Direct Write Metallizations with Organometallic Inks

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Abstract

A direct write approach using an ink jet printer to deposit solar cell metallizations is an attractive alternative to current metallization technologies. This approach can produce features with better resolution while being less expensive, simpler, more reliable and more easily automated than metallization techniques currently in use today. Inks for the deposition of silver were prepared by dissolving (hfa)Ag(COD) in toluene or ethanol. These inks were spray printed onto heated glass and Si substrates in air to give smooth, pure Ag films that adhere well to the substrates. Resistivities of ~2μΩ•cm were measured for these films, which is very close to the value for bulk Ag metal. Copper films were produced in a similar manner using inks based on (hfa)Cu(VTMS) and (hfa)Cu(BTMS). These inks are amenable to deposition using an ink jet printer. A commercial EPSON ink jet printer has been programmed for this purpose.

Introduction

Metallization processes are a critical component of the electronics industry providing the interface between the devices and the outside world. Metallization refers to the process for depositing metals onto substrates to create electric circuits necessary for communication, information exchange and energy transfer. Applications requiring metallization include microelectronic packaging, circuit boards, toys, photovoltaics and virtually all other electronic circuits. For example, strong and thermally stable materials used to protect computer chips must have some conductive material connecting the inner chip to an external circuit. Metallization accomplishes this task. Direct writing is a new approach to applying metals without the use of masks or photolithography. This is becoming an attractive option compared to other techniques in use, such as screenprinting and vacuum deposition methods.

While screenprinting is well-developed and utilizes robust equipment, it is limited in resolution, only attaining lines 100 microns wide or larger (6). This limits its viability in helping to make photovoltaics a competitive option in the world energy market. In addition, screen printing must use masks that contact the surface and these need to be developed. This method cannot give conformal deposition on textured surfaces. Another method, vacuum deposition, yields high purity films with control of the deposition rate. However, it tends to have poor surface coverage on complex surfaces and requires expensive vacuum hardware.

A novel method of increasing interest is in direct writing for metallization. Here the materials are applied directly to the substrate in the desired pattern. This eliminates the use of masks, photolithography and vacuum systems. Since this is a non-contact approach, it can be conformal and with current technology can produce lines below 20µm wide. There are a number of approaches to direct writing, based on electrostatic, electrophoretic, piezoelectric or thermal printing approaches.   The direct write method of interest here is ink jet printing. This includes thermal, electrostatic and piezo-electric printing devices. Just as these commercial printers are used to print black text in everyday life, the same printer can be used to deposit metallic gridlines on semiconductor, plastic or glass substrates using organometallic inks. Since the main hindrance to commercialization for photovoltaics today is the price of production, ink jet printing provides a cheaper alternative to current methods.

While ink jet printing has the capacity to affect the manufacturing of the entire solar cell, this paper discusses ink jet printing as a method for depositing the metallic gridlines that serve as the front and back contacts of thin-film solar cells. This method has the capability to produce continuous and uniform metal patterns with high conductivity, a property depending on the thickness, width and length of the lines printed as well as the conductive material's purity and deposition temperature. The film thickness will not depend on the substrate's surface topography (10). Ink jet printing can produce these metallic gridlines at widths of 20-40 microns. Front contacts require lines as thin as possible so as to maximize the light absorbed by the semiconductor material, thereby reducing shading losses. At the same time, the back contact does not have this coverage restriction so we seek thick films for the large back area. Ink jets can produce films as thick as 20 microns.

Solar cells absorb energy from the sun and convert it into electrical energy for useful work. Extensive research continues on optimizing the range in which semiconductor material can absorb solar radiation. Once sunlight strikes the semiconductor material, the newly excited carriers flow to the front and back contacts. Electric fields generated by the doping of the semiconductor, essentially the addition of materials either with excess electrons or deficient in electrons, direct this photocurrent outward (8). While many issues arise in making this carrier flow as efficient and successful as possible, good contact metallizations are characterized by good mechanical adhesion between the metal and semiconductor interface, high metal conductivity, low contact resistance at the interface and the ease and simplicity of the deposition process.

The research for ink jet metallization encompasses the development of the deposition process and characterization of the metallic ink's structural, electrical and physical properties coupled with development of the ink jet printing device. There are three areas of consideration in developing the ink jet printing process for metallization: 1) Modification of the ink properties to correspond to the printer design, such as orifice size of the printer nozzle and viscosity of the ink; 2) Development of the deposition process and the organometallic ink concentration to attain the desired mechanical adhesion and electrical contact to the substrate and; 3) Programming of the ink jet printer to produce gridline patterns, including the ability to make repeated passes of the printhead over the same line. This research project has focused on the second area for deposition and ink development by spraying the ink directly from an airbrush as a preliminary step towards the actual deposition by the ink jet printer. We also begin to explore the third area with the programming of the printer.

In previous ink jet printing work, D.L. Schulz and T. Rivkin performed sprays of organo-metallic inks in a nitrogen glovebox with an OMEGA 2000 airbrush (1). Copper, aluminum and silver compounds were sprayed and found to yield nearly pure metal deposits in the form of continuous films, as shown by x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM).

Towards the development of an ink jet printing device, ink jet printing has been performed by another research group to apply silver gridlines to silicon solar cells (11). In this work, a silver decanoate ink was applied to silicon wafers using an ink jet printing device, and then the wafers were annealed at 300 degrees Celsius for ten minutes (10). However, devices constructed in this manner suffered from low conductivity of the metal lines and high contact resistance.

This project simultaneously seeks to use a commercial, well-established, EPSON ink jet printer to print these gridlines, spray organo-metallic inks in air without losing the purity of deposited metal and improve the ink composition to get optimal electrical properties and adhesion to the semiconductor substrate.

The optimization of the organo-metallic ink and the programming of the EPSON printer were done separately, although the compatibility of the ink's physical properties with the printer's design and material composition was kept in mind during the project's progress. These two parts of the project will be addressed separately.

Materials and Methods

Three different inks containing silver and copper were used for the development of the metal deposition process. The following two compounds were purchased from Aldrich: (hfa)Ag(COD), (hexafluoroacetylacetonato) silver(I) (1,5-cyclo-octadiene), and (hfa)Cu(BTMS), (BTMS = Bis (trimethylsilyl)-acetylene). A second copper compound, (hfa)Cu(VTMS), (VTMS = vinyl trimethyl silane), was synthesized using the literature procedure (2). (hfa)Ag(COD) and (hfa)Cu(BTMS) compounds were dissolved in toluene or ethanol at 2 molar and 1 molar concentrations, respectively. Since copper is air sensitive, (hfa)Cu(BTMS) was dissolved in toluene under a nitrogen atmosphere and then sprayed in air. Similarly, (hfa)Cu(VTMS) was synthesized and stored in air-tight test tubes. It was sprayed in small quantities so as to minimize exposure to air during spraying.

Silver and copper compounds dissolved in organic solvents were sprayed with an OMEGA 2000 airbrush under atmospheric pressure, in a chemical fume hood. (hfa)Ag(COD) was sprayed on doped Silicon or glass substrates at temperatures between 250-420 degrees Celsius. The two copper inks were sprayed at temperatures between 160-200 degrees Celsius. These temperatures served to decompose the complex and vaporize the organic solvent with the removal of the ligands, hfa, COD, BTMS and VTMS, from the ink so that only metal deposits onto the substrate. However, temperatures could not be too high that oxidation of the metal, premature decomposition or poor adhesion occurred.

After spraying, physical and electrical characterizations were used to understand the properties and quality of the sprayed samples. X-ray diffraction (XRD) identified the composition of the thin-film samples. X-ray photoelectron spectroscopy (XPS) gave the composition of the layers deposited. We used scanning electron microscopy (SEM) to produce images of the film surface, visually verifying the film's continuity and uniformity, while atomic force microscopy (AFM) yielded a quantitative result on the surface roughness. These measurements determined the purity of the deposited metal, the presence of oxides, and the film's uniformity and density, all of which impact the conductivity. Electrical characterization included measurement of the bulk metal's thickness and conductivity, the ohmicity of the metal to semiconductor interface and the contact resistance. Film thickness measurements were taken on the Dektak profilometer and the metal conductivity was measured using the Hall System or the four-point probe. After these measurements, photolithography performed on the samples creates the contact pads, 210 x 210 microns each, etching away the silver film except for the pad areas to leave the substrate exposed. Photolithography was an intermediate step necessary for the measurement of the contact resistance in the process for deposition development. It won't be needed for the actual metallization with the ink jet printer. We used a curve tracer to determine whether the contact is ohmic, a necessary quality representing linearity between the current and voltage applied to the samples' metallic contact pads. When two different materials come into contact, the interface is ohmic if the current passing through it is proportional to the voltage drop across the interface. The samples were tested for contact resistivity by recording voltage measurements for current in the milliamperage range and plotting these values to get the best fit line in a graphing program, Delta Graph. A program based on the transmission line method, TLM & ERM developed by Tim Gessert (4), used the input data of slope and y-intercept from the graph results to calculate the contact resistivity measurements.

The piezo-electric printer was purchased from EPSON, hooked up to LPT1 port and connected to a Gateway 2000 desktop computer. The EPSON Stylus Color 740 has a 24 /48-pin printhead and reaches resolutions up to 720 by 720 dpi. The EPSON ink jet printer prints nanoparticles in a range from 50-100 nanometers (7). ESC/P2 is the EPSON printer command language. These commands for the printer were obtained from the EPSON technical web page (3). The software LabVIEW for Windows 95 was used for typing the command code and sending the code to the printer.

Results

Silver Ink

The silver organometallic ink were sprayed in air under atmospheric pressure and yielded a continuous and nearly pure silver film for spray temperatures between 300-500 degrees Celsius. X-ray diffraction verified that the film is silver, without the presence of silver oxide (Figure 1). The XRD peaks of our samples correspond to the established peaks for silver. X-ray photoelectron spectroscopy showed that oxygen and fluorine were only present on the film surface, absent before reaching a film depth of 0.0025 microns and carbon's presence dropped rapidly with increasing depth into the film (Figure 2). Additional examination under the scanning electron microscope showed the surface topography of the sprayed samples was continuous (Figures 3). The fact that the film's conductivity approaches that of bulk silver also verified that the impurities are minimal and the deposition led to a good contact.

The silver ink sprayed with toluene adhered well to the silicon substrate upon testing with tape. However, substitution of ethanol for the organic solvent failed the tape test two out of three experiments.

Thickness measurements of the deposited film ranged from 0.150 to 5.80 microns depending on the quantity of ink sprayed, the spray radius of the air brush, the temperature, the size of the substrate sample and the proximity of the spray brush to the substrate surface. We found that instrumentation limitations required that the thickness be at least 0.150 microns to get accurate metal and contact resistivity measurements.

Silver metal bulk resistivities on the order of 10^{-6} ohm-cm were attained (Table 1.). Silver has a reported bulk resistivity of 1.98e+10 $^{-6}$ ohm-cm (1).

Initial measurements indicated that we did not have ohmic contact. We tested two possibilities for improving the ohmic contact: annealing and the addition of glass frits. Annealing promotes penetration of silver into the silicon oxide layer that forms on the silicon surface (11). Glass frits have been tested in the silver slurry used in screenprinting for improving the interface contact. Glass frits are composed of silicon, oxygen, lead, boron and aluminum, of different concentrations (6). Their exact role in the contact between the semiconductor and metal contact is not well known. It is proposed that the frits facilitate the adhesion between the deposited metal and the silicon oxide present on the silicon surface after being exposed to air, serving the dual purpose for mechanical adhesion as well as improving the ohmic contact. While it was not difficult to include the frits in the ink deposition process, more experiments need to be done to see if an ohmic contact is reached after annealing near the melting point of the glass frits.

In testing various annealing temperatures between 650 to 820 degrees Celsius, we discovered how the surface behaved with changes in temperature. At high temperatures, compound light microscope observations at 1000x showed that a silver film of thickness 0.3990 microns became discontinuous. The silver appeared web-like on the silicon surface after annealing at 820 and 746 degrees Celsius for five minutes. However, at a lower temperature of 650 degrees Celsius, the film was continuous as observed at magnification 1000x. Continuity in the metallic film is essential for carrier transport from the semiconductor through the metal film to an external circuit. Samples from this same spraying, before annealing and after annealing at temperatures of 820, 746 and 650 degrees Celsius, were placed under the four-point probe attached to an oscilloscope to test for an ohmic contact. The curves were not linear but the contact barrier did have a noticeable decline for the samples annealed at higher temperatures. Annealing of the silver samples at higher temperatures seemed to increase the ohmic contact but the films need to be sprayed thicker in order to prevent the discontinuity observed under the microscope.

Ink Jet

After learning the arrangement of LabVIEW with simple codes such as paper advance and paper eject and ensuring that communication was being sent between the computer and the printer LPT1 port, we began programming vertical and horizontal lines which eventually will become the gridline pattern for the solar cell contacts. The EPSON ESC P/2 codes manual lists the commands in ASCII format. Computer language is in binary numbers, series of 1 and 0.

However, one would get lost programming in this "dinumeric" format. Instead, binary numbers are grouped into bytes, 8 binary numbers = 1 byte. In addition, two other numeric systems, decimal and hexadecimal values, were utilized in the programming process. The combination of these three numeric systems allowed us to use LabVIEW to program the printer to print lines of varying thickness, length, width and spacing to design, essentially, any straight gridline pattern. We were able to make infinitely many repeated passes, in the process for obtaining a line thickness of 20 microns. Once these tests were possible using standard black ink, we placed (hfa)Ag(COD) at 1 molar concentration in ethanol into an emptied and cleaned ink cartridge. The ink was printed in the programmed designs from LabVIEW onto high temperature resistant transparencies and plastic. Now that we have accomplished the printer programming, the next stage will be to control how the organometallic ink strikes and behaves upon contacting the substrate surface. Also, we will need to find a method for heating the substrate either during or immediately after the printing process.

Copper Ink

The copper compound, (hfa)Cu(BTMS), dissolved in toluene, was sprayed first at 400 degrees Celsius. X-ray diffraction measurements are inconclusive as to the exact composition of the deposited film, whether copper, copper oxide or some combination thereof exists. A second copper compound, (hfa)Cu(VTMS), was synthesized in-house and since it was sprayed under the nitrogen atmosphere previously at 200 degrees Celsius (1), we sprayed it at temperatures of 160 and 200 degrees Celsius.

Both copper compounds passed the tape test for mechanical adhesion. Profilometry measurements ranged from 0.62 to 3 microns thick on glass and 8.3 to 11.8 microns for n-doped silicon. Film resistivity measurements were not successful, suggesting that the material deposited had oxides or other impurities which prevent current flow through the film. Since additional experiments are needed to optimize the spray temperature to get pure copper deposited, ohmic contact and contact resistance measurements have not yet been taken.

Future Directions

The next pursuit may be in the addition of phosphorous or boron compounds in the ink. These elements would add a source of doping directly beneath the metal contacts, eliminating the need for highly doped silicon over the entire solar cell surface area. By avoiding high doping concentrations on the entire semiconductor surface, silicon's wide absorbance range of the solar spectrum would be fully utilized since the photons would strike the silicon directly, no longer being inhibited by other elements in the area between gridlines. The phosphorous and boron additions are also likely to improve ohmic contact and lower contact resistance.

In addition to pursuing an ohmic contact, a thicker film should be deposited. Thermal expansion and temperature gradients should be considered, since a thicker film will be deposited at a greater distance from the heater than with films less than six microns.

Ink Jet

With EPSON's escape code commands, ESC P/2 commands, the printer must be programmed to perform repeated line printing to reach the thickness goal of 20 microns. Then it will be necessary to determine if the printer can incorporate a heater, if it can withstand our lowest spray temperature, or whether an automated system will be developed to send the substrate to be heated between the film layering process, i.e. printhead passes over the substrate multiple times before the sample is heated nearby and returned for more ink layers. It will be necessary to explore the film's purity after annealing to see how well the ink's organic ligands detach from the silver metal to attain a highly conductive metallic film.

Copper Ink

Since copper oxidizes more easily in air than silver, we need to continue developing the variables for spray deposition, including experimentation with other copper ink formulations, substrate temperature during spraying and possibly spraying under the nitrogen atmosphere.

Conclusions

This project sheds light on the extensive possibilities for producing less expensive, continuous and uniform metal contacts for solar cells and other applications. Ink jet printing serves as an alternative to current techniques of screenprinting and vacuum deposition of the metal contacts. Direct spraying of the ink would nullify the need for masks and conserve materials. This research project has focused on the deposition and ink development by spraying the ink directly from an airbrush as a preliminary step towards the actual deposition by the ink jet printer. Programming the printer with complex commands was accomplished and (hfa)Ag(COD) at 1 molar concentration in ethanol was printed onto transparencies and high temperature resistant plastic. We developed a deposition process of spraying in air at atmospheric pressure, without the need for vacuum hardware and these depositions produced continuous and uniform silver films. While the copper film is still in the initial stages for finding a set of deposition parameters, the silver film approaches the conductivity of bulk silver and adheres to the silicon substrate when deposited in toluene.

Tables and Figures

Figures 1 and 2: Silver film deposited onto glass at 400 degrees Celsius.

Figure 1: **X-ray Diffraction (XRD) for Identification**

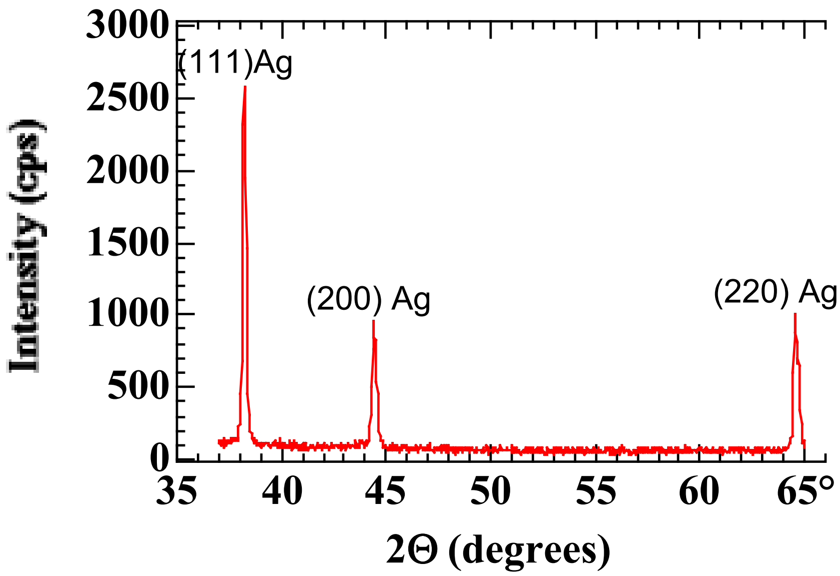
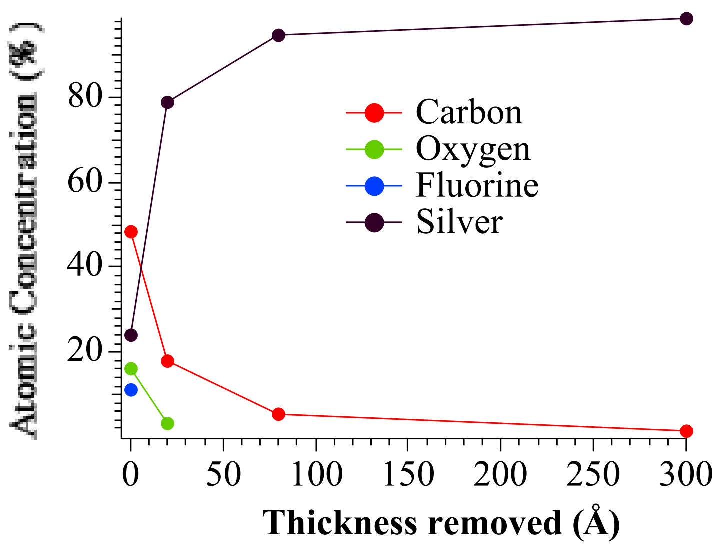


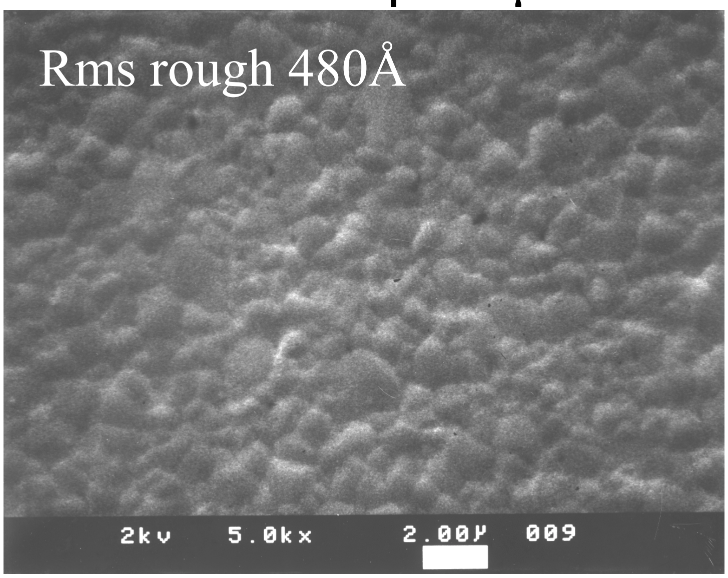
Figure 2: **X-ray Photoelectron Spectroscopy (XPS) for Composition**



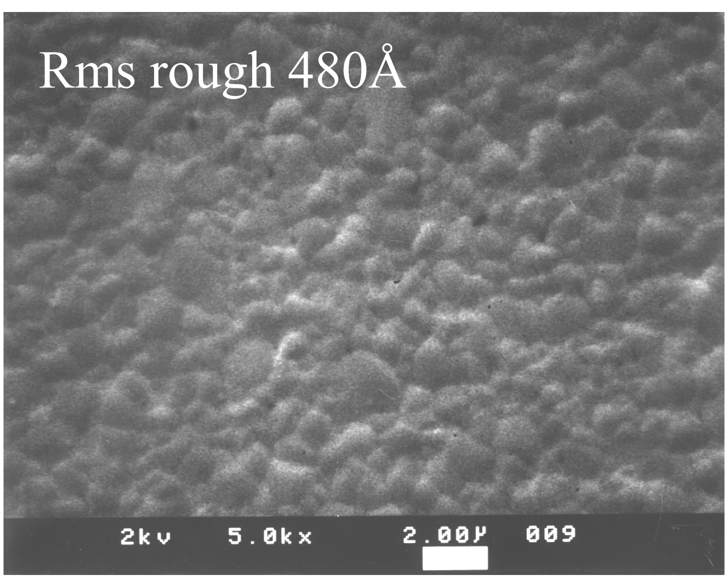
Tables and Figures continued

Figure 3: Scanning electron microscopy (SEM) shows surface morphology of silver deposited films on glass and silicon substrates at deposition temperature 400 degrees Celsius and toluene as spray solvent. Atomic force microscopy (AFM) describes the surface roughness quantitatively. Film resistance is also stated in μΩ · cm, obtained from the Hall System.

Ag on glass **$\rho \sim 2\ \mu\Omega \cdot cm$**



Ag on Silicon **$\rho \sim 2\ \mu\Omega \cdot cm$**



Tables and Figures continued

Table 1: Characterization results of the resistivity of silver deposited films for different spray deposition parameters.

Ink	Solvent	Spray Temp.	Metal Bulk Resistance	Metal Sheet Resistivity
(hfa)Ag(COD)	Ethanol	370 C	5.08 e-06 Ω-cm	0.2640 Ω/sq
(hfa)Ag(COD)	Ethanol	350 C	5.90 e-06 Ω-cm	0.0868 Ω/sq
(hfa)Ag(COD)	Toluene	420 C	2.38 e-06 Ω-cm	0.0394 Ω/sq
(hfa)Ag(COD)	Toluene	350 C	1.88 e-06 Ω-cm	0.0472 Ω/sq
(hfa)Ag(COD)	Toluene	240 C	1.21 e-06 Ω-cm	0.0021 Ω/sq

Literature Cited

1. Curtis, C.J.; Miedaner, A.; Rivkin, T.; Alleman, J.; Schulz, D.L. and Ginley, D.S. *Direct Write Metallizations for Ag and Al.* 2000: NREL.

2. Doyle, G.; Eriksen, K.A.; Van Engen, D. *Organometallics*. (4) 1985: p. 830.

3. EPSON ESP/2 command codes for printers: www.epson.co.uk/support/manuals/select/escp.htm. *EPSON ESC/P Reference Manual.* SEIKO EPSON Corporation. Nagano, Japan: 1997.

4. Gessert, Tim and Wu, Xuanzhi. *Measurement of Contact Resistivity, working report*.

5. Moller, Hans Joachim. Semiconductors for Solar Cells. Artech House, Inc. Massachusetts: 1993.

6. Nihs, J. et al. *Recent Improvements in the screenprinting technology and comparison with the buried contact technology by 2D-simulation*. Solar Energy Materials and Solar Cells. (41/42) 1996: pp. 101-117.

7. *PC Technology Guide, The*. http://www.pctechguide.com/13inkjets.htm. 16 October 1999.

8. Stone, J.L. Photovoltaics: *Unlimited Electrical Energy from the Sun.* Physics Today. September 1993: pp 22-29.

9. Sze, S.M. Physics of Semiconductor Devices. 2nd Ed. New York: John Wiley & Sons, 1981.

10. Teng, K.F. and Vest, Robert W. *Liquid Ink Jet Printing with MOD Inks for Hybrid Microcircuits.* IEEE Transactions on Components, Hybrids and Manufacturing Technology. 12(4). December 1987.

11. Teng, K.F. and Vest, Robert W. *Metallization of Solar Cells with Ink Jet Printing and Silver Metallo-Organic Inks.* IEEE Transactions on Components, Hybrids and Manufacturing Technology. 11(3). September 1988.

12. Teng, K.F. *Thick Film Ink Jet Printing, a final report*. 15 February 1988.

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