学 位 論 文 内 容 の 要 旨
DISSERTATION ABSTRACT

博士の専攻分野の名称　博士（工学）　氏名　雍 穎瓊

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Copper Fine Particles for Electroconductive Materials
(電気導電性材料用銅微粒子)

Conductive inks have received increasing attention over past few decades owing to their applications for printed devices such as light-emitting diodes (LEDs), circuit, flexible displays, radio frequency identification (RFID) tags, and photovoltaics. Because of the lowest resistivity and anti-oxidation properties in air, silver inks are the currently favored conductive inks for printed electronics. However, the high cost and low electro-migration resistance of silver inks which can cause circuit failure under high humidity, limit their applications on a large scale.

Copper, owing to its low cost, low resistivity (1.7×10^{-8} Ωm, similar to that of silver) and high electro-migration resistance, has become the promising material for conductive inks. However, copper particles suffer from the oxidation. This problem can be solved by stabilizing copper particles by surfactants. The stabilizers which act as barriers hinder the percolation paths of electrons, resulting in low conductivity (high resistivity) of the printed patterns. A conventional method to overcome the above obstacle is high temperature sintering in an oven (> 250 ℃). Nevertheless, for applications of low-cost and flexible electronic devices on heat-sensitive substrates, a low sintering temperature is essential. To decrease sintering temperature, several methods, such as laser process, decreasing particle size, photonic sintering, and using copper-based metal-organic decomposition (MOD), have been reported.

In this thesis, new strategies to obtain highly conductive copper layers by lower temperature (≤200 ℃) sintering were put forward. This thesis contains 5 chapters.

First chapter is Introduction. Recent progress of low temperature sintering for electro conductive layers is discussed. In addition, the strategies and methods of the research in this thesis is outlined.

In the second chapter, alkylamine-stabilized copper fine particles and their inks were prepared. One common way to lower the sintering temperature is decreasing particle size (<100 nm). However, this method is complicated and nanoparticles are chemically unstable during storage. In this chapter, a two-step process, in which a facile thermal oxidation process was introduced to increase the contacts between particles, was studied for effective sintering of copper fine particles (>100 nm). In the first step, copper fine particles (280 nm) were synthesized by a one-pot reaction utilizing D-isoascorbic acid as a mild reductant. For sintering processes, an oxidative preheating of the film was used for the formation of tight connections between particles. Then a following reductive sintering using a 3% hydrogen in nitrogen gas at 200 ℃ and 250 ℃ enabled the achieving of high conductivities of copper films. The results showed that the thermal-preheating step in air generated convex surfaces, nanorods

or nanoparticles among particles successfully. This was owed to the inside-out diffusion of copper ions from copper particles and the diffusion of oxygen ion in the opposite direction. The generated convex surfaces, nanorods or nanoparticles increased the contacts between particles and thus facilitated the sintering of particles in the following reductive sintering process. As a result, resistivities of 12.2×10^{-8} and 7.8×10^{-8} Ω m of copper films were achieved at 200 ℃ and 250 ℃, respectively.

In the third chapter, low temperature deposition of metallic copper from metal-organic compound systems is discussed. To achieve low resistivity at a lower sintering temperature, copper-based MOD inks with scalability and simplicity was also studied. In this work, the influence of various copper sources (i.e., copper(II) formate tetrahydrate and copper(II) acetate monohydrate) in MOD inks on the resistivity of films was compared. Commercially available copper particles (0.4-2.5 μm) were introduced into the inks to replace the organic components for higher conductivity and reliability of the obtained copper films. The results demonstrated that the resistivity of sintered copper films decreased with the decrease of size of the added commercial particles. The lowest resistivity of 2.6×10^{-7} Ω m was achieved using the inks containing 0.4 μm of added copper particles after sintering at 120 ℃ under nitrogen. In addition, polyvinylpyrrolidone stabilized copper particles (PVP-Cu) with a size range of 127 ± 20 nm instead of the commercial ones were used for preparing MOD inks to demonstrate the general applicability of this method. The resistivity of the obtained copper film using PVP-Cu particles at the sintering temperature of 100 ℃ was 7×10^{-6} Ω m. These results demonstrated that the use of copper particles to replace organic components in MOD inks effectively led to the low resistivity of film after sintering at the temperature as low as 100 ℃ under nitrogen.

In the forth chapter, in order to further decrease the resistivity, polydispersed-submicron copper particles stabilized with decomposable polymer (polypropylene carbonate, PPC) as a main part and a self-reducible copper formate/1-amino-2-propanol (CuF-IPA) complex as an additive were chosen to prepare the MOD inks. The surface modification of copper particles with PPC, using of smaller polydispersed particles, and self-reducible copper complex were favorable to obtaining highly conductive copper films at low temperature sintering. The lowest reported resistivity (8.8×10^{-7} Ω m) at the sintering temperature of 100 ℃ under nitrogen was achieved. Such a low sintering temperature with low resistivity was proved to be a result of the dual promotion effects of aminolysis of PPC with IPA and the pyrolysis of CuF-IPA complex. PPC broke down into smaller molecules by aminolysis with IPA, which reduced the steric stabilization for copper particles, and thus enabled particle coalescence and sintering more easily. The generated copper fine particles from the pyrolysis of CuF-IPA complex directly contributed for creating connections among particles and higher packing density.

The fifth chapter contains conclusions of this thesis.The methods and conductive inks developed in our study are promising for flexible and low-cost printing electronic devices.