A national laboratory of the U.S. Department of Energy
Office of Energy Efficiency & Renewable Energy

National Renewable Energy Laboratory

Innovation for Our Energy Future

Direct-Write Contacts for Solar Cells

Conference Paper
NREL/CP-520-37080
January 2005

T. Kaydanova, M. van Hest, A. Miedaner,
C.J. Curtis, J.L. Alleman, M.S. Dabney, E. Garnett,
S. Shaheen, and D.S. Ginley
National Renewable Energy Laboratory

L. Smith and R. Collins
Colorado School of Mines

J.I. Hanoka and A.M. Gabor
Evergreen Solar, Inc.

Presented at the 2004 DOE Solar Energy Technologies Program Review Meeting
October 25-28, 2004
Denver, Colorado

NREL is operated by Midwest Research Institute ● Battelle Contract No. DE-AC36-99-GO10337

Available electronically at http://www.osti.gov/bridge

Available for a processing fee to U.S. Department of Energy
and its contractors, in paper, from:
U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831-0062
phone: 865.576.8401
fax: 865.576.5728
email: mailto:reports@adonis.osti.gov

Available for sale to the public, in paper, from:
U.S. Department of Commerce
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
phone: 800.553.6847
fax: 703.605.6900
email: orders@ntis.fedworld.gov
online ordering: http://www.ntis.gov/ordering.htm

Printed on paper containing at least 50% wastepaper, including 20% postconsumer waste

Direct-Write Contacts for Solar Cells

Tanya Kaydanova[1], Maikel F.A.M van Hest[1], Alex Miedaner[1], Calvin J. Curtis[1], Jeff L. Alleman[1], Matthew S. Dabney[1], Eric Garnett[1], Sean Shaheen[1],Lee Smith[2], Reubin Collins[2], Jack I. Hanoka[3], Andrew M. Gabor[3] and David S. Ginley[1]
[1]National Renewable Energy Laboratory, 1617 Cole Blvd., Golden Colorado 80401 USA
[2]Colorado School of Mines, Golden Colorado 80401 USA,
[3]Evergreen Solar, Inc., 259 Cedar Hill Street, Marlboro, MA 01752 USA

ABSTRACT

We report on our project to develop inkjet printable contacts for solar cells. Ag, Cu, and Ni metallizations were inkjet printed with near vacuum deposition quality. Thick, highly conducting lines of Ag and Cu demonstrating good adhesion to glass, Si, and 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 silicon nitride AR layer at 850 °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. The approach developed can be easily extended to other conductors such as Pt, Pd, and Au, etc. In addition, PEDOT-PSS polymer-based conductors were inkjet-printed with the conductivity as good or better than those of spin-coated films.

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]. The inkjet effort at NREL is currently focused on metallic and polymer conductors. With appropriate inks, inkjet-printed metallizations can replace vacuum-deposited, screen-printed, and electroplated conductors in PV devices. Developing a low-cost, non-contact direct-write approaches such as inkjet printing for high-quality contacts directly contributes to achieving objectives of the Solar Energy Program for improved performance at reduced cost for PV devices.

2. Technical Approach

Organometallic 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. The inks were printed in air or N_2 on various substrates including plastic, glass, and Si (Fig. 1).

Fig 1. Inkjet printhead positioned over a glass substrate.

Additional precursor inks (proprietary composition) were developed to provide for an etching agent, so as to facilitate firing through the SiN_x AR coating in fritless Ag contacts. These precursors were inkjet-printed on SiN_x-coated Si-ribbon p/n junctions provided by Evergreen Solar, Inc., and baked at various temperatures in order to optimize etching rate and profile. Glass-frit-containing nanoparticle based Ag inks provided by Ferro were also tested in our inkjet printer. Line patterns were printed with Ferro's inks onto AR-coated substrates provided by Evergreen Solar, Inc. and annealed in a rapid thermal processing (RTP) furnace. Both composition provided for good burn through and improved contact formation.

PEDOT-PSS polymer inks were printed on glass. Ink compositions and printing parameters, such as drop generation rate, drop ejection speed, and substrate temperatures, were varied in order to achieve the highest conductivities with satisfactory resolution and good morphological properties of the printed conducting patterns.

.

3. Results and Accomplishments

Metallic coatings printed from metalorganic inks had no detectable traces of carbon or oxides (Fig. 2).

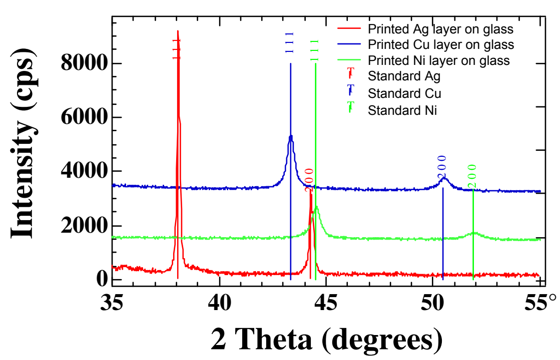

Fig 2. X-ray diffraction patterns of the spray-printed organometallic precursor inks.

A summary of important characteristics of the inkjet-printed contacts produced to date are presented in Table 1. Typical conductivities for the metallic coatings were: 2 μOhm.cm for Ag, 10 μOhm.cm for Cu and 100 μOhm.cm for Ni. Conductivity of the Ag layer is essentially that of the bulk metal, the Cu and Ni layers demonstrate approximately an order of magnitude higher resistivity than the bulk value. In general we found that the best results with Cu were obtained in inert atmosphere (N_2 or Ar). However, pure Cu coatings were obtained in air using rapid thermal processing. Similar conductivities were found for inkjet-printed metallic lines.

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)

Improving the conductivity of printed Cu and Ni metallizations is an area of active investigation. Thick (up to15 μm), highly conducting lines of Ag and Cu were printed on a variety of substrates, demonstrating good adhesion to glass, Si, and PCB (Fig. 3a,b).

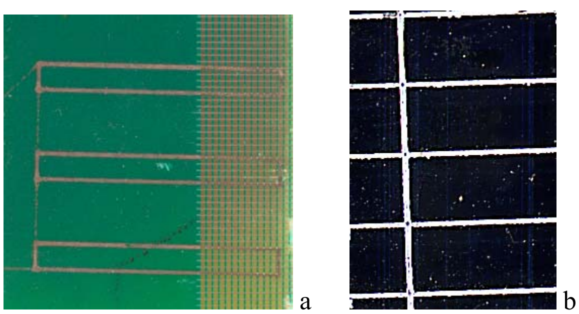

Fig. 3. 300-μm-wide, 5-μm-thick Cu lines printed on PCB in N_2 at 200 °C (a); 250-μm-wide, 10-μm-thick Ag grids inkjet-printed on a Si solar cell in air at 200 °C (b).

Ag grids were inkjet-printed on Si solar cells and fired through a silicon nitride AR layer at 850 °C, resulting in 8% cells (Fig. 3b). Next-generation multicomponent inks (including surface modifying agents) have been developed for improved fire-through contacts, leading to higher cell efficiencies. These proprietary inks greatly improve the burn through and contact formation process.

A potentially significant advantage of inkjet printing is that with multi-layer printing it allows separate writing of a contact-formation layer, and then of the metal-forming layer, leading to more control of the contact-formation process and improved conductivity of the conductor lines. Figure 4 demonstrates a 70-μm-wide, 1-μm-deep pattern etched on a AR-coated Evergreen wafer by inkjet printing and consequent thermal processing at 750 °C for 10 min of an ink containing a proprietary etching agent.

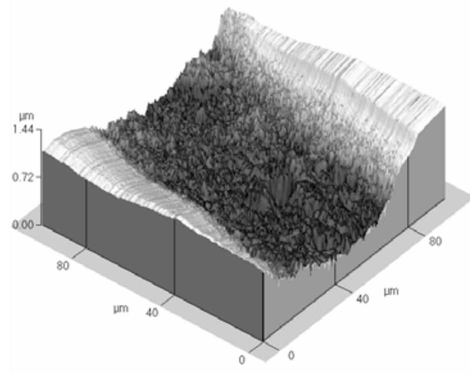

Fig. 4. 70-μm-wide, 1-μm-deep etch pattern produced by inkjet-printed "fire-through" agent in AR-coated Si wafer.

Complete burning through the SiN_x layer was observed at temperatures as low as 500 °C. Conventional, frit-containing nanoparticle Ag inks from Ferro were successfully inkjet printed resulting in 15-μm-thick, 500-μm-wide lines (Fig. 3b). 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).

Organic solar cells and organic optoelectronics often rely on PEDOT-PSS as an organic transparent contact. Uniform PEDOT lines as narrow as 300μm were printed. Film roughness, thickness, conductivity, and work function were controlled by various parameters, including type of solvent, additives (DMSO), substrate temperature, addition of a surfactant, substrate cleaning, and settings of the inkjet. Films as thin as 100 nm, as smooth as 20 nm, and as conductive as 140 S/cm have been achieved. These conductivities are equal to the best conductivities achieved for spin-coated films. The value of the workfunction (by CPD) could be varied by as much as 0.5V.

4. Conclusions

We have developed a set of tools and inks for the atmospheric direct-write deposition of various metals such as 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, improved inks for better conductivities of Cu and Ni metallizations, and integrating inkjet printing of metallic and organic contacts in device processing.

REFERENCES

[1]. D. B. Wallace, W. R. Cox, and D. J. Hayes, in Direct-Wirte Technologies for Rapid Prototyping Applications, edited by A. Pique and D. B. Chrisey (Academic Press, 2002), p. 177.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
January 2005	Conference Paper	

4. TITLE AND SUBTITLE
Direct-Write Contacts for Solar Cells

5a. CONTRACT NUMBER
DE-AC36-99-GO10337

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
T. Kaydanova, M.F.A.M van Hest, A. Miedaner, C.J. Curtis, J.L. Alleman, M.S. Dabney, E. Garnett, S. Shaheen,L. Smith, R. Collins, J.I. Hanoka, A.M. Gabor, and D.S. Ginley

5d. PROJECT NUMBER
NREL/CP-520-37080

5e. TASK NUMBER
PVA54201

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
National Renewable Energy Laboratory
1617 Cole Blvd.
Golden, CO 80401-3393

8. PERFORMING ORGANIZATION REPORT NUMBER
NREL/CP-520-37080

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSOR/MONITOR'S ACRONYM(S)
NREL

11. SPONSORING/MONITORING AGENCY REPORT NUMBER

12. DISTRIBUTION AVAILABILITY STATEMENT
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

13. SUPPLEMENTARY NOTES

14. ABSTRACT *(Maximum 200 Words)*
We report on our project to develop inkjet printable contacts for solar cells. Ag, Cu, and Ni metallizations were inkjet printed with near vacuum deposition quality. Thick, highly conducting lines of Ag and Cu demonstrating good adhesion to glass, Si, and 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 silicon nitride AR layer at 850 ^oC 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. The approach developed can be easily extended to other conductors such as Pt, Pd, and Au, etc. In addition, PEDOT-PSS polymer-based conductors were inkjet-printed with the conductivity as good or better than those of polymer-based conductors.

15. SUBJECT TERMS
PV; inkjet printable contacts; solar cells; polymer-based conductors; polymer-based conductors; multicomponent; multifunctional;

16. SECURITY CLASSIFICATION OF: a. REPORT	b. ABSTRACT	c. THIS PAGE	17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
Unclassified	Unclassified	Unclassified	UL		19b. TELEPHONE NUMBER *(Include area code)*