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Copper Conductive Ink: Cost Effective Solution for Printed Electronics

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Abstract— **Conductive ink is the most important part of any electronic product which is being printed. Various kind of conductive paste used for printing is silver, graphite and copper. Out of these silver conductive ink is widely used to form conductive electrode in printed electronics but main constraint is its price. So copper based conductive ink is the best alternative for this but it gives higher resistance compared to silver. This study focuses on low temperature ink curing and electrical characterization.**

Index Terms— **conductive ink, photo-sintering, curing, printed electronics.**

I. INTRODUCTION

1.1. Printed electronics:

Printed electronics is defined as the conventional electronic products in printed form, e.g. printed RFID etc. The advantages with conventional printing technique is short cycle times and simple material processing [3].Printed electronics has a bright future with low price. But efficiency of the printed electronics product is something which still needs to be look after.

1.2. Conductive ink:

The constituent of any printed electronics product is the conductive ink [6]. Silver conductive ink is widely been used for almost all printed electronics product. It has got high conductivity i.e. 6% more conductive than copper conductive ink. But the only constraint is its cost. Copper based conductive ink is a promising alternative to silver based conductive ink due to its lower material cost. And technically also it is at par with the silver conductive ink based on its properties which has been proved in this paper.The only limitation with copper conductive ink is its higher electrical resistivity compared to silver conductive ink. So picking one of the property i.e. curing temperature, we will try to increase the electrical conductivity of the copper conductive ink by lowering its curing temperature. By lowering the curing temperature other advantage is wide range of substrate can be used like polyimide (PI), polyethylene teraphthalate (PET), or even paper. So, the work is basically divided into two parts i.e.

low temperature curing and photosintering. This study focuses on low temperature ink curing and electrical characterization. Basically the first part of this work i.e. low temperature curing, the work is divided into 3 parts i.e.:

(a) Rheology characterization
(b) Thermal behaviour
- Thermo gravimetric analysis
- Differential scanning calorimetry

(c) Curingtest

II. BACKGROUND THEORY

In this chapter we will be dealing with the evolution or advancements of copper conductive ink. As the title deals with copper conductive ink and how we can decrease the curing temperature so that it will be comparable with silver conductive ink. So in this four year analysis scientists tried to optimize the copper conductive ink, so that a minimum curing temperature can be obtained.

2.1. Introduction of copper nanoparticles;

The microstructure of the metal particles especially the grain size could be influenced by the thermal curing process. It has been observed that the microstructures consisting of large grains are more conductive than those consisting of small grains. But large grain shows agglomeration. Agglomeration is nothing but the coarse accumulation of copper conductive particles so it would be difficult for some of the printing processes like inkjet printing to print the conductive pattern. Ink dispersions using particles of large grain size are certainly possible, but would suffer from particles precipitation and agglomeration

unless they were constantly agitated or special additives were included to help hold the large particles in suspension. The additives needed for larger particles should be of longer chain molecules with higher evaporation temperatures, i.e. they would be difficult to eliminate in the curing process. Therefore there is a need for nanoparticles. To obtain low temperature curing and sintering one must first understand the size dependence of the melting point of nonmetals. The size dependency of a nanoparticle melting point for a given material usually shows a monotonic decrease with decrease in size [4]. If we consider a cluster of size N and, for simplicity, of spherical shape, at a given pressure p we expect that the melting temperature will be a function of the size $T_m(N)$. We need to compare $T_m(N)$ with $T_m(\infty)$, which is the melting temperature of the bulk material. An important factor to be considered in the case of metallic nanoparticles sintering is the solid-liquid transitions of these nanoparticles. In order to find a solution to $T_m(N)$ we need to equate the chemical potential of the solid and of the liquid and solve the equation:

(1) $\mu_s(p,T) = \mu_l(p,T)$

Equation (1) states that the chemical potentials of a completely liquid and of a completely solid cluster are equal at the melting point. After a number of mathematical manipulations one obtains the following equation:

(2) $T_m(N) = T_m(\infty)(1 - C/N^{1/3})$

where C is a constant for each material that depends on the latent heat of material, the density of the particle, and interfacial tensions such as at the solid vapor interface and liquid vapor interface.

The precise copper nanoparticles are obtained by using thermal plasma[8]. Thermal plasma delivers the energy necessary to cause the vapourization of the metal particles. The temperature should be kept at 10,000 K. and then cooling takes place. So, the end products which we are getting are precise copper nanoparticles. So, the curing temperature of the printed copper conductive ink consisting of copper nanoparticles should be as low as possible.

2.2. Low temperature curing of copper conductive ink:

After getting copper nanoparticles the next challenge is to obtain a minimum curing temperature. Low curing temperature is obtained by taking two samples i.e. freshly prepared copper conductive pattern and aged copper conductive pattern. The test sample was isothermally aged at 85 ^oC for 7 days.

Then both the samples were cured at different temperature starting from 60 ^oC to 150 ^oC and the minimum curing temperature was found out. Here it is being found that the minimum temperature at which the sample can be cured is 60 ^oC. but after 70 ^oC the sample shows a very peculiar property i.e initially the resistance of the aged sample was less compared to freshly printed sample but after 70 ^oC the resistance of the aged sample suddenly become more than the freshly printed sample. This happens because during ageing process the printed sample comes in contact with the atmosphere and oxidation takes place. So,the resistance increases and conductivity decreases.

2.3. Photosintering:

The effects of several flash-light irradiation conditions (irradiation energy, pulse number, on-time, and off-time) and the effects of the amount of poly (N-vinylpyrrolidone) in the Cu nanoink on the flash-light sintering process were investigated.

III. METHODOLOGY

This chapter is dealing with the methods by which we can achieve low curing temperature.

3.1. Formulation of copper conductive ink:

The constituent of ink is more important for the curing process because if we are curing it with the help of heat, solvent plays a very important role. The process involves the evaporation of ink solvent during the curing process.

3.1.1.For low temperature curing:

Conductive inks are mainly made of metal particles in a retaining polymer matrix. The matrix used is a polymer, known as polymer thick film (PTF). Once printed the amount of the matrix suspending the conductive particles need to be decreased, resulting in particles conducting through physical contact, which is generally done by thermal curing. The selected copper conductive ink has a metal loading of 65wt% and an average particle size of 5µm. The weight percentage is calculated by taking the ratio of the weight of the metal particles present in the ink and total weight of the ink.

3.1.2.For photosintering:

For fabrication of Cu nanoinks, commercially available Cu nanoparticles with oxide shells (20–50 nm in diameter) were used in this study. Copper nanoparticles (3.8 g) were dispersed in a mixed solvent of diethylene glycol(3 g) and poly(N-vinylpyrrolidone) (7 g) in an ultra-sonicator for 2 h. The amount of PVP was varied to observe the effects of PVP wt% and optimize the amount of PVP in the flash-light sintering process. The Cu nanoinks were printed on polyimide (PI) substrate. The modifiers and the dispersant used for this ink constituent are diethylene glycol and poly(N-vinylpyrrolidone) respectively.

3.2.Low temperature curing of copper conductive ink

In this process sample is being cured with the help of heat. This study included rheology characterizations, thermal analysis, and actual curing tests.

3.2.1. Thermal behaviour analysis:

The thermal behavior of the studied copper ink was also analyzed using thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). The TGA analysis was conducted by heating up 40mgrams copper ink in an aluminum pan at 10°C/min from 25°C to 200°C. Meanwhile the DSC analysis was performed with the following steps: (1) The copper ink was dried in an aluminum pan at 70°C for 30mins to evaporate the ink solvent. (2) In the DSC equipment, the dried copper was heated at 10°C/min from 25°C to 200°C. Thermogravimetric analysis is used to determine the weight loss of copper conductive ink and differential scanning calorimetry is used to determine the glass transition temperature. By obtaining the glass transition temperature we will get to know a certain value so that the curing temperature above glass transition temperature is not preferred.

3.2.3. Curing of ink:

Two test vehicles were used to characterize the ink printing performance. The test vehicles were fabricated by screen-printing the copper ink on a 125µm thick PET substrate followed by heat curing the printed ink at different temperature from 60°C to 150°C for 10mins. The test vehicles were also isothermally aged at 85°C for 7 days. The performance of the deposited copper ink was determined with the conductivity, and printing uniformity. So, two test vehicles were obtained i.e. one is freshly printed and the second one is aged sample and the curing process is carried out from 60°C to 150°C and a graph is plotted between the curing temperature vs. resistance and the minimum curing temperature obtained through this process is 60°C.

3.3. Photosintering:

The spin-coated Cu nanoinks were sintered by a flash-light at room temperature and ambient conditions. The flash-light sintering system consists of a xenon flash lamp, a power supply, beam guide, a pulse controller and a reflector which is made up of aluminum [7]. The white light from the xenon flash lamp has a broad wavelength range from 380 to 950 nm . In order to optimize the flash-light irradiation conditions, irradiation energy, number of pulses, on-time, and off-time were varied as shown in the next section respectively. For monitoring of the sintering process of Cu nanoparticles in real time, a Wheatstone bridge electrical circuit shown in figure 3.1, source meter, and oscilloscope were used to measure the change in resistance of Cu nanofilms over a few milliseconds.

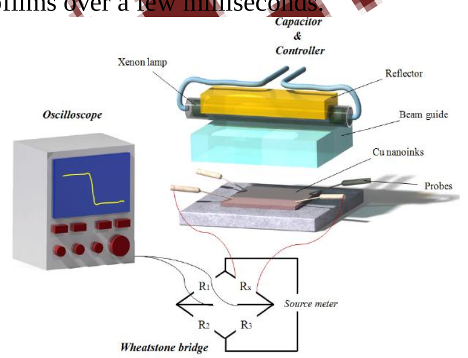

Figure 3.1. Schematic diagrams of the flash-light sintering .

The variable resistance is measured by using proportionate method or four point probe method. So the formula involved is:

$$R_1 / R_2 = R_X / R_3$$

Where

R_1, R_2 and R_3 are known resistance and R_X is the variable resistance.

So, by connecting the two potential point of R_X with that of the copper conductive

printed sample the resistance can be calculated by using the above mentioned formula. And it will be easier for analysing the variation of resistance with respect to various parameters like irradiation energy, pulse number, PVP weight percentage and on-time.

CONCLUSION AND FUTURE SCOPE

4.1. Conclusion:

The study focused on low temperature curing copper conductive ink, and electrical characterizations. By optimizing key screen printing parameters including viscosity and screen mesh size, a low curing temperature of 60°C was achieved by optimizing air-flow rate and curing profile. Then by analyzing thermal behavior, glass transition temperature obtained is 125 °C. So, the Resistance obtained in low temperature curing process is 2.45 ohm.

The curing temperature can further be decreased by sintering the copper conductive ink by using xenon flash lamp at ambient temperature i.e. it can be cured at room temperature. The Resistance obtained is 0.072 ohm by keeping all other parameters as constant like energy as 12.5 J cm^{-2},pulse number as 1,PVP 0.3 gm and on-time as 20ms.

4.2.Future scope of work:

Future work will focus on improving the quality of sintered Cu films and Cu nanoink optimization by varying various parameters like energy, on time, pulse number etc . in this study off-time was not varied so off-time can also be varied and resistance with respect to off-time can be calculated. Copper has got good shielding property i.e. the data stored inside any copper conductive printed pattern cannot be accessed by the outer source. So, copper conductive printed pattern can be used for the security purpose. So further study can be carried out on the shielding property of the copper conductive ink printed on various substrate using low curing temperature.

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