Rheological Optimization and Stability Study of Silver Nano-Ink for InkJet Printing of Solar Electrodes Using Industrial Printhead

Ravi Shankar*, A. Amert, Jon J. Kellar, and Keith W. Whites

South Dakota School of Mines and Technology
501 E. St. Joseph Street, Rapid City, SD 57701
*ravi.shankar@mines.sdsmt.edu

ABSTRACT

We have demonstrated the capability of printing silver electrodes for solar cells having line width below 100 µm using inkjet printing. To achieve this, we have produced silver nanoparticles using the polyol synthesis and have tailored the ink formulation by choosing a solvent mixture to meet the rheological requirements of industrial printheads. A solvent mixture that can suspend the ligand capped silver nanoparticle was developed while maintaining the necessary rheology. A desktop R&D printer, the LP50 developed by Pix-Dro, has been used for the jetting optimization for the printhead used here. Statistical analysis of the jetting process was conducted using printer integrated software. Typical printing parameters such as greyscale, DPI variation and substrate heating were optimized to achieve high print quality. Tests of the dispersion showed that there was no sedimentation for more than a month. Solar collector network prototypes were successfully printed on silicon and ITO substrates.

Keywords: silver nano-ink, solar cell electrodes, inkjet printing, conductive ink.

1 INTRODUCTION

Global interest in renewable sources of energy has motivated technological advancement in solar energy harvesting. Solar cells are the front runner among the photovoltaic devices and continuous efforts are being made to improve the efficiency and cost effectiveness [1]. Silicon based solar cells are already showing promise but further innovation is required to compete with traditional energy suppliers [2]. A solar panel usually consist of an array of small cells connected together where the electricity generated in individual cells is collected and transported out with a conductive grid known as a solar collector network. Screen printing has been widely used to print these solar collector networks, which is a direct contact process [1, 2]. However, due to the brittleness of silicon wafers, wafer waste during the production is usually high which increases the production cost. Also, wider and thicker lines produced by screen printing cause shadowing effects and reduces the available surface area for photon absorption and thus decrease conversion efficiency. Inkjet printing, a non-contact technique, is a versatile alternative for printing high resolution thin, conductive patterns on brittle substrates, which mininizes both wafer and material waste. However, inkjet printing requires specifically designed inks. The rheological requirement of inks greatly depend on the specific printhead in use. Inks available in the market are typically a suspension of nanoparticles in a solvent media, which needs further modification to be able to print using a specific inkjet printhead.

Considering the increasing popularity of inkjet in solar applications and flexible electronics, readily available ink suited for specific industrial printhead is highly desired. Also, the cost associated with the industrial inkjet printhead is typcally high, and improper ink formulation can cause clogging or permanent damage to the printhead. Accordingly, stable inks with proper rheology are absolutely required. We see the major challenges of ink fromulation using metallic nanoparticles for inkjet as:

- Rheological compatibility of ink and printhead
- Stability of jetting
- Stability of ink over time
- Optimization of printing parameters to achieve fine line resolution

In this study, we present a silver nanoparticle based conductive ink that has been optimized specifically for the XAAR 1001FF industrial printhead and other related printheads having similar rheological requirement. The polymer capped silver nanoparticle were dispersed in a rheologically optimized solvent media to achive stable jetting with an industrially adaptable inkjet platform.

2 INK FORMULATION

Wet chemistry based approaches for nanoparticles synthesis which includes methods like polyol process, micro-emulsion synthesis, and various one phase or two phase controlled reduction processes has been widely reported [3-6]. Due to the high conductivity and inertness of silver, we chose silver nanomaterial as the base of the ink. We used a modified polyol process to synthesize nanoparticles which yields PVP (PolyVinyl Pyrrolidone) capped silver nanoparticles [4, 6].

2.1 Experimental

In polyol synthesis, a precursor solution intially forms small nuclei or seeds which later grow into nanocrystals.

PVP capped silver nanoparticles with a size range of ~30nm to 80nm were synthesized in the ethylene glycol media using a polyol process. $AgNO_3$ (99%, Sigma-Aldrich) was used as the silver precusor salt, and both PVP (MW-55,000, Sigma Aldrich) and Ethylene Glycol (99+%, Acros organics) were used as reducing media and solvent. PVP was also used as the capping agent for the nanoparticles formed during the process. The molar ratio of PVP:$AgNO_3$ was held at 5:1. Two solutions were prepared separately, first by dissolving $AgNO_3$ in ethylene glycol and second by dissolving PVP in ethylene glycol. The PVP solution was heated at 140°C to dissolve PVP completely until it formed a clear solution. The $AgNO_3$ solution was then added dropwise to the PVP solution and the mixture was stirred for 50 minutes. The reaction was quenched after 50 minutes by transfering it into a cold water bath. Later, particles were separated by using an ultracentrifuge at 8000 rpm for 6 hours. Particles (in a pellet form) were washed with DI water and dried in air.

For conductive ink formulation, the obtained PVP capped silver nanoparticles were dispersed in a 70-30 solvent mixture of ethylene glycol and 2-butoxy ethanol. The dispersion was then subjected to sonication for 3 hours to break up agglomerates. The solution was then filtered using a 1.6 micron syringe filter. This filtered ink was used to print conductive patterns and solar prototypes using a desktop R&D inkjet printer LP50 from PixDro (OTB Solar) without further processing. A XAAR1001FF industrial printhead was used for printing which consist of 1000 nozzles. A drop-view camera attached with the inkjet platform allowed for droplet optimization during the jetting process and a print-view camera allowed the analysis of printed patterns closely.

The size and shape of the synthesized PVP capped silver nanoparticles were observed by scanning electron microscope (SEM, Zeiss Supra 25) and transmission electron microscope (TEM, Hitachi H-7000 FA). The rheological measurements for viscosity were carried out using a Bohlin CVO rheometer with a parallel plate (40 mm diameter) geometry and with a gap of 150 µm. A Kruss 100 tensiomenter was used to measure the surface tension using a Wilhelmy plate method.

3 RESULTS AND DISCUSSION

Ink formulation for inkjet printing process typically requires particle diameters below 100 nm. Due to this requirement, in our synthesis, PVP capped silver nanoparticle was synthesized using a modified polyol process [7] which yield particles in the size range of ~30-80nm. Such size distribution helps in achieving better packing of particles during sintering [8, 9]. Also, it has been reported that the sintering temperature decreases as the particle size decreases [10]. The SEM and TEM images (Figure 1) show that the particles are roughly spherical. The electron diffraction pattern shows the atomic crystal structure representing rings for various crystal planes corresponding to the silver lattice.

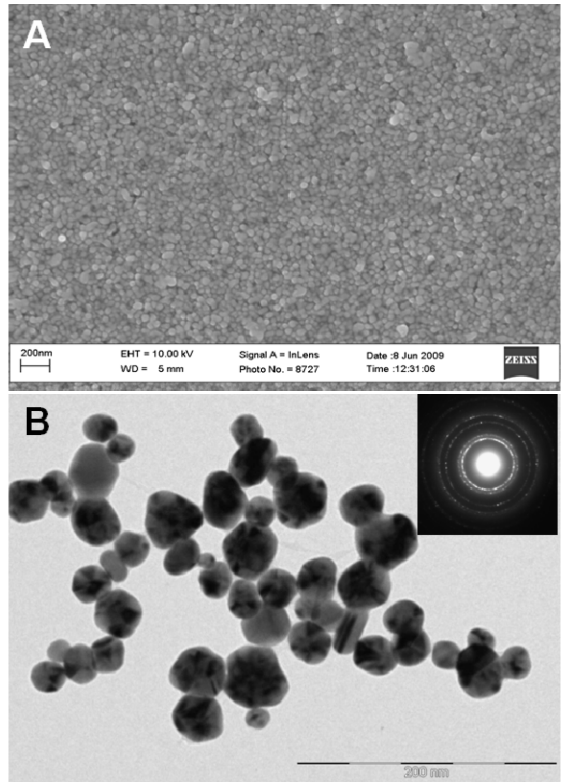

Figure 1. A) SEM image and B) TEM image of PVP capped silver nanoparticles. (Inset) Electron Diffraction pattern of silver nanoparticles showing respective crystal planes ([111], [200], [311] and [222]).

Generally, it is difficult to prepare a very stable dispersion of metal nanoparticles in a solvent due to the high density and extremely high surface energy at the particles. Accordingly, we prepared the nanoparticles with a capping agent on the surface. The capping agent not only protects from surface oxidation and agglomeration but it also act as a dispersant. PVP binds on the silver nanoparticle surface and allows the capped silver nanoparticles to disperse very easily in many polar solvents. The choice of solvent for ink formulation is important and particles that can be dispersed in a broad range of solvents allow for easier ink formulation.

Viscosity and surface tension are two important parameters for controlling the jetting of ink. Rheological measurements for many solvents were performed to meet the requirement of the printhead while maintaining the particle dispersion ability. In addition to rheology and particle dispersion ability we also considered the boiling point of the solvent. Highly volatile solvents were avoided to avoid drying of the ink on the nozzles, which can cause clogging. Selected solvents were then studied for their jetting behavior using the LP50 printer with XAAR 1001FF printheads [11].

3.1 Solvent Selection for Stable Jetting

Built-in software to the LP50 was used to study the droplet stability and other jetting related parameters. Using this software, images were captured using a drop-view camera (attached in Pix-Dro LP50 printer) during jetting. The drop formation and stability of drops can be closely watched using this camera as seen in Figure 2.

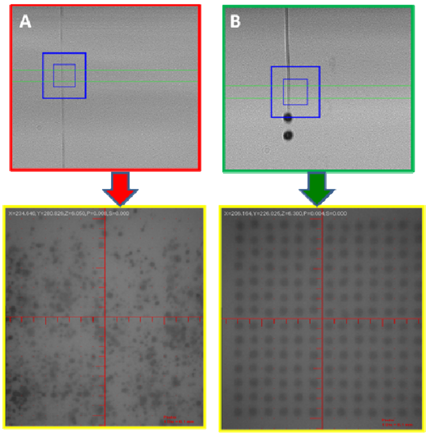

Figure 2. A) An image captured with the drop-view camera shows that the low viscosity fluid cause a continuous flow of fluid through the nozzles and result in a random spray of material on the substrate. B) A drop-view camera image showing droplet formation with optimal viscosity which results in precise drop placement on the substrate.

We performed the jetting experiment with solvents like water, ethanol, ethylene glycol, and diethylene glycol. As we see in the Figure 2, lower viscosity solvents like water or ethanol cause continuous flow from the printhead nozzles and cause random spraying on to the substrate. However, higher viscosity fluids like ethylene glycol or diethylene glycol form droplets and allow placement of droplets precisely on to the substrate. Once jetting was achieved, we next studied the repeatability of the jetting process by turning a nozzle on and off repeatedly. Figure 3 shows the difference between stable and intermittently stable droplet formation.

Intermittantly stable droplets can affect the quality of inkjet printing, we optimized the viscosity as well as the surface tension so that we obtain very stable droplets. To find a solvent base with optimal rheology, we characterized binary mixtures of water-ethylene glycol, water-diethylene glycol and ethylene glycol-2-butoxyethanol (Figure 4a and b). These solvent mixtures showed good solubility for the PVP capped silver nanoparticles for ink formulation. Viscosity and surface tension was measured for these mixtures with varying compositions. Based on our study, it was found that a 70-30 mixture of EG-2-butoxyethanol provided the most stable droplet formation. We also verified the droplet stability by running 40 steps of repeated jetting (Figure 4c). With this in mind, a 70%-30% solvent mixture was selected for ink formulation with varying weight% of PVP capped silver nanoparticles.

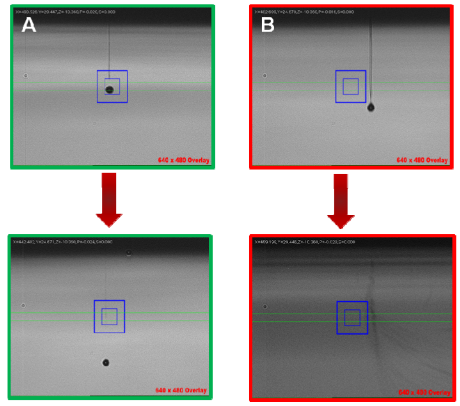

Figure 3. A) An image captured with the drop-view camera showing repeatability in stable droplet formation. B) An image showing intermittant stability in droplet formation.

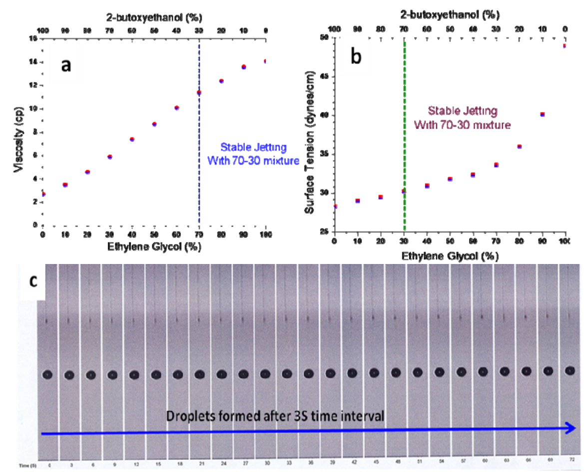

Figure 4. a) and b) shows the plots of variation in viscosity and surface tension in ethylene glycol-2-butoxyethanol solvent mixture. Dashed line represents the composition for the stable drop formation during inkjet printing. c) Droplet stability study shows uniform and stable droplet formation after succesive 3 second time interval.

3.2 Ink Dispersion Stability

To test the stability of dispersed particles in the ink, we designed an experiment. For this, an ink specimen with 20wt% silver nanoparticle loading was prepared and kept undisturbed. A fixed volume of ink was taken from the ink specimen and was transferred to a pre-weighed aluminum dish. The sample was dried in the oven at a fixed temperature to remove the solvent. The weight of dried particles was measured. The process was repeated many times with samples taken out over a period of 30 days. Any decrease in the weight of solute over a long time period indicates that the ink formulation is precipitating and is not stable. However, we found that the ink formulation using the PVP capped silver nanoparticles in 70-30 solvent mixture of Ethylene Glycol and 2-Butoxyethanol is stable and shows no sign of sedimentation (Figure 5).

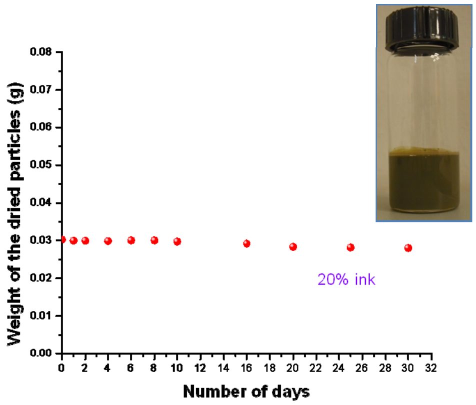

Figure 5. The plot shows the a linear variation for a period of over 30 days for the silver nano ink. (inset) A silver nano-ink specimen.

3.3 InkJet Printing

After having met the requirements for high quality droplet formation and ink stability, we optimized the printing process by varying the droplet size, DPI (droplet per inch), greyscale, and substrate heating. A multiple pass printing approach was adopted to achieve sharp edge definition as well as to increase the thickness of the printed pattern. Using greyscale 2 and 360 dpi at 100°C of substrate heating, we successfully printed conductive patterns having line widths of ~75 µm. Figure 6 shows a solar collector network prototype printed on a silicon wafer. The printed pattern was later sintered at 400°C for 4 hours.

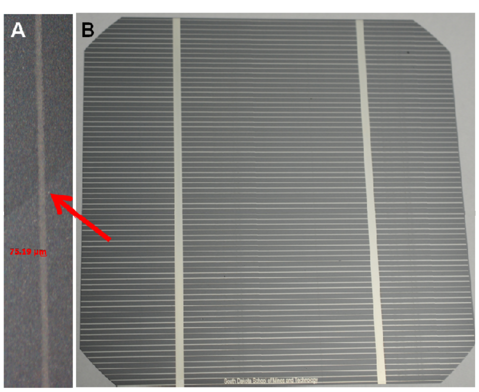

Figure 6. A) An inkjet printed conductive pattern with line width ~75 µ. B) An inkjet printed solar collector network on silicon wafer.

4 SUMMARY

We have developed a conductive ink formulation to meet the rheological requirement of the industrial XAAR 1001FF printhead. Rheological optimization was done to achieve a viscosity of ~12 cPs and surface tension ~33-35 mN/m which showed stable jetting through the printhead nozzles. A 70%-30% solvent mixture of ethylene glycol and 2-butoxyethanol was chosen as the solvent base. The as- prepared nanoparticle dispersion in ink was found very stable and showed no sedimentation over a period of more than 30 days. Inkjet printing parameters were optimized to achive conductive patterns with line widths of ~ 75 µm.

ACKNOWLEDGEMENT

This study was supported by a grant frm the National Science Foundation (NSF)/EPSCoR grant # EPS- 0903804.

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