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Conductive films prepared from inks based on copper nanoparticles synthesized by transferred arc discharge

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#### Abstract

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Copper nanoparticles (NPs) are considered as a promising alternative for silver and gold NPs in conductive inks for the application of printing electronics, since copper shows a high electrical conductivity but is significantly cheaper than silver and gold. In this study, copper NPs were synthesized in the gas phase by transferred arc discharge, which has demonstrated scale-up potential. Depending on the production parameters, copper NPs can be continuously synthesized at a production rate of  $1.2-5.5 \text{ g h}^{-1}$ , while their Brunauer–Emmett–Teller sizes were maintained below 100 nm. To investigate the suitability in electronic printing, we use ball milling technique to produce copper conductive inks. The effect of ball milling parameters on ink stability was discussed. In addition, the electrical resistivity of copper films sintered at 300 °C in reducing atmosphere was measured to be  $5.4 \pm 0.6 \,\mu\Omega$  cm which is about three times higher than that of bulk copper ( $1.7 \,\mu\Omega$  cm). This indicates that conductive inks prepared from gas-phase synthesized copper NPs.

Keywords: copper nanoparticles, conductive inks, printed electronics, transferred arc discharge, gas phase synthesis

(Some figures may appear in colour only in the online journal)

#### 1. Introduction

During the past years, printable dispersions based on conductive materials have attracted increasing attention because of the growing printed electronics market, for example, radiofrequency identification antennas (RFIDs), printed circuit boards, thin film transistors, and light emitting devices [1, 2].

Original content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI. Traditionally, electronic devices are manufactured by photolithography, vacuum deposition, and electroless plating processes. However, all these methods require expensive equipment and highly trained operators. Besides, these processes usually require environmentally undesirable chemicals, leading to a large amount of waste [3, 4]. For these reasons, many research efforts are currently being devoted to developing a convenient and low-cost processing technique. Among all the printing technologies, ink-jet printing is considered as a promising alternative to low-cost manufacture of electrical devices. Ink-jet printing is a dot-matrix patterning technique, which possesses many advantages such as high



Nanotechnology

Nanotechnology 31 (2020) 025302

	Table 1. Comparison of the throughput of copper nanoparticles reported in previous studies.							
Authors	Method	Copper source	Stabilizer	Synthesis environment	Throughput			
Deng <i>et al</i> [24] Lee <i>et al</i> [19] Stein <i>et al</i> [27] Stein <i>et al</i> [28]	Chemical reduction Chemical reduction Transferred arc discharge Transferred arc discharge	$\begin{array}{c} Cu(CH_3COO)_2\\ CuSO_4\\ Cu\\ Cu\\ Cu\\ Cu \end{array}$	CTAB and PVP PVP 	N <sub>2</sub> Ambient atmosphere N <sub>2</sub> N <sub>2</sub>	4.8 g per batch 47–50 g per batch 5.5 g per hour 69 g per hour			

accuracy, rapid deposition rate and non-contact mode [5]. To promote the application of ink-jet printing in the field of electronics, preparation of conductive inks plays a very critical role.

Currently, various conductive inks, ranging from metal nanoparticles (NPs) inks, carbon nanotube inks, and graphene oxide inks are investigated for application in printed electronics [6-10]. Since conductive inks applied for printed electronics should provide high electrical conductivity, it is obvious that the best candidates for the disperse phase are the highly conductive metals, such as Ag ( $\sigma = 6.3 \times 10^7 \, \text{S m}^{-1}$ ), Cu ( $\sigma = 5.96 \times 10^7 \text{ S m}^{-1}$ ), Au ( $\sigma = 4.42 \times 10^7 \text{ S m}^{-1}$ ), and Al ( $\sigma = 3.78 \times 10^7 \text{ S m}^{-1}$ ) [2]. Although the use of metal NPs in conductive inks and their printing by inkjet technology has been known for years, most of the relevant recent studies have focused on noble metals such as silver and gold NPs due to their high electrical conductivity and antioxidation properties [11]. Nevertheless, silver and gold are quite rare in the Earth's crust and therefore cannot be applied in large quantity. In this regard, non-noble metals, which also possess a high conductivity but are cheaper, can be considered as a possible replacement for noble metals. Copper can be a suitable candidate material due to its high conductivity (6% less than that of Ag) and lower cost [12]. A major problem is that copper possesses an inherent tendency to oxidize in ambient air. The presence of copper oxides on the surface of copper NPs can reduce the electrical conductivity and increase the required sintering temperature. Several studies address the oxidation problem, e.g. by minimizing the exposure time of Cu NPs in ambient air [13, 14], coating Cu NPs by a protective layer [15–19], or eliminating the surface oxide layer by sintering under reducing atmosphere [19–22]. Copper patterns with an electrical conductivity as high as  $2.5 \times 10^7 \,\mathrm{S \,m^{-1}}$ , which is a level comparable to that of noble metals, have been achieved through coating organic surfactants (such as PVP, oleic acid) and subsequently sintering in reducing atmosphere (such as in hydrogen or carboxylic acid with nitrogen as a carrier gas) [15, 19–21]. Nevertheless, all the employed copper NPs were prepared by wet-chemistry techniques, where the copper salts get reduced to copper and the corresponding reducing agents get oxidized.

In the past decades, various techniques have been developed to synthesize Cu NPs, including wet chemical methods as well as dry gas-phase processes. Although wetchemistry techniques offer unique possibilities of controlling particle shape and size, these approaches require inevitably precursor solutions, which commonly lead to impurities on the synthesized NPs. Besides, since chemical synthesis methods are often performed in a batch form and require a relatively long production period due to multiple steps which including stirring, centrifuging, washing and drying, most of these approaches are only appropriate for laboratory-scale synthesis but not suitable for scaling-up production [23]. To the best of the authors' knowledge, there are only a few researchers addressing this problem of scaling-up throughput. Deng et al [24] have presented a large-scale and highthroughput process for the production of copper NPs  $(d_p < 10 \text{ nm} \text{ based on transmission electron microscope})$ images) with a chemical reduction method. A throughput of 4.8 g per batch was reported by using copper acetate as the copper ions and PVP and CATB as the stabilizer. Lee et al [19] have reported a large-scale synthesis of copper NPs  $(d_p = 55 \text{ nm} \text{ based on dynamic light scattering data) by}$ chemically controlled reduction, where a high throughput of 60 g per batch was reached.

In contrast to wet chemical methods, gas-phase processes are usually continuous processes and enable to synthesize high-purity NPs, since these processes can directly and locally vaporize bulk materials to form NPs [25]. The synthesized NPs can be online deposited on a filter and collected after the production process. Recently, a transferred arc process has been developed for the synthesis of metal NPs such as copper, silver, zinc, and aluminum. It has been shown that the optimized transferred arc reactor is capable of producing pure copper NPs in the amounts of several grams per hour [26]. Copper NPs with the Brunauer-Emmett-Teller (BET) primary particle size of 83 nm could be obtained in a production rate of  $5.5 \text{ g h}^{-1}$  [27]. A scaling-up approach for high production rates, which is based on the parallelization of the number of transferred arcs (electrode pairs), has also been investigated. It was found that the production rate of copper NPs scales linearly with the number of the applied electrode pairs, whereas the primary particle size stays on the nanoscale. Based on BET measurement, the primary size of produced copper NPs is 79 nm. It has been pointed out that the particle size reduction could be adjusted by varying the carrier gas composition, applied power, or gas flow. However, the size reduction of NPs is on the expense of the production rates [28]. In table 1, an overview is given to summarize the production rates with the above-mentioned synthesis methods.

In this study, we use copper NPs synthesized by transferred arc discharge in the gas phase to prepare conductive films. Copper NPs could be continuously produced at a production rate of 1.2-5.5 g h<sup>-1</sup>, while their average primary particle size was maintained below 100 nm. Then, the produced copper NPs were used to prepare conductive inks applying ball milling. Through gravimetric observation and



**Figure 1.** Schematic of the reactor chamber applied to synthesize copper nanoparticles in this work, based on the optimized reactor by Stein *et al* [27].

scanning electron microscopy (SEM) analysis, we demonstrate that the dispersion stability is affected by the ball milling parameters. Copper inks with the metal loading of 40% by weight were applied for the preparation of copper conductive films by spin coating. Furthermore, to study their influence on the sintering process, the produced copper NPs were sintered in a different atmosphere such as nitrogen or reducing atmosphere. The electrical conductivities of sintered copper films were measured by the four-point probe method and the film thickness was determined by a profilometer. We show that copper films sintered under diluted reducing gas exhibit a low electrical resistivity, which is comparable to that of the copper patterns prepared from wet-chemistry particle synthesis.

#### 2. Experimental details

#### 2.1. Synthesis of Cu NPs in the gas phase

The optimized transferred arc reactor for metal NP synthesis has been reported earlier [26, 27]. In this study, a transferred arc reactor with crucible design 7 (figure 1) was adopted, since it was found to result in the highest production rates and smallest primary NP sizes of all the crucible designs. Furthermore, since the nitrogen arc has a significantly higher production rate than the other arcs (Ar, He, N<sub>2</sub> mixed with H<sub>2</sub>), we used N<sub>2</sub> with a purity of at least 99.9995% as the carrier gas. As shown in figure 1, there was two gas flows entering the reactor: one main carrier gas flow Q<sub>1</sub> and one cross gas flow (quench gas flow) Q<sub>2</sub>. The transferred arc can be ignited between the electrode pair in the reactor chamber. The tungsten cathode is a rod of 1.6 mm diameter, while the anode is designed as a graphite crucible, in which the desired material (copper shot, 0.8–2 mm, 99.5%, Alfa Aesar) is filled.

**Table 2.** Dispersion components and ball milling parameters applied in this work.

	Reference	Ink-1	Ink-2
Ethanol (wt%)	30%	30%	30%
Isobutanol (wt%)	15%	15%	15%
Glycerol (wt%)	15%	15%	15%
Copper NPs	_	40%	40%
Milling frequency (Hz)		30	30
Milling time (min)		180	50
Beads volume (ml)	—	4	1.5

The gas flow  $Q_1$ ,  $Q_2$ , and applied current were varied to obtain copper particles with different production rates and particle sizes. The detailed production parameters in this study used to obtain copper NPs are shown in the following section 3.1. The produced particles were directly collected from the filter and then stored in plastic vials. The collection process was conducted in the ambient air and the vials were also stored in ambient air.

#### 2.2. Preparation of copper conductive inks

Copper NPs (2.8 g) were added into a mixed solvent of ethanol (2.1 g), glycerol (1.05 g) and isobutanol (1.05 g) so that the metal loading of the ink was 40 wt%. Glycerol, isobutanol, and ethanol were all analytical grade and used without further purification. A high-energy ball mill (Mixer Mill MM400, Retsch GmbH, Germany) was used to deagglomerate copper particles in solvents. Zirconia grinding beads with a diameter of  $300 \,\mu m$  were added before ball milling to assist in reducing the copper agglomerates. The grinding jars utilized in this study have a volume of 10 ml. Ball milling parameters (milling time, vibrational frequency and beads to copper powder weight ratio) are varied to obtain a relatively stable conductive ink. Table 2 shows the detailed milling parameters as well as the corresponding ink components. After ball milling, the ink was extracted by suction syringe connected with a standard cannula ( $0.8 \times 80 \text{ mm}$ ) without using any other filter. Since the prepared inks have a high particle loading, the sedimentation process of the inks is difficult to observe visually. Therefore, the gravimetric method was used to observe the stability of produced copper inks. We extracted 50  $\mu$ l dispersion from the upper layer of prepared inks every 24 h and weighted it with an analytical balance (XS205, Mettler-Toledo AG, Switzerland), while the first measurement was conducted five hours after collecting the produced inks. In addition, a reference dispersion (table 2) without Cu NPs was prepared and weighted. The copper mass fraction can be calculated with the following equation:

$$W_{\rm Cu} = \frac{m_{\rm ink} - m_{\rm ref}}{m_{\rm ink}} \times 100\%,$$

where  $w_{Cu}$  is the copper mass fraction of the ink,  $m_{ink}$  and  $m_{ref}$  are the corresponding weight of 50  $\mu$ l dispersion, respectively. The prepared inks were then applied to produce thin copper films on glass chips (10 mm × 10 mm) by the spin coating technique (Spin 150, SPS Europe B.V. Putten) in



Figure 2. Experimental setup of sintering under reducing atmosphere with a dilution system.

ambient air. During spin coating, all the samples were rotationally accelerated to 6000 rpm (revolutions per minute) and continuously spun for one minute at a speed of 6000 rpm.

#### 2.3. Post-printing treatment—sintering

Sintering process was employed to remove the organic residues of copper films and reduce the copper oxides. Cu NPs and films were sintered with a lab-built sintering setup (figure 2), where N<sub>2</sub> (a purity of at least 99.9995%) was used as the carrier gas and formic acid (analytical grade) was filled in the bubbler as the reducing agent. A tubular furnace (MTF 12/38/250, Carbolite, England) was used for annealing the samples (copper NPs and copper films) at various temperatures for 60 min. Additionally, a ceramic boat was used as the sample holder and placed in the middle of the tube furnace during the sintering process. The gas flows Q<sub>3</sub> (50 sccm) and Q<sub>4</sub> (500 sccm) were controlled with the mass flow controllers.

#### 2.4. Characterization and measurements

Copper NPs collected from the filter were characterized by means of a BET analyzer (Gemini VII 2390a, Micrometrics instruments corporation, GA, USA). The measured specific surface area can then be used to estimate the primary particle size (BET size) of copper particles. Afterward, a transmission electron microscope (TEM, JEM-2200FS, Jeol, Tokyo) enabled to observe the morphology and surface property of the synthesized copper NPs. The microstructures of ground copper particles and sintered copper films are examined by scanning electron microscope (SEM, JSM 7500F, Jeol, Tokyo). The elemental analyses of copper NPs, as well as copper films, were determined by a scanning electron microscope (SEM, JSM 7500F, Jeol, Tokyo) equipped with an energy-dispersive x-ray (EDX) spectroscopy (Quantax, Bruker Nano GmbH, Germany) at 10 kV. X-ray diffraction (XRD) measurements were conducted to confirm the crystal phases of copper NPs as well as copper films. The x-ray diffractometer (type D8 Advance, Brunker, USA) was equipped with Cu–K $\alpha$  radiation (1.5406 Å). The thickness of copper films before and after sintering was measured by a stylus profilometer (XP-2000 Profilometer, Ambios



**Figure 3** Relationship between the production rate and primary particle diameter of the copper nanoparticles.

technology, CA, US). A four-point probe method (Keithley 4200 SCS, Cleveland, USA) was applied to confirm the sheet resistance of the sintered copper films. The electrical resistivity of the sintered copper films was then calculated by multiplying the sheet resistance and the film thickness. All the electrical conductivities reported in this work consist of averaged values from at least five measurements.

#### 3. Results and discussion

#### 3.1. Synthesis and characteristics of copper NPs

The transferred arc reactor applied to synthesize copper NPs in this study is optimized by Stein *et al* [26]. During the synthesis process, metal vapors of the desired material (copper) are generated by thermal plasma, which is realized by a DC (direct current) arc discharge. The copper vapors are immediately cooled by collisions with the flowing inert gas atoms; which induces homogeneous nucleation and subsequent condensation and coagulation to form a nanostructured solid [29]. Production parameters including applied



Figure 4. (a) TEM image showing the morphology of copper nanoparticles and (b) HRTEM images of the synthesized Cu nanoparticles showing an amorphous oxide layer, which were synthesized after three days.

current and gas flows were varied to find the relationship between the production rate and the primary particle size of copper NPs, as depicted in figure 3. The production rate displayed is based on the copper powders collected from the filter, but not on the evaporation rate of copper shots. It can be concluded that copper NPs with a larger primary particle size have a higher production rate. Theoretically, the power input of the arc is proportional to the applied current, when the electrode distance is fixed ( $\sim$ 3 mm in this work). Therefore, the larger the applied current, the more energy is supplied to the feedstock material in the graphite crucible, leading to an enhancement of material evaporation. A high material evaporation rate contributes to a high production rate, while the NP size increases significantly. This result is in good agreement with the description of Mahoney et al [29], which presented bigger primary particles and broader agglomerate size distribution with an increased evaporation rate. It can be seen that the production of the primary particle of 50 nm has a four times smaller production rate than that of 65 nm particles. As a general rule, particles with smaller size have the added benefit of lower sintering temperatures. Considering the practical requirement on Cu sample mass, copper NPs with BET size <60 nm were applied to prepare copper inks in this study.

Figure 4 shows the TEM images of copper NPs which were directly sampled from the aerosol and deposited on a TEM grid. It can be seen that copper NPs synthesized by the arc discharge process are a spherically shaped and agglomerates are present. In addition, the high-resolution transmission electron microscopy image reveals that an amorphous layer is present on the surface of each copper NPs and the layer thickness is independent of the primary particle size. The thickness of the amorphous surface layer of freshly produced copper NPs (synthesized after three days) is roughly 2 nm. It has been reported that a thin layer of 2–4 nm on the

surface of copper NPs is inevitable when wet chemical processes are used [15, 17]. The surface thin layer of Cu particles produce by gas-phase synthesis is therefore comparable to that of copper NPs synthesized by wet-chemistry methods. Because copper NPs are produced by direct evaporation of bulk copper materials, the formation of amorphous layer on the particle surface may be attributed to the impurity of carrier gas (N<sub>2</sub> with a purity of 99.9995%) and particle storage process (under ambient atmosphere).

The crystallographic characteristics of the synthesized copper NPs were analyzed by XRD with  $2\theta$  between  $30^{\circ}$  and 80°. As displayed in figure 5, the XRD pattern shows three reflections at  $2\theta = 43.4^{\circ}$ , 50.5°, and 74.0° for the (111), (200), and (220) crystal planes, respectively. These characteristic peaks represent the pure copper of a face-centered cubic symmetric (FCC) without any impurities. The average crystallite size  $d_{XRD}$  of synthesized copper NPs is calculated by the Rietveld refinement method, revealing an average primary particle size of 50 nm. EDX spectroscopy in figure 5(b) shows that the synthesized copper particles also have oxygen (O) peaks, which are attributed to the amorphous oxide layer on the surface of copper NPs. However, the XRD pattern did not show any significant Cu oxide peaks. This might be due to the presence of a very small amount of surface oxides compared to the large mass of bulk copper [30]. As previously illustrated, the main advantage of transferred arc discharge synthesis is that it is a continuous process and enables to produce pure copper NPs with a high yield. Unlike Cu NPs synthesized by the classical chemical methods, there is no surfactant as a protective layer on the particle surface. As we all know, copper NPs tend to be easily oxidized under ambient conditions in comparison to noble metals such as gold and silver. To address the oxidation problem, we suggest that the produced Cu NPs should be stored in the inert gas atmosphere and the exposure time to oxygen should be



Figure 5. (a) X-ray diffraction pattern and (b) EDX spectrum of copper nanoparticles synthesized after three days.

minimized. The presence of surface oxides could be eliminated or reduced by sintering under reducing atmosphere or adding reducing agent when preparing copper inks.

### 3.2. Effect of ball milling parameters on the dispersion stability of prepared copper inks

In the present work, we demonstrate copper NPs synthesized by transferred arc discharge are a potential alternative for the application in printed electronics, since the transferred arc synthesis is a continuous process and enables to produce copper NPs with higher purity. To study the applicability in electronic printing of conductive patterns, the produced copper NPs were applied to prepare copper conductive inks by means of ball milling technique. Because the NPs produced in the gas phase agglomerate always to large agglomerates, ball milling technique was used to disrupt the particle agglomerates, reduce them into smaller units, and therefore stably dispersed in the dispersing solvents. While the applied solvents and metal loading (40 wt% Cu) were kept constant, the major milling parameters (table 2), including milling time and grinding beads volume, were varied to obtain a relatively stable copper dispersion. Because the prepared dispersions possess a high metal loading, the dispersion stability is difficult to observe visually. In this study, we investigated the ink stability by recording the change of copper mass content in the upper dispersion. The gravimetric method used to observe the dispersion stability has been described in the previous section (section 2.2). For ideal ink, Cu NPs can be homogeneously dispersed in the dispersing solvent and Cu mass content in the ink remain constant due to the absence of particle sedimentation over a very long time. In contrast to ideal ink, over the prolonged storage time, Cu NPs may collide to each other due to Brownian motion, form large aggregates, and subsequently sediment under the influence of gravity. Therefore, less stable inks exhibit a significant mass change in the upper dispersion within a relatively short time. Figure 6 shows the change of copper mass content in the



**Figure 6.** Change of copper mass content in the upper dispersion of copper inks, which were prepared by low-energy milling (30 Hz, 50 min, 1.5 ml zirconia grinding beads) and high-energy milling (30 Hz, 180 min, 4 ml zirconia grinding beads), respectively.

upper dispersion of the produced copper inks. The copper inks were prepared by low-energy milling (Ink-2: 30 Hz, 50 min, 1.5 ml zirconia grinding beads) and high-energy milling (Ink-1: 30 Hz, 180 min, 4 ml zirconia grinding beads), respectively. It can be concluded that the dispersion stability of inks prepared from the produced copper NPs can be enhanced by decreasing the energy input of ball milling. As depicted in figure 6, inks produced with high-energy milling precipitated severely after one-day storage, and their metal loading decreased to 20 wt% after one-day storage. Nevertheless, the copper inks prepared with low-energy input could remain relatively stable for five days by showing a metal loading >30 wt% in the upper dispersion. After five days, a significant mass change in the upper dispersion was observed and a metal loading of approximately 20 wt% was recorded after two-week storage. In this study, we used copper inks



**Figure 7.** SEM images showing the microstructures of (a) unprocessed particles collected from the arc reactor, (b) copper particles after milling with high-energy input (30 Hz, 180 min, 4 ml zirconia grinding beads); (c) copper particles after milling with low-energy input (30 Hz, 50 min, 1.5 ml zirconia grinding beads).

after low-energy milling (Ink-2 from table 2) for further preparation of copper films. Besides, the applied inks were stored within five days so that all the applied inks have a metal loading >30 wt%.

To confirm the reason for different dispersion stability, SEM images were used to analyze the microstructure of copper NPs after ball milling, as shown in figure 7. It can be recognized that the copper NPs are deformed severely and displayed an irregular geometry after high-energy milling. This phenomenon results probably from the high energy milling process and the mechanical properties of the copper NPs. As illustrated by Joseph [31] and Gertsman [32], pure copper (FCC metal) exhibits high ductility as a result of its efficient crystallographic slip system, while both copper oxides (the red cuprous oxides  $Cu_2O$  and the black cupric oxide CuO) are brittle and prone to brittle fracture when grinding. Copper particles possess high ductility due to the presence of only minor amounts of copper oxides. When preparing inks with high-energy milling (30 Hz, 180 min, 4 ml zirconia grinding beads), these freshly synthesized copper particles undergo plastic deformation and re-weld to large agglomerates. Moreover, the particle agglomerates after low-energy milling did not have plastic deformation compared to the morphology of particles directly collected from the arc reactor (figure 7(a)). This finding gives a suggestion that the energy input of the ball milling process should be low to suppress the NP deformation and re-welding. But the energy supply should still be large enough to break soft agglomerates and obtain stable inks. In addition, the average size of ground copper particles with high-energy input is obviously larger than that of ground particles with reduced energy input. This can also explain the poor stability of copper inks milled with high-energy input.

As previously illustrated, the purpose of the energy supply by ball milling technique is to break the soft agglomerates of copper NPs. However, even after low-energy milling, the copper aggregates cannot be completely separated to primary NPs, as demonstrated in figure 7(c). The presence of these aggregates can accelerate the particle sedimentation and therefore deteriorate the ink stability. In the present work, the prepared copper inks were not yet optimized for long-term storage. From the point of view of further application as conductive inks, it is essential to further reduce the size of those copper aggregates in order to improve ink stability. Two strategies may contribute to enhance the copper ink stability. First, since the Cu NPs are synthesized by the transferred arc discharge method, there are no surfactant or ligand on the surface of particles. By adding the proper stabilizer or capping agents and selecting proper composition of the liquid vehicle, the copper aggregates and agglomerates in the dispersion may be prevented. Second, the milling parameters or other approaches for ink preparation should be systematically investigated. It should also be noted that the present work focuses mainly on the suitability of the synthesized copper NPs as a potential alternative for silver and gold NPs as well as chemically synthesized copper NPs in the field of printing electronics. In this regard, the ink properties, which are related to the printing performance like printability, viscosity, wettability and adhesion to substrates, long shelf time will be investigated in future work.

#### 3.3. Effect of sintering atmosphere on NPs

As mentioned above, the printed patterns based on NP inks are expected to possess a high electrical conductivity, desirably near that of bulk metal. Nevertheless, the electrical conductivity of the corresponding printed pattern can only be dramatically improved when a continuous interconnection between metallic NPs is formed. Hence, a post thermal treatment (thermal sintering) is usually applied to bond the metallic NPs and form a connected structure. In the present study, it was proved that the even the freshly synthesized copper NPs (after 3 d) were covered with a 2 nm surface oxide layer, as shown in figure 4(b). The presence of copper oxide layer can reduce the electrical conductivity of the printed patterns. Moreover, the required sintering temperature will also be enhanced, because the copper oxides have higher melting point than copper [22]. Therefore, the sintering process based on reducing atmosphere is applied to reduce or minimize the copper oxide surface layer. To investigate the effect of sintering atmosphere on the copper NPs, the following experiments were conducted. Copper NPs as prepared by the reported process were sintered under nitrogen and diluted reducing gas for 60 min at 300 °C. The gas flow is 500 sccm (Standard Cubic Centimeters per Minute) for nitrogen atmosphere. The setup of sintering under diluted reducing gas is illustrated in figure 2, where reducing gas flow through bubbler is 50 sccm and dilution gas flow of nitrogen is 500 sccm. We choose formic acid as the reducing agent filled in the bubbler because it can react with copper oxides and the formed organic copper salt can be reduced into elemental copper during sintering process [24]. Kim *et al* [20] reported that a gaseous mixture of 70% formic acid and 30% alcohol as the reducing gas enabled to obtain printed copper patterns with low resistivity (~4  $\mu\Omega$  cm). However, the appearance of sintered copper patterns displayed partially etched copper films. To address the etching problem, a dilution gas flow was added to minimize the etching of reduced copper NPs when sintering under reducing gas.

As shown by the SEM images in figure 8(b), copper NPs were sintered together to form a connected structure after sintering under diluted reducing gas. When sintering under nitrogen atmosphere, only partial necking between NPs with smaller primary size was observed, as displayed in figure 8(a). These microstructural observations demonstrate that formic acid as the reducing gas can effectively reduce the oxide surface layer of copper NPs. Thus, the copper NPs can be effectively sintered together without enhancing the sintering temperature.

#### 3.4. Electrical conductivity of sintered copper films

The influence of sintering temperature on the electrical resistivity of the printed copper films was also studied, as depicted in figure 9. All the investigated copper films were sintered under reducing atmosphere for one hour. The resistivity of sintered copper films decreases from  $46.3 \pm 1.4$  to  $5.4 \pm 0.6 \,\mu\Omega$  cm as the temperature increases from 200 °C to 300 °C. The lowest electrical resistivity of copper films sintered at 300 °C indicates that the reducing gas could effectively react with the surface oxides on copper particles and hence enhance the electrical conductivity of sintered copper films. However, copper films sintered at a lower temperature show a higher electrical resistivity. This is most likely due to the presence of organic residues from the prepared copper inks. One of the applied dispersing solvent is glycerol with the boiling point of 290 °C, which cannot be completely removed at sintering temperature <290 °C. As mentioned before, the most widely used methods to synthesize copper NPs are based on chemically controlled reduction of copper precursors. Copper NPs synthesized in the gas phase and their application as conductive inks was seldom reported. Table 3 presents the electrical resistivity of printed copper patterns reported in the literature, in which chemical reduction was used to synthesize the copper NPs. Jeong et al [17] and Park et al [11] sintered the printed copper film at 325 °C under vacuum and electrical resistivity  $>10 \ \mu\Omega$  cm were obtained. Kang et al [33] demonstrated a low electrical resistivity of 3.67  $\mu\Omega$  cm after sintering printed electrode in nitrogen at 200 °C. The low electrical resistivity is mainly attributed to the 10 times printing in order to reduce the pre-existing cracks and form a uniform thin layer. Kim et al [20] applied formic



Figure 8. SEM images of copper nanoparticles: (a) sintered under a nitrogen atmosphere; (b) sintered under diluted reducing atmosphere.



**Figure 9.** Electrical resistivity of copper films sintered at varied temperature, while all the copper films were sintered for one hour under diluted reducing gas.

acid as a reducing agent during sintering and low resistivity of  $4 \mu\Omega$  cm was achieved after sintering at 200 °C. It should be noted that Cu NPs of 7 nm were applied to form copper films. Small particles can be better sintered in low temperature in comparison with large particles, because small NPs have a higher proportion of surface atoms than large NPs [33]. In this

work, we applied copper NPs of approximately 50 nm to prepare copper films and sintered copper films at 300 °C under reducing atmosphere. The sintered copper films possess a low electrical resistivity of 5.4  $\mu\Omega$  cm, which is about three times higher than that of bulk copper. It can be concluded that copper inks prepared from gas-phase produced particles are competitive to inks prepared from chemically reduced copper NPs in terms of the resistivity of the printed patterns.

The SEM micrographs are displayed in figures 10(a) and (b), illustrating the surface morphologies of the copper films before/after sintering, respectively. It is confirmed that all the copper NPs were sintered together and a continuous film was formed. Besides, many pores are present in the sintered copper films, which may perform as the impurity in the conductive films. This could be the explanation of copper films with an electrical resistivity of 5.4  $\mu\Omega$  cm, which is about three times higher than that of bulk copper (1.7  $\mu\Omega$  cm). EDX spectra (figure 10(d)) demonstrate that oxygen and carbon along with copper are present in copper films without sintering treatment. After sintering in reducing gas for one hour at 300 °C, only copper element was observed in the EDX spectrum, indicating the organic residues from copper inks were completely removed after sintering at 300 °C. XRD spectrum of the spin-coated copper film before sintering was displayed in figure 10(d): the diffraction is mainly observed at  $43.4^{\circ}$ ,  $50.5^{\circ}$ , and  $74.0^{\circ}$  for copper with a face-centered cubic symmetry (FCC). Additionally, a minor peak for Cu<sub>2</sub>O was



**Figure 10.** (a) SEM images of a copper film before sintering; (b) SEM images of copper films after sintering; (c) XRD patterns of copper films before and after sinter; (d) EDX spectra of copper films before and after sintering, while the sintering parameters were maintained constant (300  $^{\circ}$ C, 1 h, diluted reducing gas).

Table 3. Comparison of the electrical resistivity of printed copper films with published reports.

Author	Particle size	Thickness of printed pattern	Sintering	Electrical resistivity
Kamyshny et al [2]	Bulk copper	_	—	$1.72 \ \mu\Omega \ {\rm cm}$
Kang et al [33]	10 nm	3736 nm	at 200 °C, N <sub>2</sub>	$3.67 \ \mu\Omega \ \mathrm{cm}$
Jeong et al [17]	$\sim \! 60 \text{ nm}$		at 325 °C, vacuum $10^{-3}$ Torr	11.5 $\mu\Omega$ cm
Park <i>et al</i> [11]	${\sim}45~\text{nm}$	_	at 325 °C, vacuum $10^{-3}$ Torr	17.2 $\mu\Omega$ cm
Kim et al [20]	7 nm	_	at 200 °C, reducing atmosphere	$4 \ \mu\Omega \ \mathrm{cm}$
This work	$\sim \! 50 \text{ nm}$	$\sim \! 1000 \ nm$	at 300 °C, reducing atmosphere	5.4 $\mu\Omega$ cm

also observed at  $36.6^{\circ}$ , representing the (111) plane. When freshly synthesized NPs were investigated by XRD, characteristic peaks of Cu<sub>2</sub>O were not found, as shown in figure 5(a). It can be concluded that copper oxides are mainly formed during the ball milling and spin coating processes, because both of the two processes were carried out in ambient air. Nevertheless, compared with the XRD spectrum of copper films without sintering, the diffraction peak of Cu<sub>2</sub>O disappeared after sintering in reducing gas and only diffractions of Cu were observed. This result also reveals that formic acid could react with the surface oxide of the copper NPs. One possible problem of sintering in reducing atmosphere is the possible etching problem, especially when it is applied to flexible electronics, where bendable plastic or paper substrates are used. As previously discussed, oxidation of copper NP can be minimized by storing them in inert gas and reducing exposure time to oxygen. However, a thin oxide layer on the particle surface is inevitable, which should be reacted and removed in order to obtain copper films with high conductivity. A possible alternative for this sintering under reducing atmosphere is adding reducing agent during preparing copper inks and subsequently sintering the printed pattern in a nitrogen atmosphere or under vacuum. To the best of our knowledge, Deng *et al* [24] have synthesized anti-oxidative copper paste by utilizing lactic acid as the reducing agent. Copper films after sintering in nitrogen showed anti-oxidative characteristics.

#### 4. Conclusions

Synthesis of NPs by transferred arc discharge has industrial relevance due to low cost and demonstrated scale-up potential. In this work, we demonstrated that copper NPs synthesized by transferred arc discharge are suitable for the application in printed electronics in terms of the electrical conductivity. Copper NPs can be continuously synthesized at a production rate of  $1.2-5.5 \text{ g h}^{-1}$ , where the production rate and the average primary particle size are depending on the production parameters such as applied current and carrier gas flow. The freshly produced copper NPs were determined to have a surface oxide layer of 2 nm, which is independent of the primary particle size. Copper inks prepared with lowenergy milling tend to have better dispersion stability. The prepared copper inks are subsequently applied to produce a thin film by spin coating technique. When using formic acid as the reducing atmosphere, the formic acid could effectively react with the copper surface oxide and hence enables to form a connected structure in the sintered film. Copper films sintered under diluted reducing gas were determined to have a low electrical resistivity of 5.4  $\pm$  0.6  $\mu\Omega$  cm, suggesting a potential for the replacement of silver or gold inks. Also, it could be concluded that conductive inks prepared from gasphase synthesized copper NPs are competitive to the conductive inks prepared from chemically synthesized copper NPs.

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Q Fu et al