

# **Metallizations by Direct-Write Inkjet Printing**

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C. Curtis, T. Rivkin, A. Miedaner, J. Alleman,  
J. Perkins, L. Smith, and D. Ginley

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**National Renewable Energy Laboratory**

1617 Cole Boulevard  
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# Metallizations by Direct-Write Inkjet Printing

C. Curtis, T. Rivkin, A. Miedaner, J. Alleman, J. Perkins, L. Smith, and D. Ginley  
National Renewable Energy Laboratory  
1617 Cole Boulevard, Golden, CO 80401

## ABSTRACT

Direct-write technologies offer the potential for low-cost materials-efficient deposition of contact metallizations for photovoltaics. We report on the inkjet printing of metal organic decomposition (MOD) inks with and without nanoparticle additions. Near-bulk conductivity of printed and sprayed metal films has been achieved for Ag and Ag nanocomposites. Good adhesion and ohmic contacts with a measured contact resistance of  $400 \mu\Omega\cdot\text{cm}^2$  have been observed between the sprayed silver films and a heavily doped n-type layer of Si. Inkjet printed films show adhesion differences as a function of the process temperature and solvent. Silver lines with good adhesion and conductivity have been printed on glass with 100  $\mu\text{m}$  resolution.

### 1. Introduction

A key area for improvement of photovoltaic cells is the development of low-cost materials-efficient process methodologies. Atmospheric process approaches potentially offer these advantages. Inkjet printing, as a derivative of direct-write processing, offers the additional advantages of low capitalization, very high materials efficiency, elimination of photolithography, and noncontact processing [1].

Conceptually, for Si solar cells, all device elements except the Si could be directly written or sprayed, including contact metallizations (front and rear), dopants, transparent conductors, and antireflection coatings. Our initial thrust has been in the area of developing contact metallizations. As the thickness of Si cells falls below 100  $\mu\text{m}$ , contact grids for the front and rear contacts can be inkjet printed, even on the rough surface of polysilicon, without contacting the thin, fragile substrates. At present, inkjets are capable of line resolutions  $< 20 \mu\text{m}$ , which is at least two times better than the current state of the art obtained by screen printing [2]. In addition, it is an inexpensive, atmospheric process and can be an environmentally friendly, no-waste approach.

A major challenge in applying inkjet processes for direct writing is formulating suitable inks. The inks must contain the appropriate precursors and a carrier vehicle. In addition, they may contain various binders, dispersants, and adhesion promoters, depending on the nature of the precursor and the particular application. In the case of inks for metallization, the content of the metallic ink must be adjusted to provide the required resolution, with good adhesion and the desired electronic properties for the conducting lines. Ink composition is critical because it defines the way in which the ink can be jetted, the adhesion to the substrate, and the line resolution and profile, and it can control the mechanism of metal formation.

Our specific goals are to develop inks and optimize printing parameters for highly conductive lines, achieving low contact resistance, good adhesion, and high resolution.

### 2. Approach

Overall, we have chosen to use combinations of organometallic metal precursors with metal nanoparticles. This allows essentially a mix-and-match approach between the MOD precursor and various nanoparticles which can be tailored for a particular application, e.g. doping level, thickness, and process temperature. We use organometallic precursors as both a metal-forming component of the ink and as a “glue” to bond the nanoparticles together and to enhance adhesion to the substrate. The dry organometallic compound (such as silver(hexafluoroacetylacetone)(1,5-cyclooctadiene) or Ag(hfa)(COD)) is dissolved in an organic solvent such as toluene, ethanol, or butanol. The ink is delivered by spraying or is inkjet printed on a heated substrate in the desired pattern. A silver film forms upon solvent evaporation and decomposition of the printed precursor at elevated temperature ( $\sim 300^\circ\text{C}$ ). Gaseous byproducts of decomposition leave the system, providing contamination-free metal films. To increase the silver loading of the ink and obtain higher deposition rates, silver or other metal nanoparticles may be added to the ink along with the organometallic precursor. In this configuration, silver particles comprise the main conducting volume of the resultant coating, while the organometallic constituent acts as a glue for the silver particles, providing enhanced electrical and mechanical bonding of the metal particles with the substrate and between themselves. Fine, deagglomerated nanoparticulate metal powders must be used in this ink so as to avoid clogging the 10–50  $\mu\text{m}$  orifice of the inkjet. In addition, active constituents, such as adhesion promoters, surface activators, precursors of n-dopants for selective emitters, or possibly nanosized glass frits, may be added to the ink to achieve the required electronic and mechanical properties of the contact.

For initial evaluation of new ink compositions, we have used spray deposition. In this technique, droplets of ink are deposited on heated substrates using an airbrush. This deposition technique is very similar to inkjet printing, but simpler and more robust. The relatively large nozzle opening of the airbrush makes it more difficult to clog. The main difference from the inkjet is that spray deposition is best suited for deposition of continuous films over large areas and is not spatially selective. Practice has shown that inks that spray well by this approach tend to work well in the inkjet as well.

This paper covers our work on printing Ag metallizations, but we have used the same approach to produce Cu metallizations as well. Copper MOD precursors and mixtures of MOD complexes with nanoparticles have

been used as inks to deposit Cu films. However, Cu is more easily oxidized than Ag and its conductivity is much more sensitive to impurities at the grain boundaries. Thus, the Cu inks must be deposited in an inert atmosphere, and the films produced by these inks have resistivities that are several orders of magnitude worse than bulk Cu metal [3].

### 3. Experiments and Results

Spray Deposition with Ag Metal-Organic Ink. A saturated solution of Ag(hfa)COD in toluene, filtered through a 0.2  $\mu\text{m}$  syringe filter, was used as the metal-organic Ag ink [4]. The ink was sprayed onto heated substrates in air using a hand-held Vega 2000 airbrush. During depositions, the substrates were attached using metal clips to a heated copper plate maintained at 400°C. Smooth, dense, grainy coatings were obtained on glass and silicon substrates, as can be seen in the scanning electron image (SEM) image in Figure 1. The thickness of the coatings deposited ranged from 0.1 to 4  $\mu\text{m}$ . According to X-ray photoelectron spectroscopy (XPS) the chemical content of the coatings was pure silver. A significant level

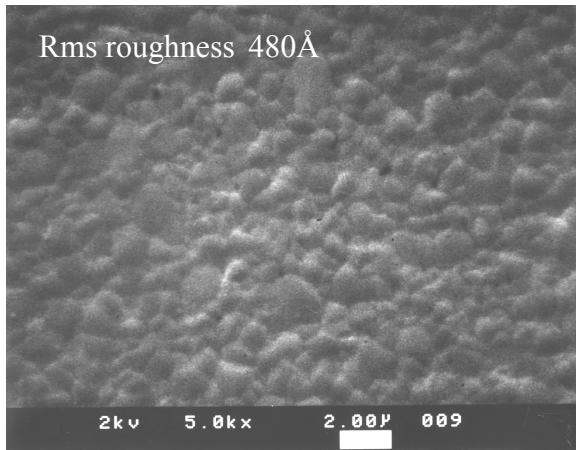


Figure 1. SEM image of Ag film spray printed on Si using ink prepared from Ag(hfa)(COD).

of oxygen, fluorine, and carbon impurities was detected at the film surface and is most likely due to post-deposition surface contamination. It rapidly decreases with depth during ion milling, and the film is >99 atom-% Ag after removing 300 Å. X-ray diffraction (XRD) analysis confirmed that the coating as-deposited consisted primarily of (111)-oriented silver grains, with a small fraction having (100) and (110) orientation. The adhesion strength of the sprayed 3.4  $\mu\text{m}$  thick silver coating on Si exceeded the adhesion strength of conventional screen printed contacts. Resistivity of the sprayed silver layer ( $2 \mu\Omega\cdot\text{cm}$ ) was very near that of bulk silver. Significantly, we were able to achieve ohmic contact (Figure 2) with a relatively low contact resistance ( $400 \mu\Omega\cdot\text{cm}^2$ ) [5] between the sprayed silver coating and the n-type layer of a diffused p-n junction silicon solar cell. The contact resistance was measured using the Transfer-Length Method (TLM) [6]. The silver pads for TLM were fabricated from the sprayed coatings

using photolithography, followed by an etch with 50 % nitric acid.

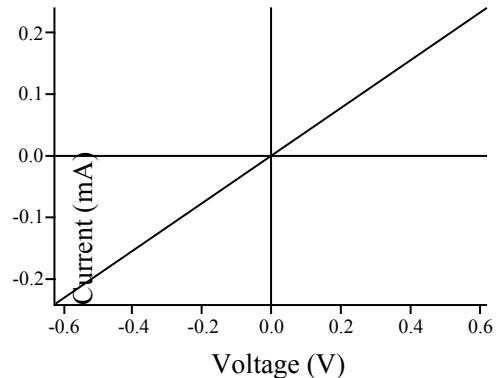


Figure 2. Current-voltage curve for Ag(hfa)(COD)-derived contact on n-type Si.

These results are significant because films with high adhesion strength and good electronic properties were achieved with a simple, one-step, low-temperature deposition process. This is in contrast to screen printed coatings, which require addition of glass frits to promote adhesion and high annealing temperatures (~700°C), or vacuum deposited coatings, which are expensive and require an additional adhesion layer, to achieve similar properties.

Spray Deposition with Composite Ag Nanoparticle/Metal-Organic Ink. Composite nanoparticle/metalorganic ink was prepared by mixing 1.0 g Ag nano-particles in a solution formed by dissolution of 1.0 g Ag(hfa)(COD) in 4 ml ethanol (1:3.9 molar ratio). This precursor was spray printed on a glass substrate heated to 300°C. As deposited, the 10  $\mu\text{m}$  thick silver layer had a relatively porous grainy structure (Figure 3). The layer in Figure 3 was characterized by good adhesion to a Pyrex microscope slide, which was confirmed with the Scotch tape pull test (15-20 lb/in). The high initial resistivity of the as-deposited silver layer ( $58 \mu\Omega\cdot\text{cm}$ ) dropped to  $2.4 \mu\Omega\cdot\text{cm}$ , near the value for bulk silver, after annealing for 30 minutes in air at 400°C.

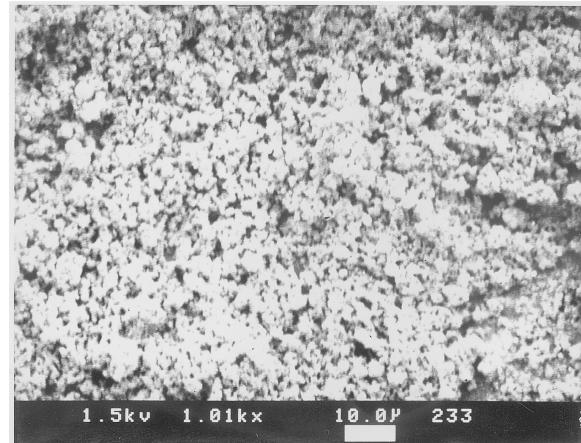


Figure 3. SEM image of Ag film spray printed on glass at 300°C using the composite ink.

The high deposition rate, along with the excellent conducting properties of the deposited silver layer from the composite ink are encouraging and we are planning to proceed to the next step – to evaluate the “printability” of the composite ink by inkjet. The primary concern is that agglomerates of the Ag particles may clog the small 50  $\mu\text{m}$  orifice of the current inkjet. Also, we need to optimize the ink composition to achieve stable particle suspension. When the Ag particles are simply mixed into the organometallic ink, they tend to sediment on the walls of the container. This may require a capping agent for the Ag nanoparticles, which would potentially solve both the agglomeration and printing problems at the same time.

#### 4. Direct-Write Ag by Inkjet Printing

Epson Printer. Simple test patterns were printed on glass and Si using the Ag(hfa)(COD) metal-organic ink with an Epson Stylus Color 740 piezoelectric inkjet printer modified to print labels on compact discs. The ink was prepared according to the recipe above, with ethanol replacing toluene as the solvent. Toluene was found incompatible with the plastic of the inkjet cartridges. The substrate was supported on an aluminum disk heated to 100°C to facilitate solvent evaporation and to prevent the ink from running on the surface. Three layers were printed on top of each other to build a reasonably thick silver coating. At the end of the deposition, the sample was annealed in air at 300°C for 20 minutes. This final annealing eliminated dark brown spots that could be seen in the coating just after the deposition. We assume that these were Ag(hfa)(COD) spots that decomposed, forming Ag during the annealing step. The average thickness of the trilayer coating was  $\sim 2000 \text{ \AA}$ , giving a deposition rate of  $\sim 700 \text{ \AA}$  per layer. Minimum feature size observed in the test pattern was 200  $\mu\text{m}$ . The surface morphology of the inkjet printed silver observed by atomic force microscopy (AFM) closely resembles the silver layers deposited by spraying, supporting the analogy between spray and inkjet printing. The resistivity of the coating measured by the 4-probe technique was  $\sim 5 \mu\Omega\cdot\text{cm}$ , which is a little over a factor of two higher than the resistivity of bulk silver. Good adhesion of the silver coating to the glass slide was confirmed with the Scotch tape pull test.

The disadvantage of using the commercial Epson printer is in lack of control over the printing conditions used. The Epson is optimized for water-based color inks. Using the same printing conditions with the ethanol-based ink resulted in reduced line quality. An optical micrograph of a single line printed on a glass slide is shown in Figure 4. It was observed that the silver accumulated at the edges of the line. This phenomenon may be understood by considering the dynamics of liquid perturbation during the processes of drop evaporation [7].

Microfab Inkjet System. The Microfab inkjet printing system is essentially a drop-on-demand piezoelectric inkjet where user control of waveform, frequency, amplitude, line pressure, and orifice size are all possible. Drops form by

voltage pulses applied to a piezoelectric actuator that creates an acoustic wave in the body of a glass capillary filled with ink. The stimulated waves break the ink meniscus off the tip of the jet at the frequency of the pulse generation. By

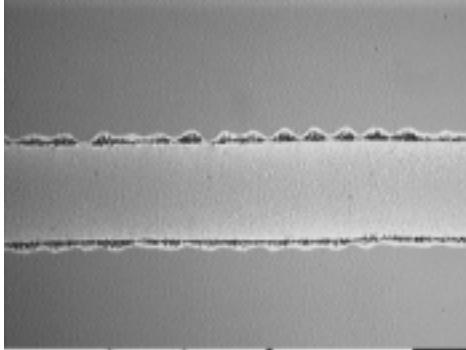


Figure 4. Single line pattern printed on glass with the Epson ink jet printer using Ag(hfa)(COD)-based ink.

The width of the line is 200  $\mu\text{m}$ .

controlling the parameters of the voltage pulse and printing variables such as the frequency of drop generation, the volume/size of the drops and the speed of the drop at ejection can be controlled. Other advantages of the new system are that the jet system does not have plastic parts and thus gives us more freedom for choosing solvents and printing at higher temperatures. Heads are available for high-temperature and nitrogen-purged printing. For the initial printing experiments, however, we used the same ethanol-based ink as employed in the Epson experiments above. Because of the relatively low boiling point of the ethanol, we had to choose a high pulse frequency (1500 Hz) and a relatively low substrate temperature (150°C) to maintain an uninterrupted jet of drops. Single-line patterns were written on a heated glass substrate by linear motion of the inkjet print-head attached to a computer-controlled X-Y table. The jet-to-substrate distance was maintained at  $\sim 1 \text{ cm}$ . To convert printed precursor lines to metallic silver, the printed substrates were heated with a heat gun to above the decomposition temperature of the organometallic compound. The lines obtained had better silver film uniformity and the same (200  $\mu\text{m}$ ) line width as those printed with the conventional Epson printer. Figure 5 illustrates a line printed with the Microfab system. The Ag is uniform across the line width. The orifice size in the Microfab inkjet system is 2.5 times larger than that of the Epson printer (50  $\mu\text{m}$  vs. 20  $\mu\text{m}$ ), and yet, the widths of the lines obtained were the same. The larger orifice size, which also delivers larger drops, gave a more uniform line with better resolution (relative to orifice size) because the Microfab system can tolerate higher substrate temperatures. At higher substrate temperatures, solvent evaporation occurs more rapidly and the ink does not have time to spread as much, leading to higher resolution. These results indicate that the Microfab inkjet should be capable of much better resolution if a smaller orifice is used. (Note that heads are available from Microfab with orifices down to 10  $\mu\text{m}$ .)

In our most recent printing experiments, we were able to achieve 100  $\mu\text{m}$  wide lines by switching to butanol-based

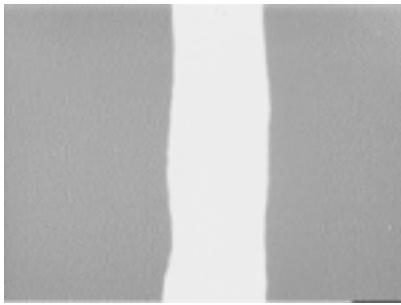


Figure 5. Single line pattern printed on glass with the Microfab ink jet printer using Ag(hfa)(COD)-based ink. The width of the line is 200  $\mu\text{m}$ .

inks. Replacing ethanol with butanol, a solvent with higher boiling temperature, allowed a reduced drop ejection rate, higher substrate temperature, and shorter jet-to-substrate distance to be used. The combination of these changes resulted in better resolution by a factor of two. An additional benefit of using the butanol-based ink is that we were able to print on a substrate heated to well above the decomposition point of the organometallic compound, thus eliminating the need for a post-deposition annealing step. Figure 6 shows individual 100  $\mu\text{m}$  drops of Ag deposited at 200°C on glass with the Microfab system using Ag(hfa)(COD) dissolved in butanol.

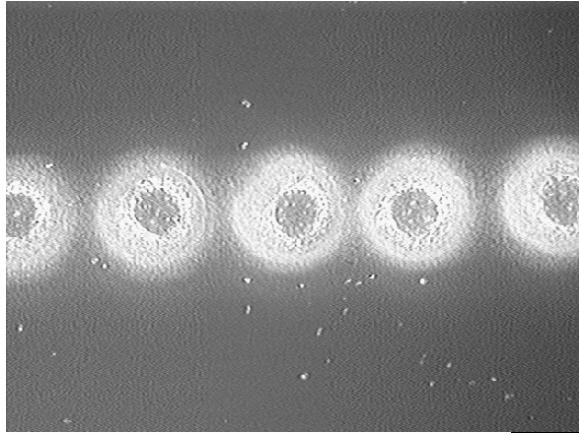


Figure 6. Individual 100  $\mu\text{m}$  Ag drops printed on glass at 200°C with the Microfab ink jet printer using Ag(hfa)(COD)/butanol ink.

## 5. Conclusion

We have demonstrated that direct MOD or composite nanoparticle/MOD deposition of Ag on glass and Si produces films with conductivities comparable to vacuum-deposited materials. Inkjet printing of the precursors produced line resolutions comparable to those obtained by current screen print technology by a non-contact approach. The deposition rates can be very high, especially for the composite inks. By going to smaller orifice size, we anticipate factors of 2 or greater improvement in resolution,

with the possibility of one pass processing. We are also investigating other metallizations using this approach.

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