Intense Pulsed Light Sintering and Reduction of Facile Copper Hydroxide Synthesis towards Printable Copper Contacts

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ABSTRACT

The printed electronics market is a rapidly growing field, with the market set to reach $3.6B by 2018. Conductive inks are used in a vast variety of technologies. Inks are typically composed of metallic particles mixed with solvents and organic binders. The organic components are burnt off by thermal treatment. In recent years copper inks are becoming common place. A drawback of copper is its susceptibility to oxidize during heating. Therefore the copper nanoparticles often need to be capped. These organic materials decompose on heating to produce a reducing atmosphere which helps prevent oxidation. We developed a low cost synthesis to produce copper hydroxide based nanoparticle inks which can be processed using Intense Pulsed Light (IPL). These nanowires were formulated into printable inks. IPL is an ultra-fast thermal processing technique using lamps to emit incoherent pulses of light from the UV to IR region. The nanoparticles absorb the light, resulting in a localized temperature rise at the surface that can sinter the particle to its neighbors. The copper hydroxide converted to cupric oxide.

Keywords: intense pulsed light, copper, printed electronics, nanoparticle, manufacturing

1 INTRODUCTION

The deposition of conductive metal traces for electronics onto various substrates is typically accomplished through physical and vapor deposition, as well as electroplating. These techniques have gained acceptance in a number of applications in electronics. Recently, there has been interest in depositing these conductive patterns utilizing more versatile techniques such as screen, inkjet and aerosol jet printing. These approaches allow for more on demand customization of the patterns as well as more affordable substrates, which can vastly reduce the costs of a number of important devices such as RFID, solar cells, flexible electronics and displays.

Inks used for the printing of conductive traces are typically composed of metal particles, binders and emulsifiers suspended in a solvent. Silver has been the metal of choice for most of these applications, but copper has begun to gain a fair amount of interest primarily because the cost is substantially lower. The deposited inks are then heated in order to remove both the remaining organics and sinter the particles to produce a conductive trace. Recently, intense pulsed light (IPL) has been utilized as a rapid and scalable technique to accomplish this heat treatment. IPL is an emerging advanced manufacturing process that illuminates light from a xenon strobe over a wide area to locally heat a film. IPL treatment has significant potential to be used as an alternative method of sintering, particularly for metal nanoparticles, as the rapid pulses would significantly reduce processing times and is also applicable to flexible substrates where traditional thermal sintering would cause irreversible damage. IPL treatment of copper nanoparticles has enabled the sintering of copper, without the use of an inert environment or vacuum, because the time-frame for heating and cooling is faster than oxidation of the copper.

In our previous work we have shown that the IPL technique can be used to reduce copper oxide nanoparticles deposited using traditional spray techniques to a conductive copper film.[1, 2] The IPL process induces a momentary (less than 1 ms) rise in temperature in a very thin film that can reach temperatures of 1000°C.[3] The IPL can induce structural changes throughout the film structure which includes grain reorientation and growth.[4] The results are the very fast processing of inks that can turn organics and oxides into highly functional films on a number of substrates including polymers. Additionally the illumination area of the IPL is large making this technique appropriate to roll-to-roll coating platforms.

In this work we explore an alternative system to the oxide nanoparticle ink that should display improved ink stability and faster processing. The ink continues to be processable in room temperature in water and can be rapidly converted into a conductive film. The nanoparticle ink is composed of a copper nitrate hydroxide ($Cu_2(OH)_3NO_3$). The films are investigated using XRD, SEM and FTIR.

2 EXPERIMENTAL

The synthesis of the $Cu_2(OH)_3NO_3$ was accomplished in a completely aqueous system through the drop wise addition of a basic solution to an copper salt solution. In this case the salt was copper nitrate ($Cu(NO_3)_2.2.5H_2O$, Alfa Aesar, 99.99 %), the base was potassium hydroxide (KOH, Sigma Aldrich, 98%) and deionized water was used for both solutions. All reactions were done at room temperature and did not require any inert atmospheres.

The $Cu_2(OH)_3NO_3$ inks were adjusted for viscosity by adjusting the water content in the mixture. The pastes were then manually screen printed with a squeegee using a 200 mesh screen in a 15 mm x 15 mm square pattern.

The deposited inks were exposed to an IPL process of 40 pulses at varying energy intensities and the pulse duration was maintained at approximately 2 ms per pulse. The IPL unit used was a Sinteron 2000 by Xenon Corporation.

The analysis of the films included XRD using a Bruker AXS D8 X-ray diffractometer using Ni- filtered Cu-Kα radiation with a step size of 0.02° and a scan speed of 0.5 sec/step. A FEI Nova NanoSEM 600 with an accelerating voltage of 2-3 kV and a working distance of 5 - 6 mm was used to study the morphology and extent of sintering of the deposits.

3 RESULTS AND DISCUSSION

There have been several reports that detail the synthesis of nanoparticles of copper, copper oxides and copper hydroxides. Most of these methods include very involved synthesis techniques which include high temperatures, washing steps and inert atmospheres. All of these are typically relegated to batch processes that can also increase the cost of manufacture. Other issues such as ink stability and solids concentrations further impact the ability to reduce the cost of printing copper.

By choosing a printing technique with high solids content, there is a lot less need to produce an ink with uniform size and morphology. Thus, during this work we did not attempt to optimize the synthesis for size and or shape, but were looking to produce nanoscaled material with uniform composition. The resulting synthesis produced a $Cu_2(OH)_3NO_3$ nonocomposite ink of several different morphologies as shown in Figure 1. XRD analysis of this material indicated that the synthesized material was predominately $Cu_2(OH)_3NO_3$ (Figure 5).

The deposition of the inks can follow a number of different traditional printing techniques as the viscosity of the dispersion is simply adjusted using different solvents and organic binders. In this study we employed the screen printing process as a means to print the materials onto a glass substrate. The screen printing technique is well known and very versatile printing very fine patterns at extremely high speeds. A picture of the screen printed film is shown in figure 2. The printed size is approximately 15 mm x 15mm.

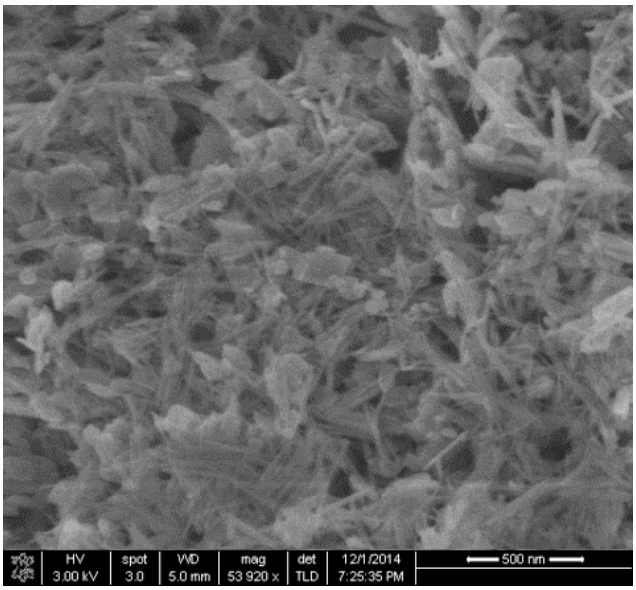

Figure 1. SEM image of the as synthesized $Cu_2(OH)_3NO_3$, which shows that the ink consists of several morphologies.

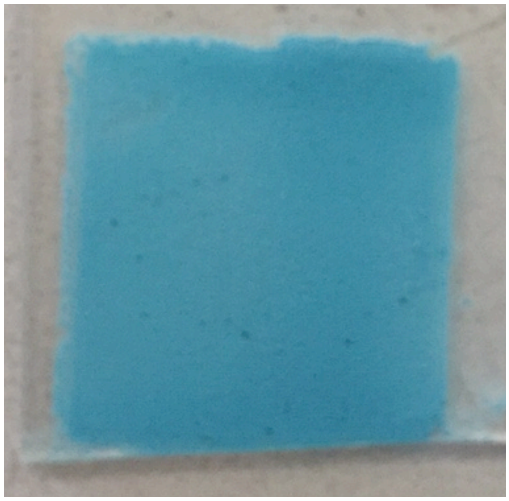

Figure 2. Photograph of the printed sample, where the printed area is approximately 15 mm x 15 mm.

The deposited films include a fair amount of water that must be removed in order to develop a conductive paste. The IPL process is therefore designed to remove the unwanted water, as well as reducing and sintering the nanoparticles. The decomposition of the $Cu_2(OH)_3NO_3$ can be accomplished at relatively low temperatures. Thermo gravimetric analysis (TGA) was used to confirm the temperatures needing to be reached in order to (1) remove the remaining solvent from the film, and (2) induce the loss of OH and NO_3 from the film in the form of H_2O and

HNO_3. The results shown in Figure 3, show that there is significant decrease in the weight of the samples starting at a little more than 125°C and lasting approximately 100°C.

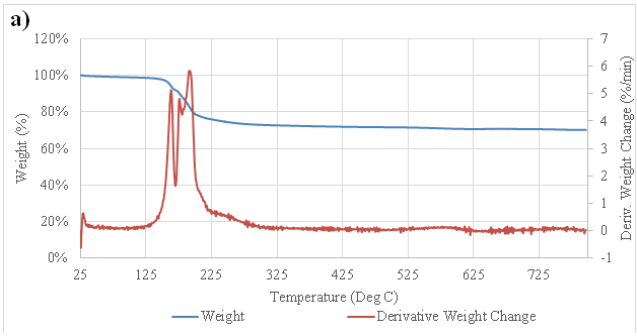

Figure 3. TGA results of the $Cu_2(OH)_3NO_3$ films showing the removal of the residual water, OH and NO_3 groups.

The final stage of the process is to convert the material from $Cu_2(OH)_3NO_3$ to an oxide or to copper. This is accomplished using IPL. The films were subjected to 40 pulses of light using a 2 ms flash duration. Several energy intensities of 10.1, 12.8, 15.8, 19.2, 22.9, 26.8, 31.1 and 35.7 J/cm^2 were used in this study. The SEM of the films sintered at the highest setting are shown in Figure 4.

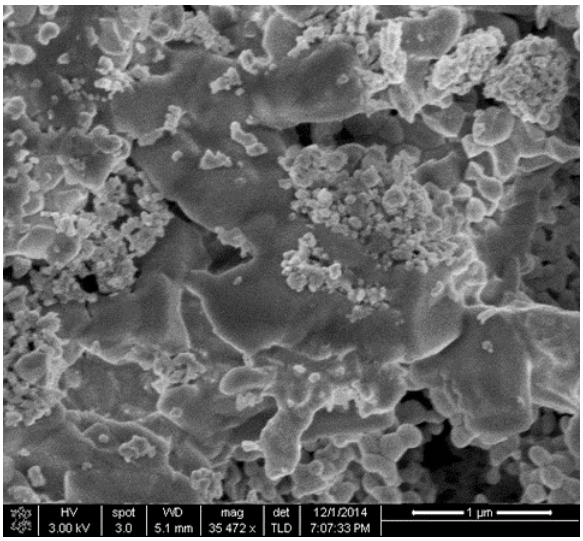

Figure 4. SEM image of the $Cu_2(OH)_3NO_3$ film after 40 IPL pulses at 35.7 J/cm^2.

The results of IPL processing the films at the highest intensities demonstrate a fair amount of sintering throughout the sample. The films also show a high degree of melting due to the use of a low melting point copper precursor ($Cu_2(OH)_3NO_3$). XRD analysis of the films demonstrated that the films did not convert to copper as desired as shown in Figure 5. However, we have previously demonstrated that the IPL method can be used to reduce oxides of copper into elemental copper by utilizing reducing gases. Therefore an organic binder with a low thermal decomposition temperature (< 150°C) was added to the $Cu_2(OH)_3NO_3$ paste prior to printing. The films were then IPL processed using the same method reported above. During this heat treatment the organic molecules decompose into gases which subsequently reduces the $Cu_2(OH)_3NO_3$ to copper (Figure 6).

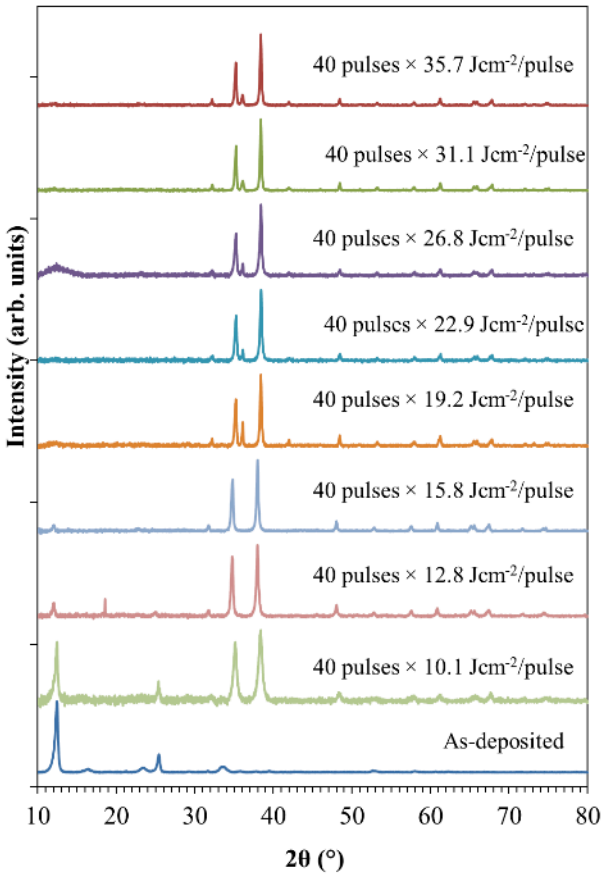

Figure 5. XRD analysis of the films as-deposited and after IPL processing at several different light intensities. The diffractogram for the as-deposited film was indexed to the $Cu_2(OH)_3NO_3$ ICDD(00-003-0068), while the IPL treated films were indexed to CuO ICDD(00-001-1117).

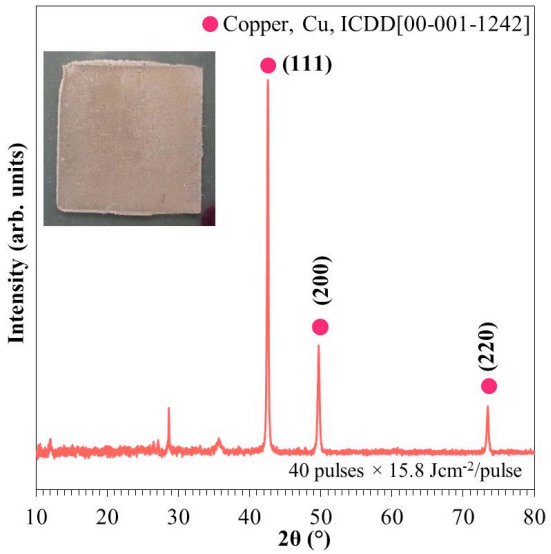

Figure 6. XRD and photograph of the films deposited with an organic binder and IPL processed.

4 CONCULSION

In this study we have synthesized $Cu_2(OH)_3NO_3$ nanoparticles using a very simple method. The nanoparticles are synthesized and stable in water, and the method does not require any elevated temperatures or inert atmospheres. The SEM images show that the morphology of the resulting materials includes wires and particles. The IPL processing of the films does result in the sintering and melting of neighboring nanoparticles resulting in a bulk thin film. However, the XRD results show that the $Cu_2(OH)_3NO_3$ converts to oxides of copper. In order to reduce the films to copper, the addition of an organic molecule with a low thermal decomposition temperature in to the inks formulation was necessary. The addition of this molecule was necessary to decompose into a reducing gas during heat treatment. More work is required to reformulate the ink to optimize the reducing atmosphere initiated during the IPL process.

5 REFERENCES

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