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Multi-Layer Inkjet Printed Contacts for Silicon Solar Cells

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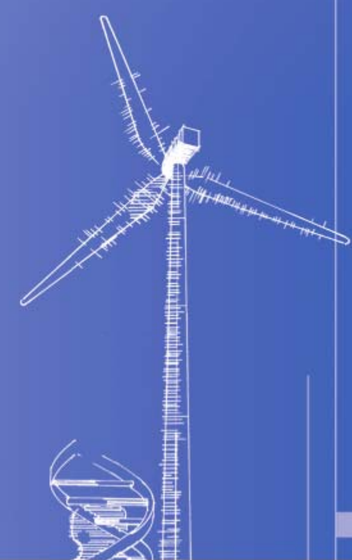

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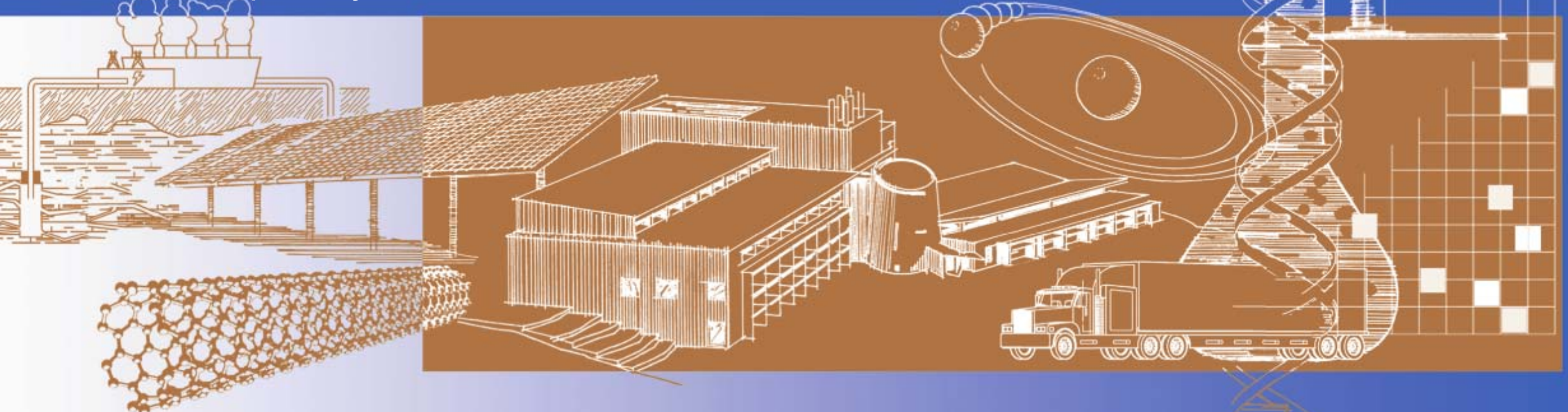

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MULTI-LAYER INKJET PRINTED CONTACTS FOR SILICON SOLAR CELLS*

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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^oC 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^oC, 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%.

INTRODUCTION

Inkjet printing is rapidly becoming a viable alternative to the existing deposition approaches for a variety of inorganic and organic electronic materials[1]. With appropriate inks, it can replace vacuum deposition, screen printing and electroplating for depositing metallizations. 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 may be easily 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/multicomponent structures. We report here on ink-based approaches to printing Ag, Cu and Ni metallizations with near vacuum deposition quality. This approach can by analogy be extended to other conductors such as Pd, Pt and Au.

INKJET-PRINTED METALS

Organometalic compounds of Ag, Cu and Ni in organic solvents (proprietary compositions) were used as the precursor inks for inkjet and spray printing of the metallic layers and patterns. When spray-printed with an airbrush on heated glass substrates at 200-250^oC in air, the metal precursor inks fully decomposed forming metallic coatings without detectable traces of carbon[2] or oxides (Fig. 1).

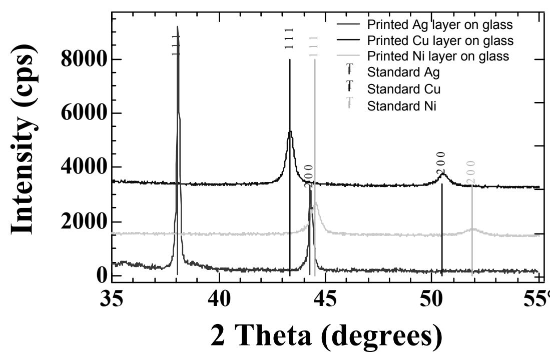

Fig 1. X-ray diffraction patterns of the spray-printed organometallic precursor inks.

The inkjet printing apparatus is pictured on Figure 2. It consists of a stationary drop-on-demand piezoelectric inkjet 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 printing parameters and patterns were controlled by computer using LabView. Printing parameters such as substrate temperature and translation speed, as well as the inkjet driving parameters, the frequency and amplitude of the controlling voltage pulses, were optimized to achieve the best resolution and highest conductivity for Ag and Cu metals.

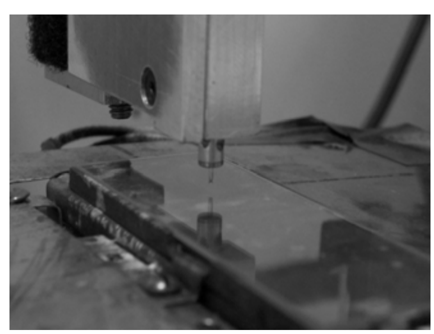

Fig. 2. Inkjet printhead positioned over a glass substrate.

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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 (Figure 3a,b). 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, including the one characterized in Fig. 1, were obtained in air using rapid thermal processing.

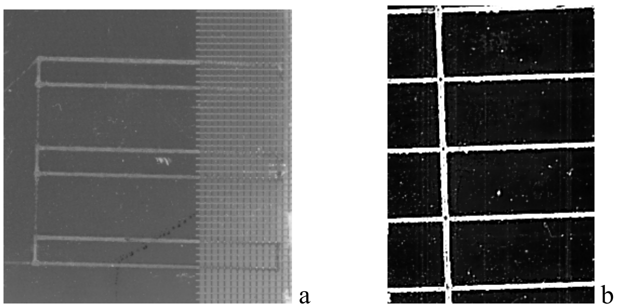

Fig 3. (a) 300µm wide, 5-µm thick Cu lines printed on PCB in N_2 at 200^oC. (b) 250µm wide, 10µm thick Ag grids inkjet-printed on a Si solar cell in air at 200^oC.

A summary of the important characteristics of the inkjet-printed contacts produced to date is presented in Table 1. Typical resistivities for the metallic coatings were: 2µOhm*cm for Ag, 10µOhm*cm for Cu and 100 µOhm*cm for Ni. The resistivity of the Ag layer is essentially that of the bulk metal, the Cu and spray-printed Ni layers demonstrate approximately an order of magnitude higher resistivity than the bulk values. Improving conductivity of printed Cu and Ni metallizations is an area of active investigation.

Table1. Important Characteristics of Printed Conductor Patterns

Material	Thick ness (µm)	Line-width (µm)	Resistivity (µΩ·cm)	Printing temperature (^oC)
Ag	1- 15	100-250	2	200
Cu	1-15	200-300	10	250
Ni	4		100	250
Fire-through agent	1-5	70-200	NA	200

INKJET-PRINTED SILVER GRIDS ON CRYSTALLINE SILICON SOLAR CELLS

Pure Ag grids

Ag lines 250 µm wide and 10 µm thick were inkjet-printed on silicon nitride coated Si ribbon p/n junctions provided by Evergreen Solar, Inc. 1µm thick Al back contacts were deposited by e-beam evaporation. The two contacts were co-fired in a single annealing step at 850^oC 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 (Figure 3b). In this experiment, the ohmic contact between Ag and Si was formed through the SiNx layer without the use of glass frits to enhance etching. The high temperature and long time required for the penetration of the Ag through the AR coating[3] can be detrimental for the junction. Facilitating the process of etching through the AR coating is desirable to lower the temperature and time of annealing for the inkjet-printed contacts. In order to achieve this goal, we explored printable etching agents and multi-component inks.

Table 2 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 2. 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%

Pure Ag grids with etching underlayer

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 multicomponent 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. Figure 4 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^oC for 10 min. Complete penetration of the SiN_x layer was observed at temperatures as low as 500^oC.

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.

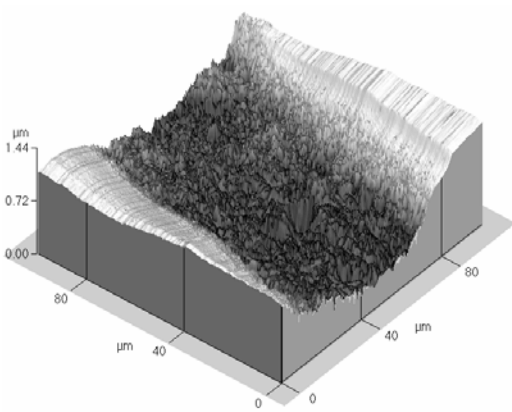

Fig. 4. AFM image of the 1µm deep, 70µm wide etch pattern produced by the inkjet-printed “fire-through” agent on an AR coated Si wafer

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 cell performance.

Future work will focus on improved resolution, multicomponent/multifunctional inks for enhanced contacts and improved inks for better conductivities of Cu and Ni metallizations.

ACKNOWLEDGEMENTS

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