Ambient Temperature Synthesis and Sintering of Conductive Aqueous Copper Inks

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ABSTRACT

Conducting films are becoming increasingly important for the printed electronics industry with applications in various technologies including antennas, RFID tags, photovoltaics, flexible electronics and displays. To date, expensive noble metals have been utilized in these conductive films, which ultimately increases the cost. In the present work, more economically viable copper based conducting films have been developed for both glass and flexible PET substrates, using copper and copper oxide nanoparticles. The copper nanoparticles (with copper (I) oxide impurity) are synthesized by using a simple copper reduction method in the presence of Tergitol as a capping agent. Various factors such as solvent, pH and reductant concentration have been explored in detail and optimized in order to produce a nanoparticle ink at room temperature. Secondly, the ink obtained was used to fabricate conducting films by intense pulse light sintering (IPL) of the deposited films. These conducting films had sheet resistances (R_s) as low as 0.12 Ω/□.

Keywords: intense pulsed light, printed electronics, copper

1 INTRODUCTION

The direct printing of conductive materials has garnered a fair share of interest from researchers and industry in the past few years. The advantages primarily stem from a cost savings over traditional techniques such as vacuum deposition and photolithography. The reduction in costs are reflected by large area scalability, efficient materials usage, reduced energy processes and the availability of existing manufacturing capacity. The ability to process onto polymeric substrates using roll-to-roll manufacturing further improves the economics and opens up new opportunities. The conductive ink market is expected to exceed $3B in the next few years in a wide array of end point uses including antennas, RFID tags, photovoltaics, flexible electronics and displays. As an example, the photovoltaic industry is expected to become a major consumer of silver for conductive current collectors that are typically deposited using screen printing techniques and sintered using thermal processing.[1]

Solution phase inks and pastes for the direct printing of conductive lines are typically composed of metallic particles (spherical, flake and wires and may include dimensions less than 100 nm) suspended in an organic solvent or binder. Silver in the form of flakes is the most predominant material used in the direct printing of conductive lines. There have been a number of applications utilizing silver nanoparticles (NP)s in inkjet formulations and sintering using lower temperature methods such as inert gas plasmas[2-3], microwaves[4] and intense pulsed light (IPL)[5-6]. These inks and processes reduce the overall cost of devices and have gained some advantage in the flexible electronics industry but nevertheless still rely on a relatively expensive material.

Inexpensive materials such as copper (Cu) that utilize the lower temperature sintering processes above would further reduce the costs associated with conductive patterns. Cu and silver have very similar electrical conductivity; however, Cu is significantly less expensive. Despite this, silver is commonly used in printed electronics primarily due to its stability in air. Cu tends to rapidly oxidize under ambient conditions, which significantly reduces conductivity and higher processing temperatures to sinter.[7] To overcome these shortcomings, Cu inks have been developed utilizing reducing capping agents on pure Cu NPs in order to produce conductive patterns at temperatures between 200°C and 320°C[8-9] and using inert gas plasmas.[10] However, these inks rely on pure Cu NPs using relatively complex processes that inevitably add cost.

IPL sintering is one technique that has been used to sinter pure Cu NPs dispersed in an ink formulation.[11] A fast flash, approximately a millisecond in duration, from a Xenon lamp is used to emit incoherent pulses of light from the UV to IR region. The NPs absorb the light, resulting in a localized temperature rise at the surface that can sinter the particle to its neighbors. The outcome of the extremely short pulse time is process having very fast kinetics and as a result sintering can occur without oxidation.[11-12] To date, the Cu inks used with IPL sintering have been produced using commercially available Cu NPs. These particles are commonly created by an energy intensive process that includes the resistive heating of the metal precursor followed by vapor condensation, to produce spherical NPs.

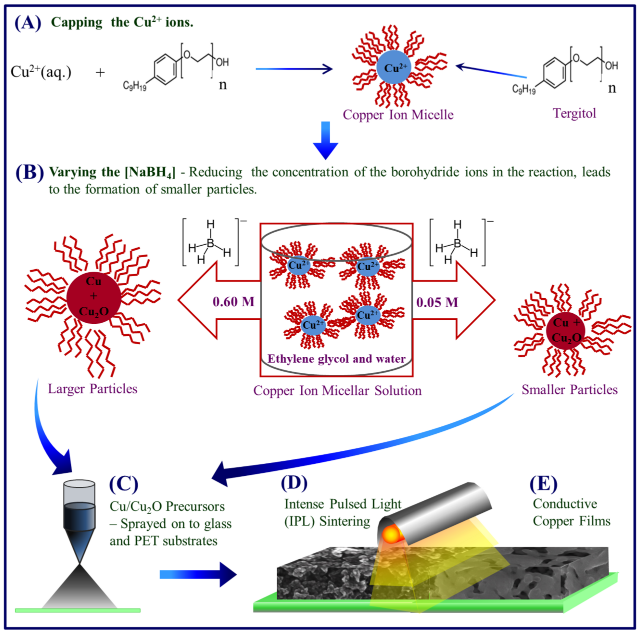

Figure 1. Schematic representation of the synthetic route for the fabrication of the copper nanoparticulate inks and the IPL sintering of the ink films to produce conductive copper films.

This work includes both a water-borne synthesis of a nanoparticle (NP) ink and a low temperature sintering technique shown schematically in Figure 1.[13] The initial work focused on the optimization of the NP synthesis yielding a degree of control over the particle size and oxide concentration using sodium borohydride ($NaBH_4$). TEM micrographs of the Cu NP ink obtained using 0.05 M and 0.6 M $NaBH_4$ show the formation of particles with diameters ranging from 10-15 nm and 100-120 nm respectively. These inks were sprayed onto a substrate using an air assisted micro-sprayer and after solvent evaporation resulted in a nanoparticulate film of mixed Cu and Cu oxides. This film was processed using IPL to both sinter neighboring particles and reduce the surface oxides producing a conductive Cu thin film.

2 RESULTS

The original assumption was that inks with a high percentage of Cu would produce Cu films with the lowest sheet resistance. The optimization of the mixture of NPs for the fabrication of conductive coatings was done by varying three synthetic conditions as follows: 1) the solvent system, (2) the pH of the reaction and (3) the concentration of the reducing agent, $NaBH_4$, used in the reaction. Aqueous inks are desirable as a low cost and environmentally friendly solution and the synthesis of the NP ink was accomplished by dissolving a $Cu(NO_3)_2$ into water creating Cu^{2+} ions in solution.

The use of water as the solvent causes oxidation of the Cu and necessitates the addition of a co-solvent to minimize the formation of Cu oxides. Earlier reports on the synthesis of micron sized nickel particles in non-aqueous solvents showed that ethylene glycol is a very good solvent for obtaining oxide-free metal nanostructures.[14] Subsequently, ethylene glycol was added to the reaction to reduce the formation of oxides while increasing the Cu yield. The overall concentration of reagents was kept the same. At pH of 11, in the presence of ethylene glycol a mixture of Cu and Cu_2O was obtained (Figure 2c) at a ratio of approximately 3:1. The increase in the yield of Cu in the ink suggests a reducing environment was generated by the presence of the ethylene glycol co-solvent.

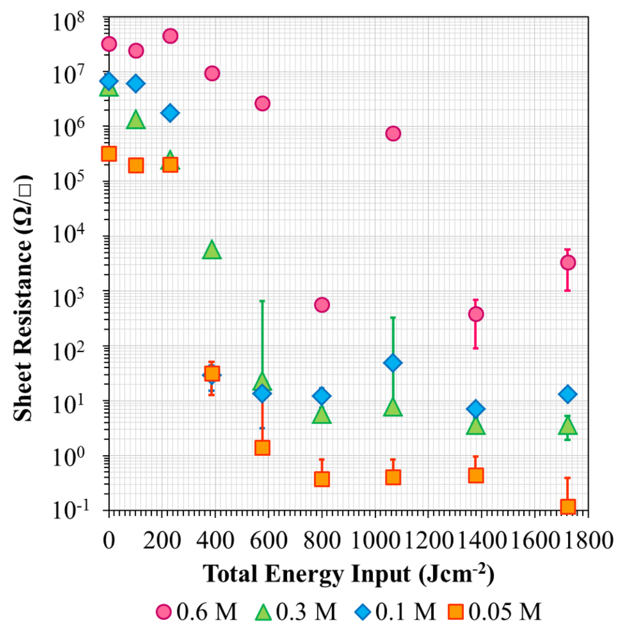

Figure 2. Sheet resistance vs. total energy input during the IPL treatment. The films were fabricated from the 0.6, 0.3, 0.1 and 0.05 M $NaBH_4$ inks. The error bars were calculated using the standard error.

Figure 2 shows the R_s of the Cu/Cu_2O films deposited from the 0.05, 0.1, 0.3 and 0.6 M $NaBH_4$ inks with varying energy inputs. The total energy input was changed by increasing the energy densities (ED) of the pulses. Films deposited from the ink obtained using 0.6 M $NaBH_4$ displayed R_s's greater than 100 Ω/□, even after a total energy input of 1723 Jcm^{-2} was applied to the film, using pulses with a maximum ED of 34.5 Jcm^{-2}. In contrast, under similar conditions, the films deposited from the 0.3, 0.1 and 0.05 M inks, produced R_s's lower than 10 Ω/□. These films also display an inflection point at a total energy input of ~350 Jcm^{-2}, where the R_s changes from MΩ/□, to less than 100 Ω/□. This indicates that pulses with a minimum ED of 15.5 - 19.0 Jcm^{-2} are required to reduce and sinter the Cu/Cu_2O films. The lowest sheet resistance of 0.118 Ω/□ was obtained from the 0.05 M ink, after 1723 Jcm^{-2} was applied to the film. It should be noted that the films are deposited over a wide area (10 cm^2) as we are trying to demonstrate a bulk Cu film technique. The bulk resistivity can be found by the product of the sheet resistance and the film thickness ($r=t*R_s$), the film thickness is 7.97 µm, yielding a bulk resistivity of 9.40×10^{-5} Wcm.

3 CONCLUSION

An economically viable method for fabricating conducting Cu films on both glass and flexible plastic substrates has been developed (Figure 3). The low viscosity and moderate pH make these inks scalable to printing techniques such as ink jet, screen printing and gravure. In addition, the optimization of both the synthetic and processing conditions as reported here allows for greater latitude in the ability to scale up and manufacture conductive Cu films.

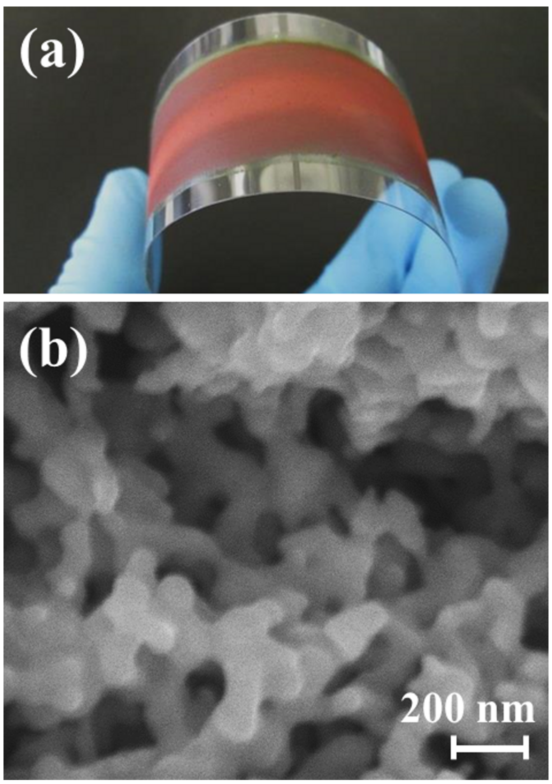

Figure 3. (a) Photograph and (b) SEM of the IPL sintered Cu/Cu_2O film on PET using 1 pulse with an ED of 22.4 Jcm^{-2} in air.

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