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Multi-Layer Inkjet Printed Contacts to Si

C.J. Curtis, M. van Hest, A. Miedaner,
T. Kaydanova, L. Smith, and D.S. Ginley

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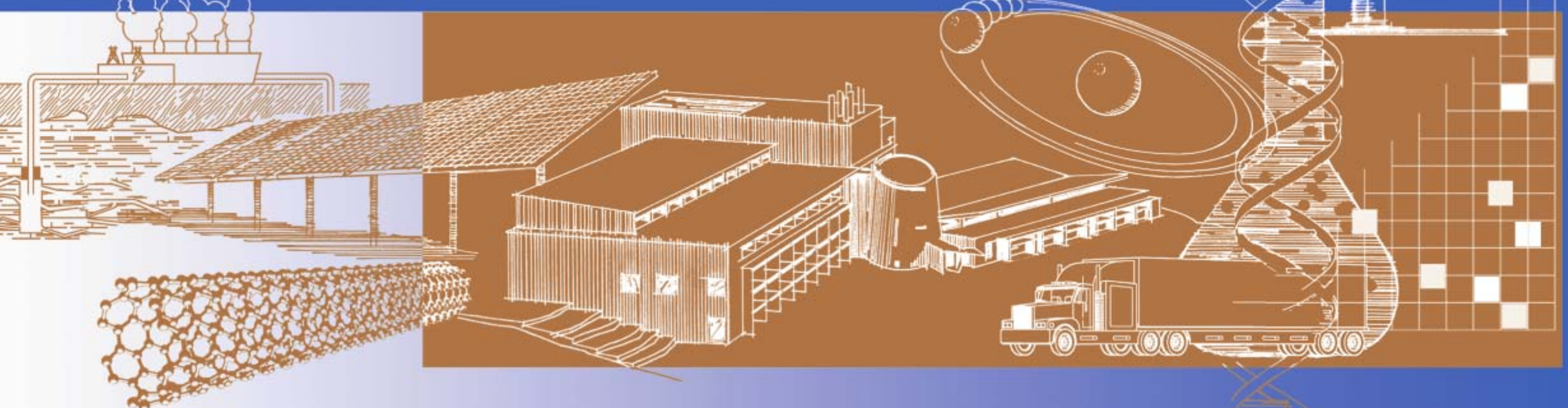

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Multi-Layer Inkjet Printed Contacts to Si

Calvin J. Curtis, Maikel van Hest, Alex Miedaner, Tanya Kaydanova, Lee Smith, and David S. Ginley
National Renewable Energy Laboratory, Golden, Colorado, calvin_curtis@nrel.gov

ABSTRACT

Ag, Cu, and Ni metallizations were inkjet printed with near vacuum deposition quality. The approach developed can be easily extended to other conductors such as Pt, Pd, Au, etc. Thick highly conducting lines of Ag and Cu demonstrating good adhesion to glass, Si, and printed circuit board (PCB) have been printed at 100-200°C in air and N_2 respectively. Ag grids were inkjet-printed on Si solar cells and fired through the silicon nitride AR layer at 850°C, resulting in 8% cells. Next generation inks, including an ink that etches silicon nitride, have now been developed. Multi-layer inkjet printing of the etching ink followed by Ag ink produced contacts under milder conditions and gave solar cells with efficiencies as high as 12%.

1. Objectives

Inkjet printing is rapidly becoming a viable alternative to the existing deposition approaches for a variety of inorganic and organic electronic materials[1]. For metallizations, with appropriate inks, it can replace vacuum deposition, screen printing, and electroplating. The NREL research effort is focused on inkjet printed metallic conductors and other materials necessary to form high-quality contacts. The advantage of inkjet printing is that it is an atmospheric process capable of resolution higher than in screen printing (features as small as 5µm have been produced using an inkjet). It is a non-contact, potentially 3D deposition approach, which makes it ideally suited to processing thin and fragile substrates. The composition of the inks can easily be tailored by the addition of elements such as adhesion promoters and doping compounds to optimize mechanical and electronic properties of the subsequently processed contact. In addition, inkjet printing is inherently suited for printing multilayer/multi-component structures. Development of inkjet printing for deposition of high-quality solar cell contacts contributes directly to achievement of the objectives of the Solar Energy Program for improving performance and reducing the cost of PV devices.

2. Technical Approach

Metal-organic compounds of Ag, Cu, and Ni dissolved in organic solvents (proprietary compositions) were used as precursor inks for inkjet and spray printing of metallic layers and patterns. These inks were printed in air or N_2 on a variety of substrates including glass, Si, and PCB. Ag contact grids were inkjet printed onto SiN_x-coated Si ribbon p/n junctions supplied by Evergreen Solar, Inc.

The inkjet printing apparatus is pictured in Fig. 1. It consists of a stationary drop-on-demand piezoelectric inkjet print head from Microfab Technologies with a 50-micron orifice. A resistive substrate heater plate positioned on an X-Y stage directly under the inkjet serves to provide heating and x-y positioning to 1 µm. The printed pattern, substrate position and translation speed, as well as the print head driving parameters are controlled through a LabView interface.

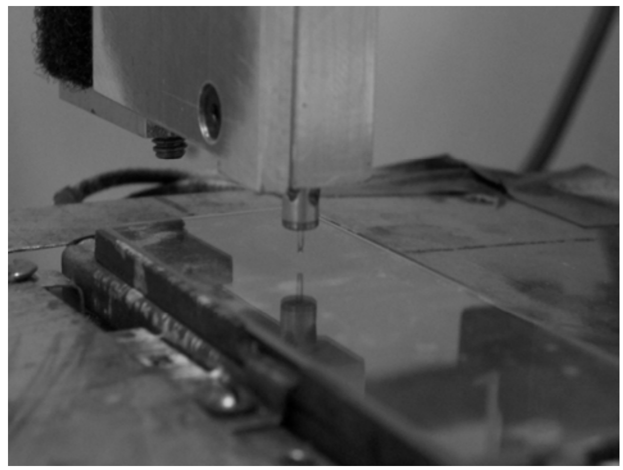

Fig. 1. Inkjet print head positioned over a glass substrate.

Additional inks (proprietary compositions) were developed to provide an etching agent to facilitate penetration of the SiN_x AR coating during processing and promote contact formation. These inks were printed on Evergreen substrates and annealed at various temperatures to optimize the etching rate and profile.

3. Results and Accomplishments

3.1 Printed Metal Inks

Thick (up to 15µm), highly conducting lines of Ag and Cu were printed on a variety of substrates, demonstrating good adhesion to glass, Si, and PCB. The inkjet parameters for Ni printing have not yet been optimized. In general, we found that the best Cu deposits were obtained in an inert atmosphere (N_2 or Ar). However, pure Cu coatings were also obtained in air using rapid thermal processing. Typical resistivities for the metallic coatings were: 2 µOhm*cm for Ag, 7 µOhm*cm for Cu and 100 µOhm*cm for Ni. The resistivity of the Ag layer is essentially that of the bulk metal; the Cu lines are about five times more resistive than bulk, while spray-printed Ni layers show approximately an order of magnitude higher resistivity than the bulk value. Improving the conductivities of printed Cu and Ni metallizations is an area of active investigation.

3.2 Inkjet Printed Ag Grids on Si Solar Cells

Silver lines 250 µm wide and 10 µm thick were inkjet printed on SiN_x-coated Si ribbon p/n junctions provided by Evergreen Solar. Al back contacts 1µm thick were deposited by e-beam evaporation. The two contacts were co-fired in a single annealing step at 850°C for 10 min in air, forming a solar cell with 8% efficiency, Voc=0.529V, Jsc= 22.67mA and a fill factor of 0.65. In this experiment, the ohmic contact between Ag and Si was formed through the SiN_x layer without the use of glass frits. The high temperature and long time required for the penetration of the Ag through the AR coating[2] can be detrimental for the junction. Facilitating the process of burning through the AR coating is desirable to lower the temperature and time of annealing for inkjet printed contacts.

Table 1 summarizes the processing and performance for Si cells with inkjet printed contact grids. The first generation is the cell just described, the second generation used Ag ink modified for better line width, and the third used the etching under layer described below.

Table 1. Summary of line dimensions, processing temperatures and efficiencies for Si cells with inkjet printed contacts.

Generation	1st	2nd	3rd
Line thickness	10 µm	15 µm	15 µm
Line width	400 µm	250 µm	220 µm
Deposition temp	180°C	180°C	180°C
Annealing temp	850°C	850°C	750°C
Efficiency	8%	8%	10%

3.3 Ag Grids with Etching Under Layer

A significant advantage of inkjet printing is that it allows multi-layer printing so that separate writing of the contact formation layer and then the metal forming layer is possible, leading to more control of the contact formation process and improved conductivity of the conductor lines.

Next generation multi-component inks (including surface modifying agents) have been developed to obtain improved fire-through contacts. These proprietary inks greatly improve the burn through and contact formation process. Fig. 2 depicts a 1µm deep, 70µm wide etch pattern obtained by inkjet printing an ink containing a proprietary etching agent on a SiN_x coated Si substrate, followed by thermal processing at 750°C for 10 min. Complete penetration of the SiN_x layer was observed at temperatures as low as 500°C.

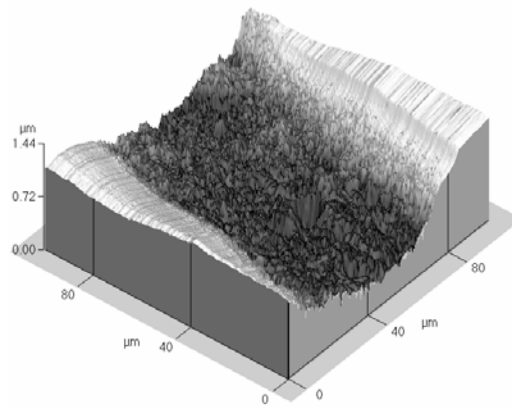

Fig. 2. AFM image of the 1µm deep, 70µm wide etch pattern produced by the inkjet-printed "fire-through" agent on an AR- coated Si wafer.

Experimental solar cells have now been fabricated using this process. These cells were formed by sequential printing of the etching agent layer followed by the deposition of the Ag lines from organometallic precursors as described above. Back contacts were screen-printed using Al paste. However, annealing of the structure has proven to be more difficult than anticipated. Short (40 sec) anneals at 550°C in our lamp RTP furnace have yielded poor results due to non-uniform overheating and penetration of the contact layer too deep into the Si substrate. Short anneals in a conventional furnace have given better results (Table 1, 3rd generation), but the lack of good control of the time-at-temperature has limited the performance of these cells. However, cell efficiencies as high as 12% have now been observed. Further development of the ink composition and optimization of the annealing process are underway and should result in improved efficiencies.

4. Conclusions

An atmospheric, direct-write deposition technique has been developed for metals including Ag, Cu, and Ni. Line widths, conductivities and thicknesses are comparable to or better than those produced by screen printing. It has also been demonstrated that new inks and multi-layer printing can improve the contacting process for Si photovoltaics and lead to better performance.

ACKNOWLEDGEMENTS

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