridge (center) and ultrasonic spray nozzle (bottom).

Ultrasonic spraying can also be used to deposit large area contacts, such as back contacts. Metal grid patterns are printed on a hot substrate in order to obtain the best conductivity. Printing on a hot substrate ($T < 200^{\circ}\text{C}$) has the benefit of not needing a secondary anneal step in order to obtain pure and conductive material [3]. This is for example suitable for contact to TCOs and organic photovoltaics directly.

RESULTS

Metalization

Fig. 2 shows the line dimensions for printed silver and nickel as a function of the number of layers printed. It can be seen that the line width is almost independent of the number of layers, therefore making it very easy to thicken the material to the desired thickness. In this example the line width for nickel and silver are $80\ \mu\text{m}$ and $110\ \mu\text{m}$ respectively.

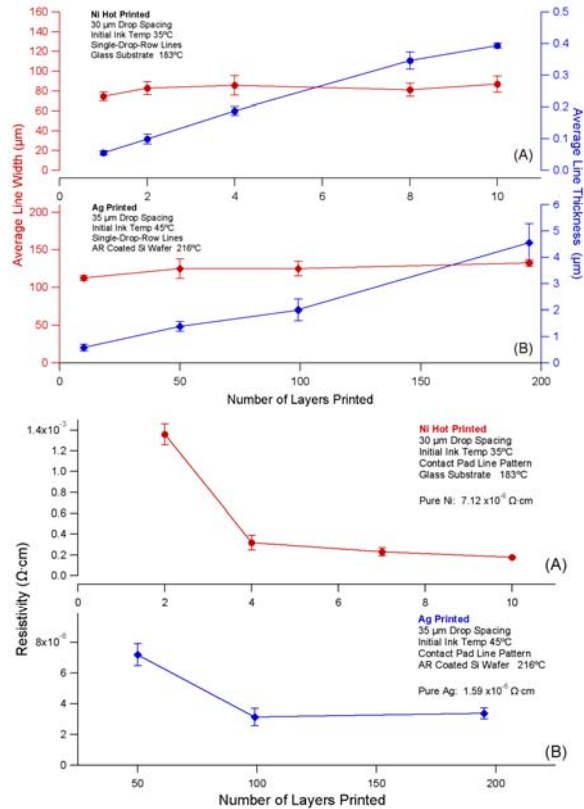


Fig. 2: Line width, thickness (top) and resistivity (bottom) as function of the number of layers printed using the nickel (A) and silver (B) inks.

Also it can be seen in Fig. 2 that the thickness increases continuously with the number of layers. Even though in the shown example that the thickness per pass is of the order of $50\ \text{nm}$ increasing the MOD precursor loading concentration in the ink and decreasing the drop spacing can increase this number to about $1\ \mu\text{m}$ per pass. By optimizing the printing

conditions the line width can be significantly reduced to our currently best of around $30\text{-}40\ \mu\text{m}$ (see fig. 3). This number can be improved even more by changing the nozzle diameter on the inkjet system. This however would reduce the line thickness per pass due to a reduction in droplet diameter and volume.

The resistivity of the lines as function of the number of passes is also shown in fig. 2. It can be seen that for silver a resistivity of $3 \times 10^{-6}\ \Omega\text{cm}$ is obtained, which is close to that of bulk silver ($1.6 \times 10^{-6}\ \Omega\text{cm}$). Optimizing the printing conditions has obtained resistivity as low as $2 \times 10^{-6}\ \Omega\text{cm}$ for silver. The resistivity of inkjet printed silver lines is significantly better than that of screen printed silver lines, which are typically in the range of 5 to 10 times bulk resistivity. In the case of printed nickel the resistivity does not reach number as close to bulk as for silver. This is most likely due to the formation of small amounts of nickel oxide. Using the nickel ink in an inert environment will likely reduce the resistivity significantly.

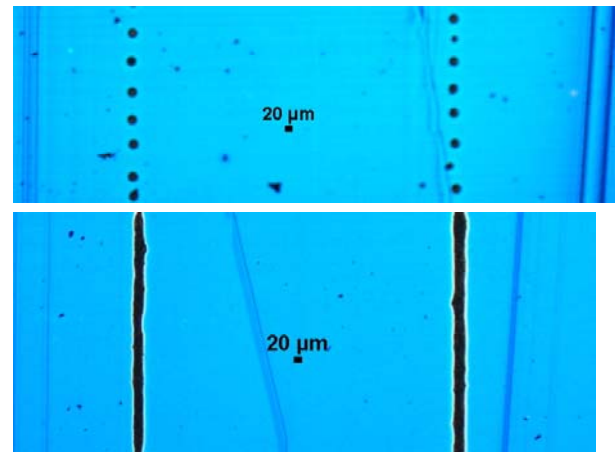


Fig. 3: Micrograph images of inkjet printed silver lines using a metal-organic decomposition precursor. Lines and individual drops printed on SiN_x -coated ribbon silicon.

Screen-printing pastes contain frit material that facilitates the burn-through process of the printed grid lines through the silicon nitride anti-reflection coating typically present on top of a silicon photovoltaic device. An ink to replace this frit material has been developed that can be printed in between the silicon nitride and the silver grid lines (see fig. 4) to facilitate burn-through. This ink will etch through the silicon nitride at relatively low temperatures ($< 750^{\circ}\text{C}$). Using the burn-through ink in combination with the silver ink has produced silicon-based cells with efficiencies similar to or better than those produced using conventional screen-printed contacts. The best contact resistance for inkjet printed contacts using inkjet printed burn-through material and inkjet printed silver was found to be $7\ \text{m}\Omega\text{cm}^2$ which is below that of screen-printed contacts. Using the burn-through layer approach also reduces the amount of

silver that is needed since the inkjet printed silver has better conductivity than the screen-printed alternative.

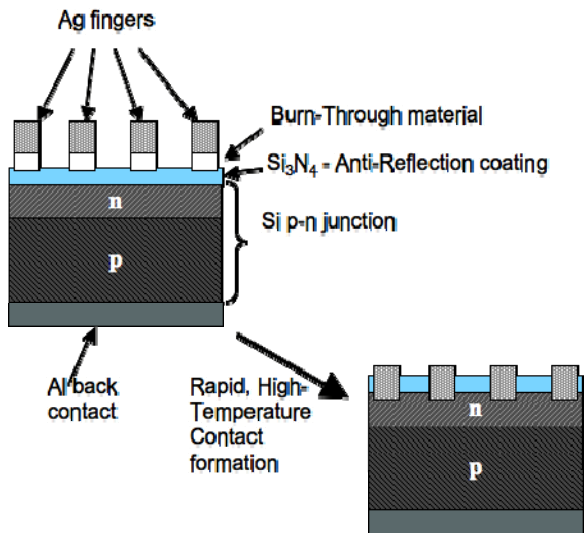


Fig. 4: Schematic of using a separate burn-through material in combination with pure silver to produce contacts for silicon photovoltaic devices with SiN_x anti-reflection coating.

Printed contacts are not limited to silicon-based photovoltaics, but they can also be used for contacts to CuInSe_2 and organic thin film photovoltaic devices. Also it should be possible to replace silver with a less costly material such as copper. If copper is used for metallization on silicon photovoltaic devices a buffer layer of some kind needs to be introduced to prevent copper from diffusion into the silicon, which would negatively affect the efficiency. A candidate buffer material would be nickel. Changing metallization material from silver to a cheaper material would contribute to a reduction in production cost of photovoltaic devices.

Transparent Conductive Oxides

Another field for which inks have been developed are the deposition of transparent conductive oxides (TCOs). TCO layers are used in thin film photovoltaic devices, such as CIGS, CdTe and organic photovoltaics. TCOs are also used in heterojunction wafer silicon devices and as an alternative to the SiN_x anti-reflection coating. The later has the potential to

reduce the number of grid lines and therefore reducing the shadow losses on a device. Using a non-vacuum technique for the deposition of TCOs will contribute to a reduction in production cost. Inks have been developed for a variety of TCOs, e.g. amorphous indium zinc oxide and doped zinc oxides. Initial testing is underway and the results are very promising. Conductivities comparable to vacuum deposition processes can be obtained [4,5].

CONCLUSIONS

Using direct-write approaches in photovoltaics for metallization and contact formation can significantly reduce the cost per watt of producing photovoltaic devices. This is accomplished in two ways. First the direct write deposition techniques can be used under atmospheric conditions, which eliminates the need of costly vacuum deposition techniques. Second better resolution in comparison to screen-printing can be obtained, resulting in higher efficiency devices.

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REFERENCES

- [1] T. Rivkin, C.J. Curtis., A. Miedaner, J. Alleman, D. L. Schulz and D. S. Ginley, "Copper and silver inks for inkjet printing.", *198th International Symposium of the Electrochemical Society.*, 2000.
- [2] T. Rivkin, C.J. Curtis., A. Miedaner, J. Perkins, J. Alleman, and D.S. Ginley, "Direct Write Processing for Photovoltaic Cells.", *IEEE 29th Photovoltaics Specialists Conference.* 2002
- [3] A.L. Dearden, P. J. Smith., D.-Y. Shin, N. Reis, and P. O'Brein, "A Low Curing Temperature Silver Ink for Use in Ink-Jet Printing and Subsequent Production of Conductive Tracks", *Macromol. Rapid Commun*, 2005, **26**, pp. 315-318
- [4] G.G. Choi, S.-J. Seo, and B.-S. Bae, "Solution-Processed Indium-Zinc-Oxide Transparent Thin-Film Transistors", *Electrochem. Solid State Lett.*, 2008, **11** pp. H7-H9
- [5] M.L. de la Olvera, H. Gomez, and A. Maldonado, "Doping, vacuum annealing, and thickness effect on the physical properties of zinc oxide films deposited by spray pyrolysis", *Solar Energy Mater. and Solar Cells*, 2007, **91**, pp. 1449-1453

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