Electrical Characterization of Printed Nanocrystalline Silicon Films

Cooperative Research and Development Final Report

CRADA Number: CRD-07-00241

NREL Technical Contact: David Young

CRADA Report
NREL/TP-7A10-50944
May 2011

Contract No. DE-AC36-08GO28308

NOTICE

This report was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or any agency thereof.

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/help/ordermethods.aspx

Cover Photos: (left to right) PIX 16416, PIX 17423, PIX 16560, PIX 17613, PIX 17436, PIX 17721

Printed on paper containing at least 50% wastepaper, including 10% post consumer waste.

Cooperative Research and Development Final Report

In accordance with Requirements set forth in Article XI.A(3) of the CRADA document, this document is the final CRADA report, including a list of Subject Inventions, to be forwarded to the Office of Science and Technical Information as part of the commitment to the public to demonstrate results of federally funded research.

CRADA number: 07-241

CRADA Title: Electrical Characterization of Printed Nanocrystalline Silicon Films

Parties to the Agreement: Innovalight

Joint Work Statement Funding Table showing DOE commitment:

Estimated Costs	**NREL** Shared Resources
Year 1	$ 300,000.00
Year 2	$ 00.00
Year 3	$ 00.00
TOTALS	$ 300,000.00

Abstract of CRADA work:

This CRADA helped Innovalight characterize and quantify their ink-based selective emitter technology. Controlled localized doping of selective emitter structures via Innovalight Silicon Ink technology was demonstrated. Both secondary ion mass spectrometry and scanning capacitance microscopy revealed abrupt lateral dopant profiles at ink-printed boundaries. Uniform doping of iso- and pyramidal surfaces was also verified using scanning electron microscopy dopant contrast imaging.

Summary of Research Results:

Innovalight worked closely with NREL to provide experiment-specific wafers with typical dopant patterns used in their ink-based selective emitter technology to confirm their dopant profiles. The following pages are taken from a paper written for the IEEE Photovoltaic Specialists conference in June 2010. The paper summarizes the joint research done under this CRADA and contains no confidential, protectable, or proprietary information.

LOCALIZED DOPING USING SILICON INK TECHNOLOGY FOR HIGH EFFICIENCY SOLAR CELLS

K. Alberi[1], G. Scardera[2], H. Moutinho[1], R.C. Reedy[1], M.J. Romero[1], E. Rogojina[2], M. Kelman[2], D. Poplavskyy[2], D.L. Young[1], F. Lemmi[2] and H. Antoniadis[2]
[1]National Renewable Energy Laboratory, Golden, CO, USA
[2]Innovalight Inc., Sunnyvale, CA, USA

ABSTRACT

Controlled localized doping of selective emitter structures via Innovalight Silicon Ink technology is demonstrated. Both secondary ion mass spectrometry and scanning capacitance microscopy reveal abrupt lateral dopant profiles at ink-printed boundaries. Uniform doping of iso- and pyramidal surfaces is also verified using scanning electron microscopy dopant contrast imaging.

INTRODUCTION

A selective emitter is a front-contact solar cell configuration in which surface regions under the front contacts are heavily doped to improve ohmic contact, while remaining surface regions are lightly doped to minimize charge carrier recombination and improve blue light response [1-4].

Although theoretically able to achieve high conversion efficiency, in practice such gains are only realized if high localized doping is achieved on textured surfaces without also damaging charge carrier generation in the bulk Si material. In addition, even if technically feasible, in order to be commercially viable and widely implemented, the selective emitter manufacturing process must also be relatively simple, cost-effective and easily incorporated into existing production lines

In practice, selective emitter formation by conventional photolithography, laser-patterning, or etch-back techniques often fails to meet at least one of the abovementioned criteria due to high cost, difficult process control, defect formation and excessive lateral dopant diffusion, among other issues [5-8].

In contrast, implementation of the Innovalight Cougar™ Platform with Innovalight Silicon Ink allows solar cell producers to overcome these barriers. A portfolio of simple to implement technologies, the Innovalight Cougar Platform enables the manufacture of a selective emitter solar cell with a single-step non-masking diffusion. Innovalight Silicon Ink is a highly engineered silicon nanoparticle colloidal dispersion, implemented for both high volume ink-jet and screen printing deposition, and further optimized to be produced and delivered in commercial volumes. In fact, demonstration of this technology using screen printing on monocrystalline 125 x125 mm Cz-Si wafers has resulted in efficiencies as high as 19% [10]. Here we present further details on the efficacy of localized doping by Si ink and demonstrate uniform doping on textured surfaces.

EXPERIMENTAL

Lateral and depth doping profiles of the selective emitter were investigated by secondary ion mass spectrometry (SIMS) and scanning capacitance microscopy (SCM). Multiple SIMS measurements were performed at various locations spanning two fingers of a Cougar device pattern. A complete contacting pattern with fingers and busbars was printed onto a saw damage etched wafer and subjected to a diffusion process. Ink regions were stripped prior to measuring. The SIMS measurements were performed on a Cameca IMS-5F. The impact energy of the primary Cs^+ ion beam, purified by a mass filter, was 14.5 keV at an incident angle of 25° from the surface normal. The primary current was approximately 65 nA focused into a spot approximately 40 μm in diameter. Negative secondary ions generated from the sample were accelerated normal to its surface and were detected at 4.5 keV. The mass spectrometer was focused for high mass resolution to separate the ^{31}P signal from the $^{30}Si^{1}H$ mass interference. For depth profiles, secondary ions, counted by electron multiplier and Faraday cup detectors, were collected from a 60 μm diameter area in the center of a raster-scanned 150 μm x 150 μm region. For imaging, secondary ions from a 250 μm x 250 μm square area were collected minus 10% to minimize effects from the crater walls.

Localized doping was further verified by performing SCM measurements directly at the edges of Silicon Ink printed regions. Silicon Ink fingers were printed onto a polished wafer and subjected to a drive-in step. SCM measurements were performed on a Veeco Dimension 3100 microscope with Nanoscope IIIa electronics and Pt/Ir-covered Si tips. The specimen surface was not polished in order to preserve the surface doping profile. Instead, the positions of the ink lines after printing were marked with a focused ion beam, the ink was stripped, and front and back metal contacts were deposited. The sample was then heated to 300 C for 20 minutes in air, with UV exposure during the last minute, to form a uniform surface oxide. Measurements were taken at the boundary of the ink-printed regions away from the FIB marks to determine the extent of lateral dopant diffusion.

The doping uniformity on textured surfaces was evaluated by scanning electron microscopy (SEM) dopant contrast imaging, which overcomes the limitations such structures present to conventional doping analysis techniques such as SIMS and spreading resistance. Silicon Ink fingers were printed onto both random pyramid textured and iso-textured wafers and subjected to a diffusion process. Ink layers were stripped prior to imaging. Measurements were taken on an FEI NanoSEM 600 with a 2 keV electron beam and a current of 50-100 pA. The contrast between p and n-type regions was enhanced by turning off the extraction field on the through-the-lens detector.

RESULTS AND DISCUSSION

The highly localized doping achieved using Silicon Ink technology is attributed in part to its high print fidelity. Screen printed Silicon Ink fingers maintain print fidelity after selective emitter formation as shown in the optical microscope images of Fig. 1. No line bleeding is observed after drive-in. The localized doping suggested by the optical microscopy results are verified in greater detail using SIMS and SCM measurements.

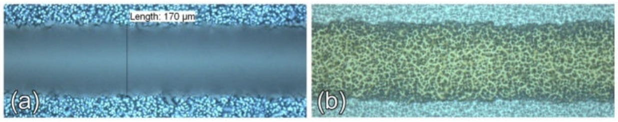

Figure 1: Optical microscope images of a Silicon Ink finger on a random pyramid textured wafer (a) after screen printing and (b) after selective emitter formation.

Depth profiles of ^{31}P in a saw damage etched wafer were measured by SIMS both on and off heavily doped ink-printed contact regions (indicated by the points in Fig. 2a) and are displayed in Fig. 2b. Consistently high surface doping is achieved within the contact regions, while the ^{31}P concentration at various locations, both close to and far away from the ink-printed regions, does not deviate.

The SIMS ^{31}P image, shown in Fig. 2c, demonstrates the transition in the doping concentration between the heavily and lightly doped regions. The lateral resolution of this measurement is limited by the beam spot size diameter (estimated to be 40 µm).

The lateral spread of ink-printed dopants after diffusion was further investigated by SCM, which is capable of sub-micron 2D carrier concentration profiling [11]. Figure 3 displays a differential capacitance image of the ink-printed line edge as well as a linescan of the signal across the boundary. The region of low signal (far left) indicates a high electron concentration coincident with the heavily doped contact region, while the higher negative signal corresponds to the lower doping level of the wafer in the "non-ink" region. Although SCM does not yield quantitative values for the doping concentration in each region, such an abrupt increase in the magnitude of the signal suggests that the P concentration decreases to that of the wafer over a lateral distance of only a few microns. Thus, on the merit of lateral dopant confinement, printed Silicon Ink appears to be far superior to other dopant pastes, where the dimensions of the doped region can increase by several hundred microns after drive-in [8].

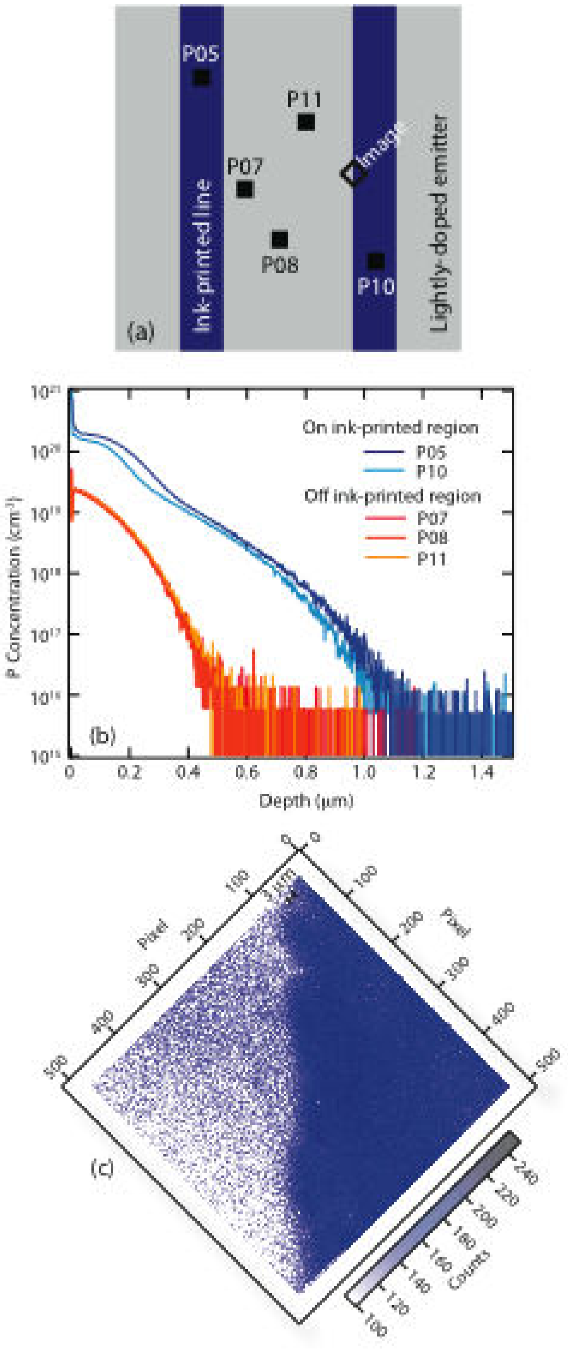

Figure 2: Phosphorous SIMS profiles of ink-printed (heavily doped) and non-ink (lightly doped emitter) regions shown in (a). (b) depth profiles and (c) ^{31}P ion image.

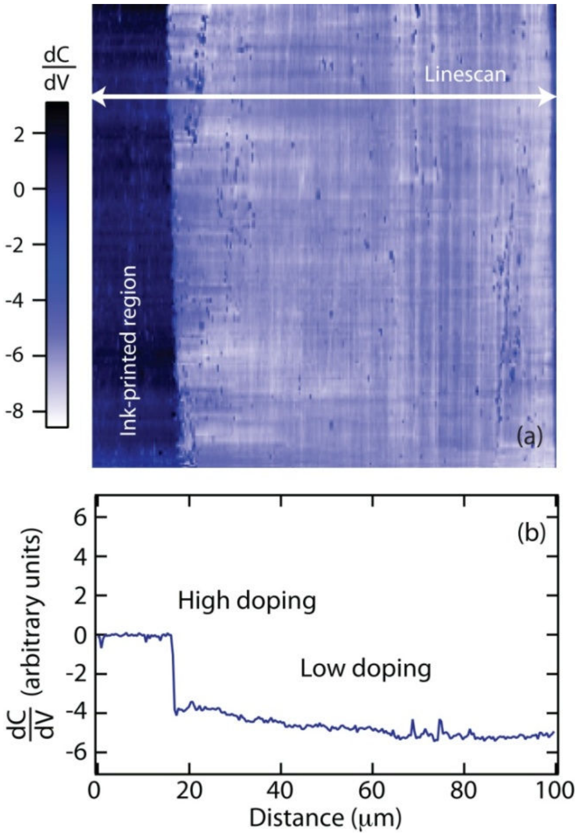

Figure 3: (a) SCM dC/dV scan of edge of ink-printed region (far left) on top of a lightly doped wafer and (b) dC/dV linescan at the position indicated in (a).

Finally, homogeneous doping via Silicon Ink is demonstrated on iso-textured and random pyramid textured wafers by cross-sectional SEM dopant contrast imaging, shown in Fig. 4. The Silicon Ink formulation has been optimized to allow uniform, conformal coverage of textured features like random pyramids thus enabling homogeneous doping. Here, the contrast between p and n-type material is driven by differences in the Columbic attraction and repulsion of secondary electrons with surface charge, resulting in a disparity in the efficiency of their collection [12]. In both instances, the dopant coverage and depth are uniform across the surface.

CONCLUSIONS

Innovalight Silicon Ink presents an industrially viable pathway for highly localized selective emitter formation. High doping is achieved while maintaining a sharp interface between printed and non-printed regions. This technology also allows for effective doping of textured surfaces.

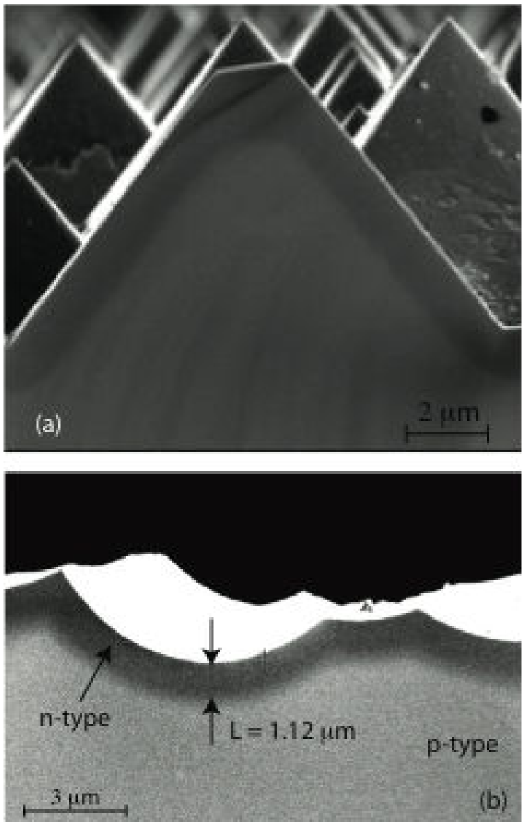

Figure 4: SEM dopant contrast micrographs of (a) pyramid and (b) iso-textured wafers showing high uniform doping from the Silicon Ink printing process

ACKNOWLEDGEMENT

The authors would like to thank Anna Duda for sample preparation help. We also acknowledge support under CRADA CRD-07-241.

REFERENCES

[1] M.M. Hilali, A. Rohatgi, B. To, “A review and understanding of screen-printed contacts and selective emitter formation”, *Proceedings of the 14th Workshop on Crystalline Silicon Solar Cells and Modules*, Winter Park, CO, USA, August 2004

[2] D.-H. Neuhaus, A. Munzer, “Industrial Silicon Wafer Solar Cells”, *Advances in OptoElectronics* 2007, pp. 1-15

[3] B. Raabe, H. Haverkamp, F. Book, A. Dastgheib-Shirazi, R. Moll, G. Hahn, “Monocrystalline silicon – future cell concepts”, *22nd EU PVSEC*, 2007

[4] D. Kray, M. Aleman, A. Fell, S. Hopman, K. Mayer, M. Mesec, R. Muller, G.P. Willeke, S.W. Glunz, B. Bitnar, 33rd IEEE PVSC, 2008

[5] M.D. Abbott, J.E. Cotter, K. Fisher, “N-type bifacial solar cells with laser doped contacts”, *32nd IEEE PVSC*, 2007

[6] A. Knorz, A. Grohe, C. Harmel, R. Preu, J. Luther, “Progress in Selective Laser Ablation of Dielectric Layers”, *22nd EU PVSEC*, 2007

[7] F. Book, B. Raabe, G. Hahn, “Two Diffusion Step Selective Emitter: Comparison of Mask Opening by Laser or Etching Paste”, 23rd EU PVSEC, 2008

[8] M. Edwards, J. Bocking, J.E. Cotter, N. Bennett, “Screen-Printed Selective Diffusions for High-Efficiency Industrial Silicon Solar Cells”, Prog. Photovolt: Res. Appl., **16**, 2008, pp. 31-45

[9] H. Antoniadis, Proc of 34th IEEE Photovoltaic Specialist Conference, 7-12 June 2009, Philadelphia, PA, USA

[10] H. Antoniadis, “All Screen Printed Mass Produced Selective Emitter Solar Cells”, presented at this conference, 2010.

[12] C.C. Williams, “Two-Dimensional Dopant Profiling by Scanning Capacitance Microscopy”, Annu. Rev. Mater. Sci., **29**, 1999, pp. 471

[11] S.L. Elliott, R.F. Broom, C.J. Humphreys, “Dopant Profiling with the Scanning Electron Microscope – A Study of Si”, J. Appl. Phys., **91**, 9116, 2002

Subject Inventions listing: None

Report Date: 2-14-2011 Responsible Technical Contact at Alliance/NREL: Dr. David L. Young

This document contains NO confidential, protectable, or proprietary information.