Nanotechnology and Its Contribution to Technical Inks for Printed Electronics

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Abstract

Printed electronics is an emerging manufacturing technology with applications in consumer electronics including future display products. Direct deposition methods such as inkjet printing can be used to deposit droplets of ink directly onto a substrate using an additive method. A wide variety of materials including dielectrics, metals, organic semiconductors, etc., can be printed. Metalic nanoparticles, in particular, are used for metalic inks due to the quantum confinement effect observed in these metalic inks when the size of the particles is less than 100 nanometers. For example, copper nanoparticle inks for inkjet printing are a promising substitute for more expensive silver- or gold-based inks for consumer electronics applications. However, because of the relatively high melting temperature of copper and tendency to oxidize in ambient atmosphere the utilization of copper in the printed electronics industry was delayed. This paper we will present novel inkjettable copper nanoparticle inks for use with Kapton substrates. Copper is a common material in electronics and less expensive than noble metals. Potential applications for printable copper inks range from polymer based flexible circuits, metalization and printable transistors for backplanes among others.

1. Introduction

Metal conductors on printed circuit boards (PCBs), flex tape connectors and other flexible substrates are generally copper (Cu) lines that are either laminated onto the PCBs or deposited by electro-plating techniques. These technologies are standard and well known in the industry. Patterning the copper material to form conducting lines and leads between the electrical components requires photolithography and etching steps in order to define the copper line pattern from the blanket copper film. These processes use harmful chemicals that generate hazardous waste, adding significant cost to the products made. The cost is further increased by the time and labor necessary for the etching and photo-patterning process steps.

Presented here are novel copper inks suitable for printing techniques, including inkjet, that can form highly conductive copper traces or lines on a variety of substrates at room temperature without the utilization of inert atmosphere. By transitioning to printing techniques, the cost of the products can be reduced because the Cu deposition and patterning are done in a single process step. Furthermore, since printing is an additive process it eliminates the need for harsh etching and photo-patterning chemicals. In such a way the processes become environmentally friendly, thus further lowering the cost of the product.

Copper nanoparticle inks suitable for printing were shown to be a promising substitute for silver or gold-based inks for electronics applications.[1][2][3][4] The desire to use copper ink for inkjet limits the size of the copper nanoparticles in the ink to a nanometric level (less than 100 nm). In addition to the size requirements it is highly desirable to develop a material that can be processed at temperatures lower than 100 degrees C (ideally room temperature) in air. Obviously, these are serious challenges regarding the development of inkjet printable copper. In particular, copper nanoparticles are easily oxidized in air under ambient atmospheric conditions in comparison to noble metals for example. In this work many of these obstacles have been overcome and the of copper inks for both piezo-electric and aerosol printing heads have been demonstrated[5]. Direct current (dc) resistivities as low as 3.3×10^{-6} Ω-cm were observed.

In this paper the properties of the printable nanoparticle copper inks are discussed and structural and electrical characterization methods are reported.

2. Nano-requirements for metalic inkjet printing

Nanotechnology comprises all sciences, technologies and applications concerned with the properties of matter from two or three molecules binding together until the first aggregate of the same molecules is created achieving the same chemical, physical and biological properties as the bulk material.

Typical inkjet nozzle diameters are on the order of one micron. If the metalic particles are too large, they will plug the nozzle and printing will simply stop. For inkjet printing, the average particle size needs to be less than 50nm and the nanoparticles must be well dispersed in the ink. The largest particle allowed is approximately 100nm in order to avoid plugging due to agglomeration with other particles.

Ink dispersions using particles larger than 100nm 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 would likely be longer chain molecules with higher evaporation temperatures, i.e. they would be difficult to eliminate in the drying and curing steps following printing.

3. Nano-effects in metalic nanoparticles

To achieve low temperature drying and sintering one must first understand the size dependence of the melting point of nanometals. The size dependency of a nanoparticle melting point for a given material usually shows a monotonic decrease with decrease in size and may show also irregular variations.

First, let us justify the experimental results of the observed monotonic trend of decreased melting point with the size decrease of the nanometalic particles.

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 metalic 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:

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

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[6] one obtains the following equation:

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

where C is a constant for each material that depends on the latent heat of melting per particle, the density of the particle, and interfacial tensions such as at the solid vapor interface and liquid vapor interface.
This model can be refined[7] by including the possibility of surface melting that may be the case in the sintering process. In this case the melting process is considered to start at the surface of the nanoparticle and the melting temperature is found by imposing the equilibrium condition on the solid core/liquid shell particle. This model is even further complicated and expanded[8] for metallic particles specifically. In this case, a new variable ξ was introduced that is the characteristic length of the interaction among atoms in liquid metals in addition to taking into account the effective interaction between the solid-liquid and liquid-vapor interfaces. This effective interaction is repulsive and favors the formation of a liquid shell between the solid core and the vapor as shown in Figure 1. Obviously, the equation will be much more complex, but in the limit $\xi \to 0$ we obtain the simple equation (2).

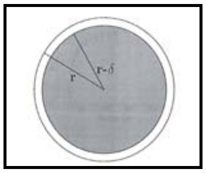

Figure 1. A particle with the solid core and a liquid shell

It is believed that the solid core/liquid shell model is more accurate and fits the experimental data much better. In fact, some researchers[9] found out that this solid core/liquid shell model fits very well for copper at $N = 500$ for copper. For example, below we have a comparison (Figure 2) of theoretical and experimental melting points of tin clusters[10] showing clearly that this approach can predict theoretically the drop in the melting temperature of tin clusters *vs.* size. It is clear that in many cases the melting point of a material drops with the size of the particle and is particularly pronounced in the size range below 100nm.

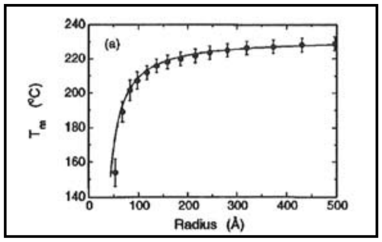

Figure 2. Comparison of theoretical and experimental (solid lines) melting points for tin clusters.

Another important characteristic of nanoparticles in ink is the behavior of the absorption spectrum of the nanoparticles in suspension. Studies have shown[11] that the absorption spectra of nanoparticles in suspension depend on size and shape of nanoparticles. Furthermore, the absorption spectra are strongly dependant on agglomeration effects as shown in Figure 3.

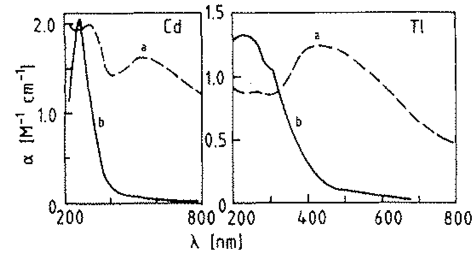

Figure 3. Absorption spectra of agglomerated (a) and isolated (b) particles of cadmium and thallium in water.

Furthermore, the absorption spectra of nanoparticles behave vastly different than the absorption spectra of the bulk material. It was found that a dependency of these absorption spectra exist on the size and shape of the nanoparticles[12] due to their strong relation to the mean free path of the electrons in the specific material. As we deal with nanoparticles, quantum confinement effects at the nanolevel will have an influence on their absorption spectra.

These nano-effects were carefully studied and employed to apply a sintering method that is different from the usually employed thermal curing process. By lowering the melting temperature of copper nanoparticles and controlling the agglomeration effects in the ink, special UV flash lamps were devised to cure the printed copper metalic traces by very short UV pulses in a process called “photosintering”[13].

In order to understand the photosintering process we need to consider the anomalous heat capacity of nanoparticles[14]. In the formation and melting of the nanoclusters we have a region of coexistence of two or more phases, which results in a peculiar behavior of the heat capacity. The equilibrium between two phases, whether in a bulk form or nanocluster form, can be described by an equilibrium constant:

$$K_{eq}(T) = \exp(-\Delta F/KT) \qquad (3)$$

whereby ΔF is the free energy difference between the solid and the liquid and can be expressed in terms of chemical potential as

$$(4) \qquad \Delta F = N\Delta\mu$$

As a result the equilibrium constant can be written as below:

$$(5) \qquad K_{eq}(T) = exp(-N\Delta\mu / KT)$$

where N is the number of particles in the system and $\Delta\mu$ is the mean difference in the chemical potentials of the two phases. Hence, even if $\Delta\mu/KT$ is very small (approximately 10^{-10}), but N is on the order of 10^{20}, then the thermodynamically unfavored phase is so unfavored that it is simply unobservable. However, if N is of order of 10 or 1000, then as long as each phase persists long enough to establish conventional properties by which we recognize it as such, it can be quite easy to find ranges of temperatures and pressure in which two or even more phases may coexist in thermodynamic equilibrium. Indeed, in the case of copper nanocluster melting or solidifying there may be situations where isomers may coexist, which as a result may induce the anomalous heat capacity behavior. We need to take this into account, as well as other variables, when we try to model the photosintering process as temperature induced phase transitions in copper nanoclusters. This type of modeling requires extensive molecular dynamics and jump-walking Monte Carlo simulations[15], which needs to treat solid-solid transformation, solid-liquid transformation and cooling below the solidification point phenomena. This is very complex requiring several million of configurations and averaging these simulations over different clusters with the same size.

The complication of the modeling is even more extensive if one needs to take into account coalescence. The process is so complex that one must take into consideration the coalescence between two solid clusters, a liquid and a solid cluster and two liquid clusters. Furthermore, while the coalescence of two liquid clusters takes place rapidly, the process of coalescence of two solid clusters takes much longer.

Researchers concluded[16] that coalescence of two solid clusters is a complex process, which takes place on a very slow time scale and may involve either the formation of a single domain cluster or complicated grain structures presenting grains. What exactly happens depends on size and structure of the initial clusters, so it may be a function in our photosintering case of the initial size of copper nanoparticles that we use. I would like to stress that this modeling is very complex and no one in the world has full control and understanding.

4. Experimental results

Copper nanoparticles with average size of approximately 70nm were utilized by dispersing them in a liquid medium in a proprietary formulation of ink. The ink contains dispersants to prevent nanoparticle aggregation along with other modifiers to control parameters such as viscosity and surface tension. Obviously the requirements of these parameters depend on both the nature of the substrate and the chosen printing method. After inkjetting the copper ink onto a Kapton substrate the traces were dried at temperatures less than 100°C and then photosintered to fuse the copper nanoparticles into metalic copper. The rapid photosintering leads to metalic conductors that have low resistivities (the average 5-7 μΩ-cm) with good adhesion to Kapton substrates as characterized by standard tape peal testing (ASTM D3359-02). Photosintering process was done in air and leads to both reduction of the native thin layer of copper oxide to copper and the fusion of these copper nanoparticles into a metalic film. Figure 4 shows SEM images of the dried ink before and after sintering.

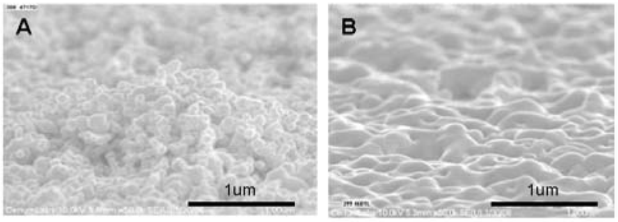

Figure 4. A) SEM images of uncured deposited ink, and B) cured ink after photosintering

Figure 5 shows the depth profile of a copper film after sintering studied by XPS. One can observe that a small quantity of oxygen is absorbed on the surface of the copper film but very rapidly we have over 90% copper in the film and very little oxygen is present.

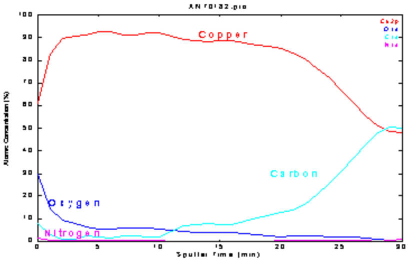

Figure 5. XPS depth profile for photosintered copper film

Two types of inkjet printers were utilized: Dimatix DMP-2800 piezo-inkjet printer having 16 continuously operating nozzles and an aerosol inkjet OPTOMEC M^{3}D® printer that has an integrated IR laser mounted on the printer that is also able to photosinter the copper ink. Figure 6 shows copper lines on Kapton achieved by inkjetting the copper ink and then photosintering using high power UV photocuring lamp. Figure 7 shows a 30 μm copper trace deposited by the Optomec aerosol printer that is IR laser-sintered on glass substrate.

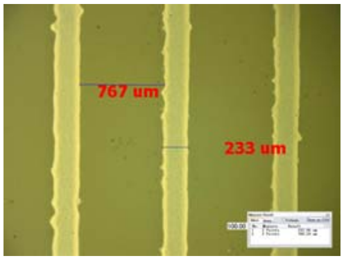

Figure 6. Image of longitudinal patterns of copper traces using Dimatix DMP-2800 X100

We also demonstrated photosintering using a UV laser as required by the absorption spectra of the copper inks (Figure 3). Although the absorption of copper inks in IR is lower than UV, the IR laser power on the Optomec printer is sufficient for achieving complete photosintering.

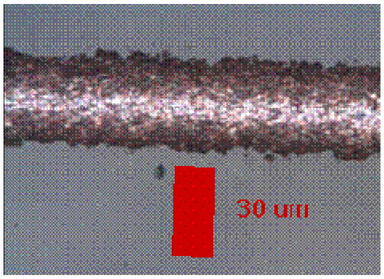

Figure 7. Optomec M^{3}D$^®$ aerosol-jetted copper ink trace laser-sintered on glass substrate

5. Conclusions

We presented a formulation of copper ink that is inkjettable, the drying temperature is less or equal to 100°C and the photosintering process is performed at room temperature without the need of inert atmosphere (Figure 8). Repeatable copper traces are achieved with resistivities between $5x10^{-6}$ to $7x10^{-6}$ Ω-cm. Initial wide-band electrical characterization results up to 20 GHz show [17] that the RF attenuation using the inkjettable copper ink on Kapton is comparable if not better than similar traces using silver (Ag) ink.

Based on our understanding of the nanoparticles' behavior and the photosintering mechanism, we achieved an optimal copper ink as follows:

- The ink contains copper nanoparticles less than 100nm in dispersion.
- We devised a suitable passivation of the copper nanoparticles during their production compatible with the ink formulation.
- The nanoparticles have a narrow size distribution which utilizes proper choice of vehicles and dispersants.
- The copper ink is inkjettable and optimized for photosintering.
- The photosintering is executed in air at ambient temperature.
- Additives to the ink were identified to control viscosity, surface tension and surface wetting on Kapton.
- The copper ink does not include any toxic materials and the dispersion is stable for at least six months in storage.
- We achieved control of the agglomeration and as a result of the inks' spectral behavior.

Figure 8. Inkjetted copper ink printed on flexible substrate

We believe that these characteristics of our copper ink technology will be adopted by the cost sensitive printed electronic industry to replace silver and gold based inks. The significant cost reduction in conductive inks will continue to drive down the cost of consumer electronics, including displays, and will enable new printed electronics applications in the future.

6. References

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