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Conductive film by spray pyrolysis of self-reducing copper–silver amine complex solution

Sira Suren, Walailuk Limkitnuwat, Phenfar Benjapongvimon, Soorathep Kheawhom *

Computational Process Engineering, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand

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ABSTRACT

In this work, a facile method was demonstrated to prepare conductive film deposited on glass and polyimide (PI) substrates using spray pyrolysis of a copper–silver complex solution in nitrogen atmosphere. The copper–silver amine complex solution was prepared by mixing together the copper(II) acetate monohydrate, silver oxide, ammonia solution and di-ethanolamine. Four-point probe analysis, scanning electron microscopy (SEM) and X-ray diffraction (XRD) analysis were employed to investigate the properties of the conductive film obtained. The effects of various parameters including spray pyrolysis temperature, molar ratio of copper to silver, type of substrate and annealing time were investigated. The volume resistivity of the film was decreased by using either higher spraying temperature or longer annealing time. In addition, the volume resistivity was also decreased by adding silver. At spray pyrolysis temperature 200 °C and annealing time 25 min. The conductive film with volume resistivity of 19.0 μΩ cm, which is 11 times higher than the resistivity of bulk copper, could be fabricated using molar ratio of copper to silver 0.8:0.2 on glass substrates. Copper oxide was not observed on the film deposited on the glass substrates. In contrast, the film deposited on the PI substrates contained copper oxide and exhibited resistivity 5 times higher than that deposited on the glass substrates.

1. Introduction

An electrically conductive layer is an important component of electronic devices. Traditionally, photo-lithography and wet processing (developing, etching and striping) is widely adopted to fabricate this layer. However, this process is time consuming and expensive. Moreover, the procedure requires using a large volume of chemicals thereby producing a large amount of etchants and cleaning liquids that pollute the environment.

A printing process, which is an additive process, is considered a promising alternative technique for fabrication of a conductive layer owing to low cost, low waste, low temperature, and simple process [1–4]. The process is done using various printing techniques including ink-jet [3,5], screen-printing [6,7], spin-coating [8], spray-coating [9–11], and other methods. Among these methods, spray pyrolysis is one of the most promising techniques to deposit various different materials in thin film form on various substrates owing to its simplicity and inexpensiveness [12,13].

In general, widely used conductive inks are based on a suspended solution of metal nanoparticles [14–16] or a solution of metal–organic compounds or metal complexes [17–22]. Metal nanoparticles are generally synthesized using complicated processes, and various toxic wastes are generated throughout these steps. Moreover, organic compounds used as capping agents are inevitably present in nanoparticle inks because of the high surface energy of metal nanoparticles.

Silver [21,23,24] is the most commonly used conductive ink because of its high electrical conductivity and stability in air. However, the high cost of silver limits wide industrial application. Further, silver conductive lines exhibit low electro-migration resistance which leads to premature failure of electronic components [25].

Copper [18,19] is a potential alternative because copper is significantly cheaper and it has considerable high conductivity. However, copper has a great affinity for oxygen and it is easily oxidized in air forming a copper oxide layer. Consequently, copper oxide drastically reduces electrical conductivity.

Yabuki et al. studied the synthesis of copper complex ink by mixing copper formate with N-octylamine [18]. Synthesized complex ink was coated on a glass substrate and calcined at 140 °C for 60 min in nitrogen atmosphere. The minimum electrical resistivity of 20 μΩ cm was obtained.

Kim et al. also synthesized copper complex ink by mixing copper formate together with hexylamine. The complex ink was printed on a glass substrate and annealed at 200 °C for 2 min in nitrogen atmosphere followed by reduction with formic acid gas at 250 °C for 2 min. The lowest electrical resistivity obtained was 5.2 μΩ cm [19].

Farraj et al. presented copper complex ink made of copper formate and 2-amino-2-methyl-1-propanol [20]. This complex ink is stable in

* Corresponding author.
E-mail address: soorathep.k@chula.ac.th (S. Kheawhom).

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air and decomposes at 140 °C. The lowest resistivity of 10.5 μΩ cm was obtained by inkjet printing and annealing at 190 C under nitrogen atmosphere.

Laser sintering of copper complex ink made of copper formate, isopropyl alcohol, hexylamine and 2-amino-2-methyl-1-propanol was studied [8]. The ink was spin-coated on a polyimide (PI) substrate followed by ultraviolet laser sintering under nitrogen atmosphere. The minimum resistivity reported was 19.25 μΩ cm.

Fabrication of copper conductive film with a low resistivity of 5 μΩ cm was further demonstrated [17]. The ink composed of copper formate and blended amines of octylamine and dibutylamine was coated on a glass substrate and calcined at 140 °C under nitrogen atmosphere.

Self-reducible and alcohol soluble copper-based metal–organic decomposition ink was also presented [26]. The copper conductive film with resistivity of 9.46 μΩ cm was fabricated on a glass substrate by annealing at 350 °C under nitrogen atmosphere.

Conductive copper lines were again fabricated by inkjet printing of copper ethylene glycol carboxylates, followed by thermal sintering between 175 and 220 °C under inert conditions [22]. The resistivities of 12.3 μΩ cm on a glass substrate and 66.6 μΩ cm on a PI substrate were observed.

Recently, attention has been paid to studies on copper complex inks. However, copper complex inks require post processing whereby copper-ion precursors are converted to copper and then sintered to a contiguous copper conductive film. As copper is sensitive to oxygen in the atmosphere, sophisticated conditions are usually required to suppress the formation of copper oxide.

In this work, a facile method was demonstrated to fabricate conductive film using spray pyrolysis of a copper–silver complex solution. In this technique, metal ion reduction, deposition and sintering processes occur sequentially in the same chamber. The paper is organized as follows. In Section 1, the background of printed electronics as well as copper complex inks was introduced. In Section 2, experimental details including materials used, spray pyrolysis setup, and characterization techniques used are presented. In Section 3, all experimental results are presented and discussed. Reaction and thermal analysis of copper–silver complex ink are investigated. In addition, the effects of spray pyrolysis temperature, molar ratio of copper to silver, type of substrate and annealing time are also studied. Finally, the paper is concluded.

2. Experimental

2.1. Materials

All chemicals used were of analytical grade. Silver oxide (Ag_2O) and copper(II) acetate monohydrate ($Cu(CO_2CH_3)_2\ H_2O$) were bought from Ajax Finechem and Carlo Erba, respectively. Di-ethanolamine ($HN(CH_2CH_2OH)_2$, DEA, 98.5% purity) and ammonia solution (NH_4OH, 25% wt/wt) were purchased from Ajax Finechem and QRCTM, respectively. These reagents were used as received without further purification. Glass (Sigma-aldrich) and polyimide (PI, Dupont Kapton 100HN 25 μm.) were used as substrates.

2.2. Preparation of copper–silver di-ethanolamine complex solution

A varying amount of silver oxide (57.94, 11.59, 5.79 and 0 mg) was dissolved in 5 mL of 25% wt/wt ammonia solution. Then, the solution was stirred at 35 °C for 15 min and a varying amount of copper(II) acetate monohydrate (0, 79.86, 89.84 and 99.82 mg) was added to the solution. The solution obtained was further stirred at 35 °C for 15 min. This solution is denoted as copper–silver ammonia solution. DEA solution was prepared by mixing 1 mL of deionized DI water and 4 mL of DEA. The copper–silver ammonia solution and DEA solution were mixed together, and stirred at 35 °C for 15 min. in order to prepare the copper–silver di-ethanolamine complex solution (copper–silver complex ink).

2.3. Fabrication of the conductive film by spray pyrolysis

The setup for spray pyrolysis system is shown as in Fig. 1. The spray pyrolysis system mainly consists of an air blast atomizer made of stainless steel, a stainless steel reaction chamber, and heaters. A similar design has been used in [12]. The atomizer used high speed nitrogen gas to produce an aerosol. The reaction chamber is a vertical cylindrical tube of diameter 20 cm and of length 30 cm. Heaters were installed at the wall of the chamber and just below the substrate holder made of stainless steel mesh of diameter 9 cm and of thickness 0.2 cm. With heaters installed, a maximum temperature of 250 °C can be attained over a uniform cylindrical zone inside the chamber. The substrate holder was placed in the uniform zone of the chamber and its temperature was measured using a thermocouple placed just below the substrate holder. The temperature of the furnace was maintained and controlled with a temperature sensitivity of 1 °C. The spraying of the complex ink was carried out. Further, the moving arrangements of an atomizer were employed in order to achieve uniform deposition.

In each experiment, conductive film (15 mm × 15 mm) was fabricated on glass or PI substrates by spray pyrolysis of 5 mL synthesized complex inks in nitrogen atmosphere at 150 or 200 °C. Initially, nitrogen gas was flown into the chamber at a flow rate of 10 L/min for 20 min in order to remove the air from the chamber and reach an inert atmosphere. In all experiments, spraying time was 3 min. Subsequently, 10 L/min of nitrogen gas was continuously flown to the chamber and the complex inks were sprayed at the rate of 1.67 mL/min for 3 min (spraying time). The samples were then further annealed inside the chamber for a varying annealing time of 5 to 35 min while 10 L/min of nitrogen gas was continuously being fed into to the chamber during the annealing process.

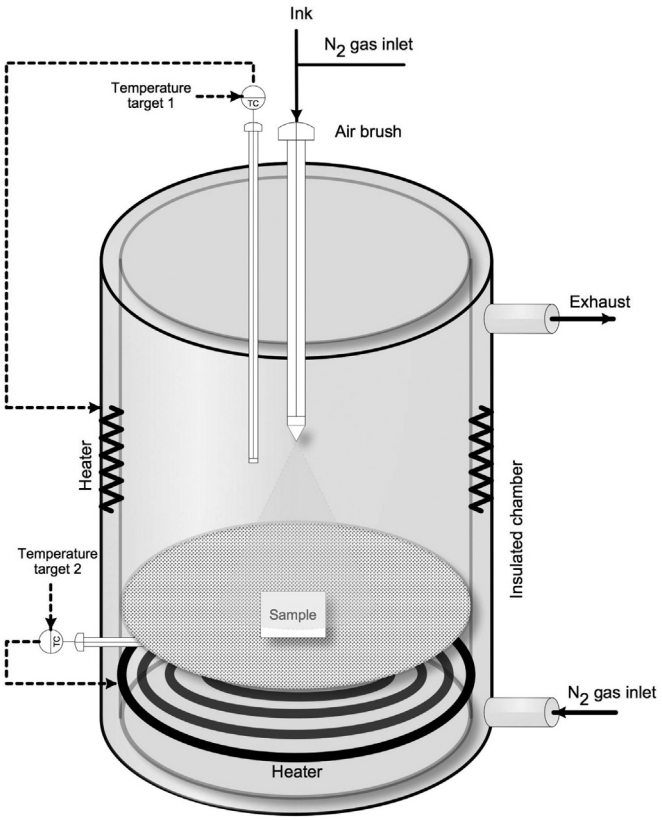

Fig. 1. Schematic setup for spray pyrolysis system.