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Metallic nanoparticles for conductive inks

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ABSTRACT

Conductive inks are mainly based on metallic particles. At the moment silver flake inks govern the market but other solutions appear constantly. These include more economical materials such as copper and copper oxide flakes and metallic nanoparticles having improved performance. Nanoparticle based inks allow novel applications to be created through new material combination possibilities. Improved performance typically means higher conductivity at lower sintering temperature, inkjet printability and possibility to create thinner patterns with higher resolution. Main challenge is the high cost of manufacturing nanoparticles. Other challenge is for example high investments on R&D actions to create stable ink formulations. This presentation gives an overview of metallic particles used in conductive inks at the moment. In addition, an economical gas phase synthesis method to manufacture metallic nanoparticles for example for conductive inks is presented. Method has been developed by VTT Technical Research Centre of Finland and is operated in pilot scale at the moment.

Keywords: Conductive ink, metallic nanoparticle, printed electronics.

1. Introduction

The global market demand for high quality and low cost electronic components requires fabrication techniques that are both faster and cheaper compared to traditional production methods [1,2]. In this regard different printing methods using conductive inks have been researched and developed for decades under the name printed electronics. There is an increasing demand for printable conductive tracks (Fig. 1) in many different application areas such as smart packaging, flexible displays, OLEDs, thin film transistors, OPV and smart textiles.

Screen printing with silver flake inks is already established commercially and other printing methods such as inkjet (non-contact), gravure and flexography are used to manufacture products and demonstrators of printed electronics [3]. All printing methods require conductive ink with active material in order to create the conductive pattern on the substrate. Due to the ever increasing cost of silver metal and need for thinner films and lines and lower sintering temperature, lower cost and higher performance solutions have been developed. In the presentation we list metallic particles most commonly used in conductive inks and propose an economical synthesis method to manufacture different metallic nanoparticles, for example for conductive inks.

Figure 1 – Printed silver and carbon conductors (Source: DuPont)

2. Conductive ink composition

Conductivity (S/m) describes the performance of a conductor after the printing and sintering processes [1, 2]. In addition to conductivity of active material in the ink uniformity of the printed layer affects the performance of printed pattern. Ink formulations based on metal particles having high conductivity such as Ag and Cu offer a clear advantage over other conductive materials such as organic polymers. Metal particle size and morphology affects final conductivity of the printed pattern through layer uniformity and good particle contact.

Inks are in fluid state in the printing process and particle dispersion in the ink should be stable against aggregation and precipitation in order to have appropriate performance in the process and product [1, 2]. After deposition on the substrate ink should wet the surface properly, dry and adhere to the substrate. Metallic particles are brought into contact on substrate, in order to achieve conductivity, by different sintering methods. Sintering is a process of welding particles together at temperatures below their melting point. For all above reasons ink formulation is a complex process requiring considerable amount of R&D actions.

In addition to metallic particles inks contain solvent (aqueous, organic or oxygenated organic solvents), binder (for example epoxy) and stabilizing agent (for example PVP or polyelectrolytes), and possible additives [1, 2]. Ink dispersion stability and solid content, surface wetting and sintering process affect uniformity of the printed pattern. Sintering process should decompose organic polymers used in inks and bring metallic particles into contact. Impurities originating from ink formulation (organic stabilizers and binders) decrease the conductivity of printed pattern.

3. Metal particles in conductive inks

At present most conductive inks are based on micron size Ag flakes [1, 4]. Ag powders (nano-sized particles) have been commercially available for some years. Other metals used in inks are Cu and CuO. Also these metal particles can be purchased in different particle sizes and morphologies (particles and nanowires) from tens of nanometers to micron scale flakes.

Ag possesses the highest electrical conductivity among metals (6,3 * 10^7 S/m) and is resistant to oxidation but has a high and fluctuating price (approximately 500 €/kg in January 2014) [1, 4, 5]. Inks based on Ag flakes have conductivity 4-5 times lower than pure metal and price two to three times of bulk Ag. Typically nanoparticle based inks are considerably more expensive than inks based on flakes due to higher price of nanoscale metal particles and special ink formulation.

Cu has almost the same conductivity (5,96*10^7 S/m) than Ag but is considerably less expensive (approximately 5 €/kg in January 2014) [1, 4, 5]. The challenge with Cu is its rapid oxidation in the air. Oxides are not conductive which delimits Cu usage in printed electronics applications. Cu can be protected in ink formulation by using protecting agents such as ligands [1, 2]. Low cost inks based on CuO contain agent which reduces oxide back to metallic copper in photonic sintering process. Still Cu ink usage, if not protected or shielded in the application, is limited to only certain, usually shorter life-time products.

Advantages of nanoparticles over flakes are ability to reach same conductivity with thinner and finer printed pattern with less metallic particles, ability to use non-contact printing method with fragile substrates and ability to use lower sintering temperature which allows cheaper and temperature sensitive substrates such as plastics and paper to be used [1, 3, 4, and 5]. The main challenge is the manufacturing cost and obtaining stable fluid dispersion in inks.

3.1. Future prospects

Recently, Ag coated Cu particles (flakes and nanoparticles) have been researched and developed to bring benefits of both metals into the particle and conductive ink formulation [1, 2, 6]. In addition, carbon nanotubes and graphene are getting attention as a potential active material in conductive inks.

Although nanoparticle products are generally more expensive today, it is anticipated that volume manufacture will drive production costs down when a high volume application adopts such technology [1, 5]. Health and safety issues in nanoparticle production chain and usage in application are under investigation.

Largest market ($ 2,86 billion in year 2012) is for Ag flake based screen printing inks and they are mainly used to print interconnects in PV manufacturing process [1, 3, 4]. Other applications for conductive ink are conductors in glucose sensor strips, automotives, and RFID antennas. Potential future applications are transistors, wearable electronics, OLEDs and electroluminescent devices, touch screens and sensors for packaging. Thus, potential market for different conductive inks is large. At the moment the conductive ink market size, in other applications except PV's, is still relatively modest but forecasted to grow as new products are getting ready to be commercialized.

4. Production method for metal nanoparticles

VTT has developed a new award winning process (*) for synthesis of metallic nanoparticles based on gas-phase reduction of metal chloride precursors [7]. The aim has been to scale up the synthesis from laboratory to the pilot scale capable of daily production of 200-3000 g/d of metallic nanopowders.

Figure 2 – VTT Pilot unit TIPU for synthesis of metallic nanoparticles

The objective of the pilot unit TIPU (Fig. 2) is to demonstrate economical and sustainable production of nanoparticles. The targeted production costs for the metallic nanopowders is in the order of 100 €/kg. The reactor allows continuous week long operation, where pure metal powders are produced in one-step process starting from inexpensive precursor materials. The process is energy efficient and operating in atmospheric pressure, which directly influence the investment costs of the facility. The pilot unit TIPU is constructed using refractory materials commonly applied in the industry. In addition, the facility consumes very little water and produces minimal amount of liquid waste.

The transfer time of the particles through the facility is in the order of seconds. In practice, all material has experienced uniform temperature history, which relates to rather uniform particle size and structure. . An example of copper particles synthesized with the pilot reactor is presented in figure 3. The size distribution of the particles estimated from SEM images was approximately normal with mean diameter of 133 nm and standard deviation of 54 nm. According to electron diffraction measurements, all particles had a fcc crystal structure. The growth of the nanoparticles can easily be controlled by adjusting the feed rate of the precursor as well as the gas flow rates within the unit. Online monitoring and control has enabled operators to observe, that changes in the production rate take place in seconds as the conditions within the facility has been adjusted.

The metal particles can be coated in-situ with graphitic carbon as the particle synthesis takes place [8, 9]. Therefore, the coating also allows controlled reduction of the diameter of the produced powder. Carbon coating protects the particles during handling and storage against oxidation and sintering. According to TGA analysis oxidation of e.g. carbon coated copper nanoparticles in air start at about 200°C, whereas the non-coated particles oxidise already at room temperature. Carbon coating also facilitates mixing the metal particles in polymer matrix as well as functionalization of the particle surface.

TIPU pilot is also an example of safe-by-design principle with special emphasis on operator training and guidelines. Sophisticated online measurement techniques allow the synthesis process to be remotely operated. The powder treatment and packaging is integrated into the pilot unit to maximize both quality and safe handling of the materials.

(*)Printed Electronics Europe 2014 – Best Technical Development Materials Award

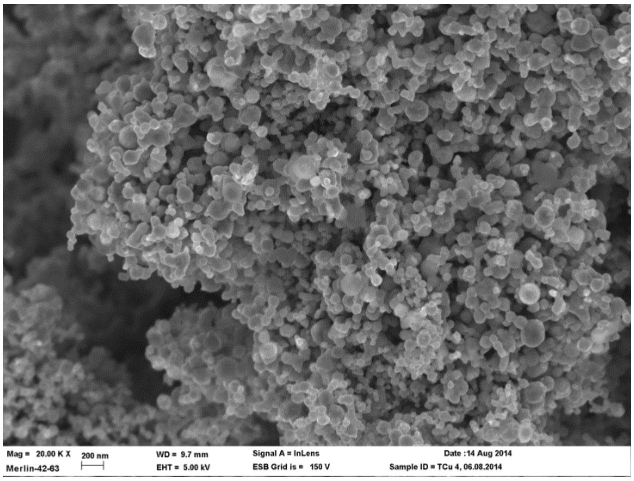

Figure 3 – An SEM image of Cu particles synthesized in VTT nanomaterial pilot TIPU.

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