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Direct Write Contacts for 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 PCB have been printed at 100-200^{o}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^{o}C resulting in 8% cells. Next generation multicomponent inks (including etching agents) have also been developed with improved fire through contacts leading to higher cell efficiencies. PEDOT-PSS polymer based conductors were inkjet printed with conductivity as good or better than that of spin-coated films.

INTRODUCTION

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 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 easily extended to other conductors such as Pt, Pd, Au etc.

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^{o}C in air, the metal precursor inks fully decomposed forming metallic coatings without detectable traces of carbon[2] or oxides (Fig. 1).

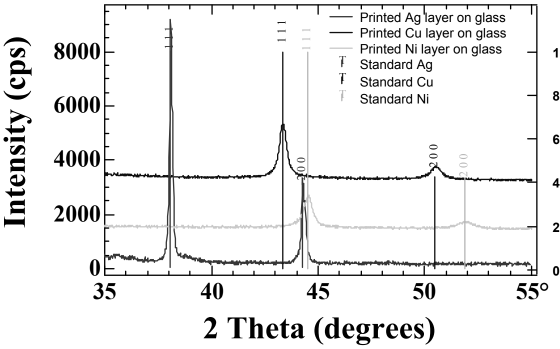

Fig 1. X-ray diffraction patterns of the spray-printed organometallic precursor inks.

The inkjet printer set up is pictured on Fig. 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. 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.

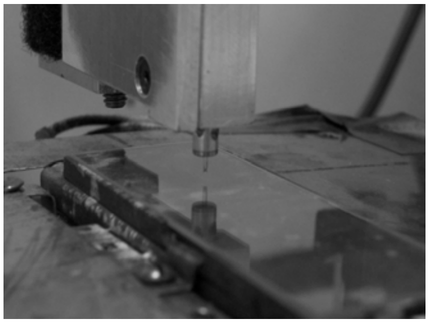

Fig. 2. Inkjet printhead positioned over a glass substrate.

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 shown in Fig. 1, were obtained in air using rapid thermal processing.

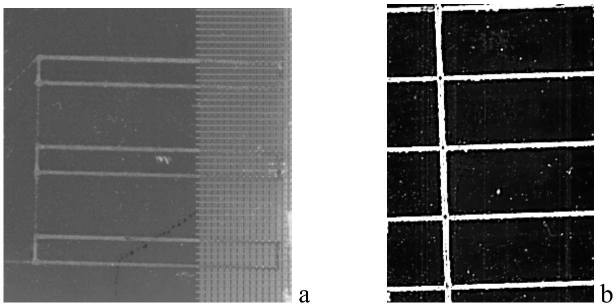

Fig 3. (a) 300μm wide, 5-μm thick Cu lines printed on PCB in N_2 at 200°C. (b) 250μm wide, 10μm thick Ag grids inkjet-printed on a Si solar cell in air at 200°C.

A summary of the important characteristics of the inkjet-printed contacts produced to date is presented in Table 1. Typical conductivities for the metallic coatings were: 2μOhm*cm for Ag, 10μOhm*cm for Cu and 100 μOhm*cm for Ni. The conductivity 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	Thickness (μm)	Line-width (μm)	Resistivity (μ□□□.cm)	Printing temperature (°C)
Ag[(1)]	1- 15	100-250	2	200
Ag[(2)]	1- 15	300-600	7	250
Cu	1-15	200-300	10	250
Ni	4		100	250
PEDOT:PSS	0.1	300	700	50-75
Fire-through agent	1-5	70-200	NA	200

(1) – Ag from metalorganic ink developed at NREL
(2) – Ag from frit-containing nanoparticle ink (Ferro)

INKJET-PRINTED SILVER GRIDS ON CRYSTALLINE SILICON SOLAR CELLS

Pure Ag grids

250 μm wide, 10 μm thick Ag lines 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°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 (Figure 3b). In this experiment the ohmic contact between Ag and Si was formed through the SiNx layer without the use of glass frits. 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 burning 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 two independent directions described below.

Grids from glass containing silver inks.

Glass-frit containing inks analogous to screen-printed pastes in composition but with nanosized Ag particles were supplied by Ferro. The small particle size of the Ag powders used in these inks make them suitable for inkjet printing with the 50μm jet. They were successfully printed resulting in 15μm thick, 500μm wide lines (Figure 4).

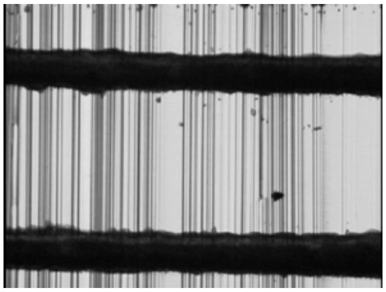

Fig. 4. 100x microscope image of the 15μm thick, 500μm wide Ag lines inkjet printed from Ferro's frit-containing ink

Using these inks, ohmic contacts were achieved at much lower temperatures (650°C, 750°C) with a very short annealing cycle (less than a minute). Further optimization of the ink composition and printing processes is underway.

Pure Ag grids with etching underlayer

Simultaneously we explored another approach to reduced times and temperatures for processing inkjet-printed silver contacts. 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. Fig. 5 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.

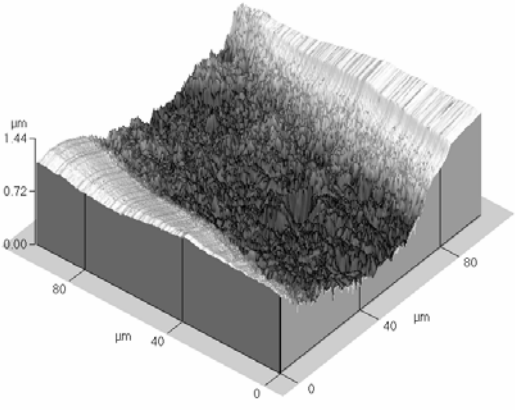

Fig. 5. AFM image of the 1µm deep, 70µm wide etch pattern produced by the inkjet-printed “fire-through” agent on an AR coated Si wafer

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 Ferro’s 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, but the lack of good control of the time-at-temperature has limited these cells to modest efficiencies. Optimization of the annealing process is underway and should result in improved efficiencies.

INKJET-PRINTED PEDOT-PSS CONTACT FOR ORGANIC SOLAR CELLS

Organic solar cells and organic optoelectronics rely in many cases on thin films of PEDOT as an organic TCO. We report on an extension of the inkjet printing process to high performance PEDOT lines and films.

An aqueous suspension of PEDOT/PSS (Baytron P HCV2) was obtained from Bayer. It was printed both as-received and diluted with water or ethyl alcohol, and with additives such as dimethyl sulfoxide (DMSO) and surfactant (Surfynol 2502 from Air Products) in order to achieve highly conducting and smooth PEDOT-PSS films and patterns. Uniform PEDOT lines as narrow as 300µm were inkjet printed on glass substrates (Fig. 6).

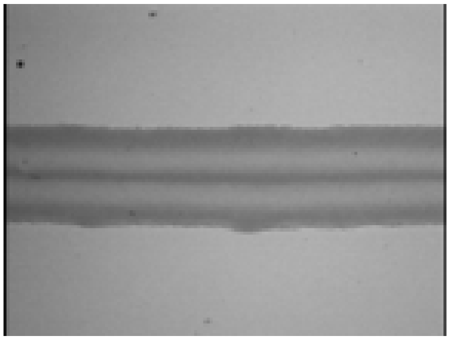

Fig. 6. 50x microscope image of the 300 µm wide PEDOT line inkjet printed on ITO

Continuous films were produced by printing overlapping adjacent lines. The distance between the printed lines was varied for each ink composition in order to achieve smooth films. It was found that film roughness, thickness and conductivity were controlled by various parameters including type of solvent, dopant, substrate temperature and the settings of the inkjet. The smoothest films were achieved by printing at 50°C. The inkjet-printed films were consistently more conducting than films spin-coated from the same ink (Table 2).

Table 2 – Inkjet-printed versus spin-coated films

Sample description	Thickness (nm)	Rough-ness (nm)	Conduc-tivity (S/cm)
Inkjet Printed PEDOT	350	24	4.3
Spin-coated PEDOT	160	2.5	3.1
Inkjet - 1:1 PEDOT/water	150	24	4.7
Spincoat – 1:1 PEDOT/water	60	2.5	3.7
Inkjet – 1:1 PEDOT/water +5% DMSO	300		33
Inkjet – 1:1 PEDOT/water + 5% DMSO +1% Surfynol	300	40	51
Inkjet – 1:1 PEDOT/water + 1% DMSO +1% Surfynol	180	35	31

The increased conductivity of the inkjet versus spin-coated films is not entirely understood, but may be due to preferential polymer alignment or orientation that occurs with longer drying time. The best conductivity of 51 S/cm was achieved by adding 5 wt% DMSO and 1% Surfynol. The increase of conductivity with DMSO has been previously demonstrated for spin-coated films [4, 5]. The surfactant Surfynol was added to the ink to improve the wetting properties of the polymer for smoother films. However, it not only produced visibly more uniform and smoother films, but it also increased the conductivity by a factor of about 1.5, which has not been observed before. Finally it was found that the value of the workfunction (by CPD) for the inkjet-printed polymer could be varied by as much as 0.5V by various additives. This is instrumental for matching the workfunctions of the PEDOT-PSS layer with other layers in the device.

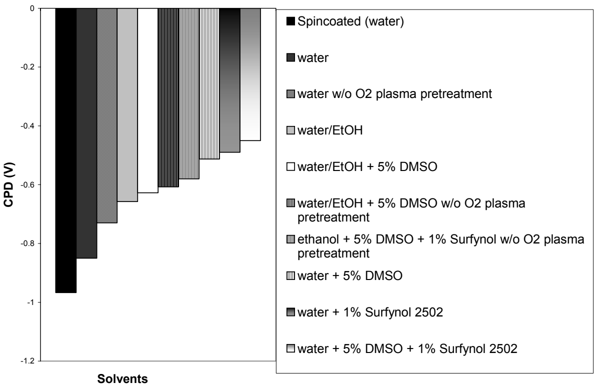

Fig. 7 – Contact Potential Difference (CPD) of PEDOT films printed under identical conditions with various solvents and substrate pretreatments.

CONCLUSIONS

In summary, we have developed atmospheric direct-write deposition of metals including Ag, Cu and Ni. Line widths, conductivities and thicknesses are comparable to or better than those produced by screen printing. We have shown how new inks can improve the contacting process for Si photovoltaics. We have demonstrated inkjet printed patterns of highly conductive PEDOT polymer for contacts in organic photovoltaic cells. Future work will focus on improved resolution, multicomponent/multifunctional inks for enhanced contacts and improved inks for better conductivities of Cu and Ni metallizations.

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14. ABSTRACT *(Maximum 200 Words)*

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