



Blended Copper and Nano-Silver Screen-Printed Circuits on FTO-Coated Glass

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Abstract

Using a mixture of micro-copper and nano-silver in the production of screen-printed circuits has the potential to reduce material costs and cost variability. The fundamental premise of this study involved dispersing silver nanoparticles among the larger copper microparticles at selected ratios and subsequently sintering in order to establish their resultant electrical and physical performance. Commercial materials were mixed, printed, and sintered at two thermal regimes on fluorine-doped tin oxide (FTO)-coated glass substrate. The inclusion of 25% silver provided an appreciable reduction in electrical resistance from 4.21 Ω to 0.93 Ω , with further silver additions having less impact. The thermal regime used for sintering had a secondary impact on the final electrical performance. The addition of silver reduced the adhesion to the FTO substrate, with reduced film integrity. The results show that blending inks offers the advantage of enhancing material conductivity while simultaneously reducing costs, making it a compelling area for exploration and advancement in the field of electronics manufacturing.

Keywords Nano silver · copper inks · conductive ink · sintering

Introduction

The conductive circuit serves as an essential element in every electrical or electronic device.^{1,2} Although silver boasts excellent conductivity, stability in organic suspensions, and a commendable life span, its relatively high cost and susceptibility to price fluctuations are drawbacks.^{3,4} Copper ink, with its demonstrated applications in radio-frequency identification (RFID) aerials, hybrid silicon/printed flexible circuits, and thin film transistor electrodes, emerges as a promising alternative material.⁵

These applications focus primarily on polymer substrates, particularly polyimide, due to its ability to withstand higher sintering temperatures, along with its flexibility and compatibility with reel-to-reel processes. The objective of this study is to investigate a mixed ink consisting of copper nano/microparticles and silver nanoparticles that can be sintered at lower temperatures. This concept draws inspiration from

existing literature and the promising outcomes of previous studies utilizing the combination of copper nano/microparticle ink. One advantage of using larger particles in the copper ink is the reduction in oxidation levels due to the lower surface area-to-volume ratio.^{1,6} Copper nano/microparticle ink typically necessitates high sintering temperatures, which align with the sintering requirements of the nano-silver ink (250–500°C).⁷ Furthermore, copper ink encounters issues with oxidation during storage and processing, which can be mitigated by blending it with silver. The higher surface area of copper nanoparticles leads to a quicker oxidation rate compared to larger particles. The existing literature has explored the potential of blended ink to decrease sintering temperatures,³ but it has not examined the application on glass substrates coated with a fluorine-doped tin oxide (FTO) surface, which is the substrate of choice for many third-generation photovoltaics (PV), where material costs are critical. Therefore, the goal of this study is to assess the viability of using a silver–copper ink on FTO glass substrates and to determine whether it offers any potential improvements over conventional silver ink.

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Methods

The copper microparticle ink was supplied by Intrinsic (IMCE4118) and selected from a previous study, as it exhibited the lowest oxidation under H_2/N_2 atmosphere sintering, provided good conductivity, and was stable, showing no drift in resistance after 4 weeks of sintering. The sintering time and temperature were set within the operational window of copper ink and nano-silver ink. The silver ink was supplied by AGFA (ORGACON) and is a well-established material known for its high conductivity, low deposition, and ability to support high-resolution patterning applications. The 30–40 g blends were mixed manually, and 20 samples were produced from each batch. The mixing was carried out manually with three ratios of silver-copper ink as shown Table I.

The single metal and mixed ink were screen-printed using an ATMA semi-automatic printer, with an image consisting of areas that allowed for characterization of fine lines (200–600 μm wide). The images were printed to Tec-7 FTO-coated glass from NSG (nominal sheet resistance of 7 Ω/sq), with a 110-34 polyester mesh on an automatic ATMA flatbed printing machine. A Lenton model CSC 12/90/600H tube furnace was used, which could be sealed at either end and filled with a sintering atmosphere of a mix of 5% hydrogen and 95% nitrogen. Figure 1 shows the method steps.

After drying for 10 min at 80°C, the samples were subjected to two thermal regimes. The first involved a 30-min treatment at 250°C, which was determined to be the optimum temperature for copper material. The second regime followed the supplier's recommendation for silver ink, specifying a temperature of 275°C for 10 min. The TQC

test kit was used in this test to measure the adhesion. A JEOL JSM-7800 scanning electron microscope was used for surface analysis.

Results

At 25% silver content, the adhesive performance of the ink was mostly unaffected, with a small increase in the area removed as the silver content increased to 54% (Table I). As the silver content increased to 75%, more of the film was removed by tape, leading to complete delamination under testing. This behavior is similar to that observed with nano-copper ink, where sintering of copper nanoparticles reduces adhesion. It is believed that the sintering of nanoparticles and formation of a denser conductive film negatively impacts the ink–substrate interface (Table II).

All electrical characteristics showed improved conductivity when the silver content was increased (Fig. 2). The copper 600-micron line resistance was 4.21 Ω , while the silver was 0.16 Ω (Fig. 2a). There was an initial sudden reduction as silver was added followed by a more gradual decrease as silver content increased further. This was common for both thermal sintering regimes. Similar trends were observed for the sheet resistance, Fig. 2b, contact resistance, Fig. 2c, and absolute resistivity, Fig. 2d.

The inference which can be drawn from these results is that the sintering of the copper provides a less conductive feature than that produced from the silver ink. This is likely a result of the oxidation of the copper material during the wet, drying, or sintering process, resulting in a less densely packed film with microparticles. The film density and ease of a conductive pathway can be seen in Fig. 3, where the silver nanoparticles sinter to form a more continuous film.

X-ray diffraction was used to identify changes in the structure and possible oxidation due to the sintering process. Figure 4 shows the diffraction peaks observed at 2θ 111, 200, and 220 planes in all mixed inks, indicating the presence of copper and silver. The relative intensities of the peaks are in line with the ratios of the silver and copper components. No additional peaks are visible due to the sintering process, indicating little chemical change during

Table I Mixed ink ratio

| % (g) | Ag (g) | Cu (g) | Total W | % Ag-Cu |
|--------------|--------|--------|---------|---------|
| 25 Ag, 75 Cu | 7.59 | 22.71 | 30.30 | 25 |
| 54 Ag, 46 Cu | 20.37 | 17.24 | 37.61 | 54 |
| 75 Ag, 25 Cu | 30.17 | 9.85 | 40.02 | 75 |

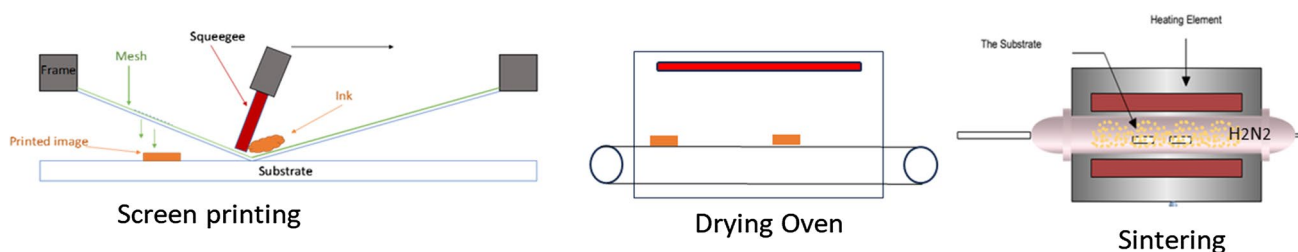
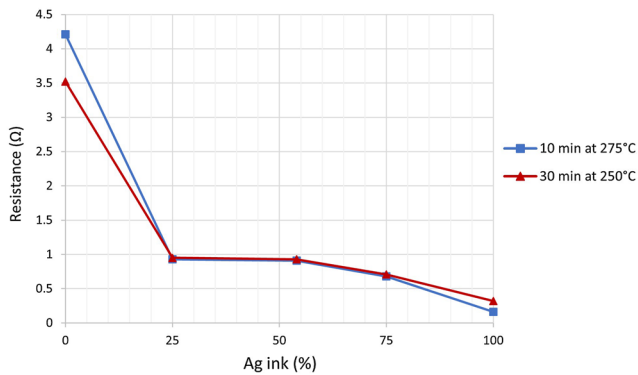


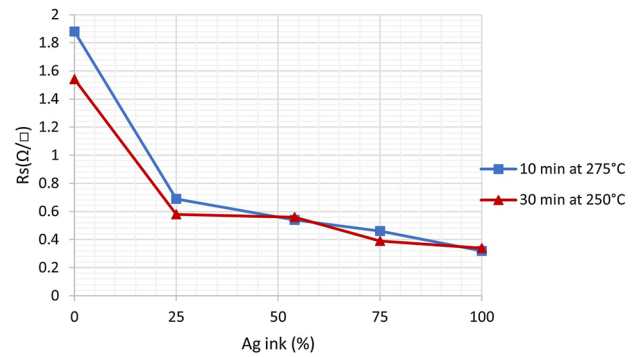
Fig. 1 Schematic diagram to explain the method steps.

Table II Physical characteristics of conductive films sintered at 250° C for 30 min

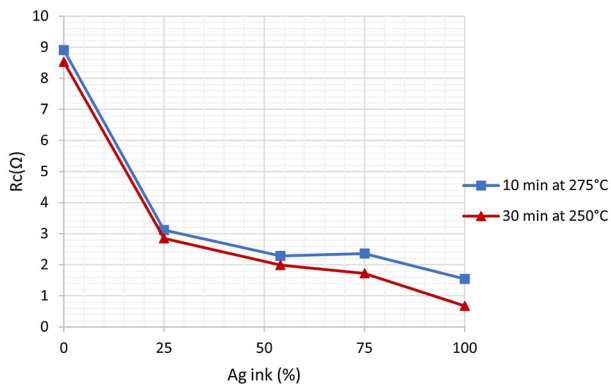
| %Ag | 0 | 25 | 54 | 75 | 100 |
|-------------------|----|----|----|----|-----|
| Sample after test | | | | | |
| Tape after test | | | | | |
| % Tape removed | 15 | 15 | 22 | 35 | 71 |
| Scratch | 5B | 5B | 4B | 3B | 1B |



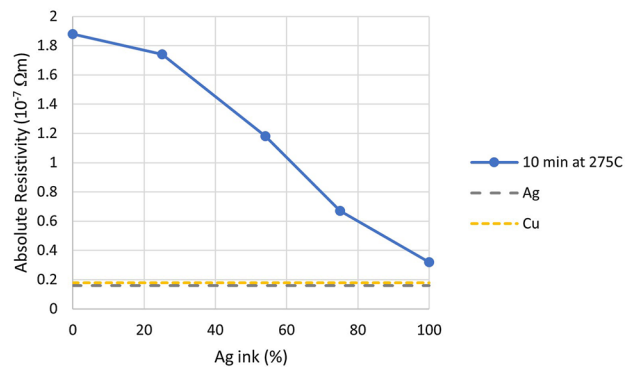
(a) Line resistance for a 30 mm x 600 micron line



(b) Sheet resistance



(c) FTO- conductive film Contact Resistance



(d) Absolute resistivity

Fig. 2 Electrical characteristics of the mixed inks sintered at the two thermal regimes: (a) line resistance, (b) sheet resistance, (c) FTO-conductive film contact resistance, and (d) absolute resistivity.

the sintering process. Three characteristic copper peaks are clearly present at 2θ values of 43.27° , 53.42° , and 74.12° , corresponding to (111), (200), and (220), respectively. These

characteristic peaks confirm that a face-centered cubic (FCC) copper phase is present. There is also no evidence of the Cu_2O phase at 36.6° , which indicates that minimal

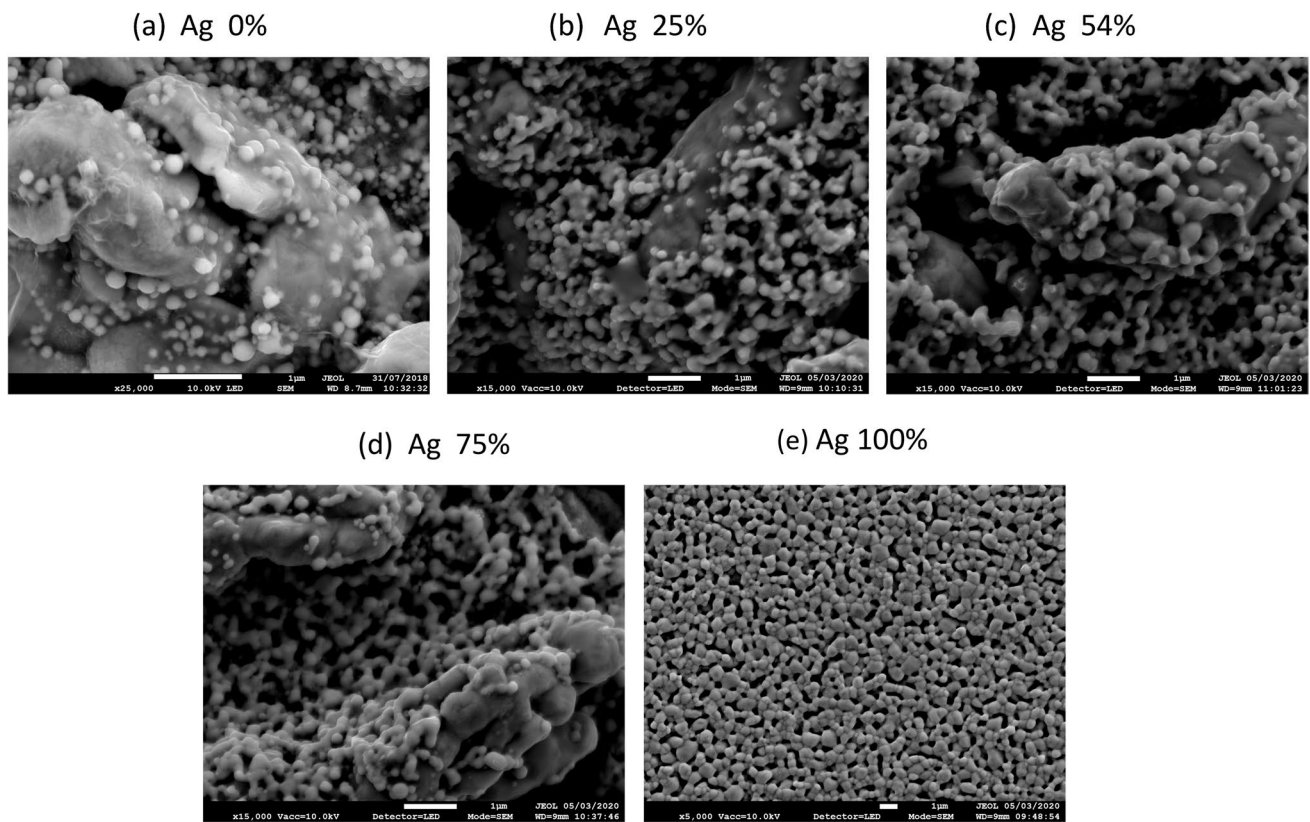


Fig. 3 Microstructure of the sintered conductive films.

oxidation has occurred. Also, the presence of peaks at 2θ values of 26.2° , 38.19° , and 44.22° is indicative of a layer of silver, which should provide extra protection to the copper against oxidation.⁸

Discussion

This study addresses several points that have both scientific and practical implications. Firstly, it demonstrates that incorporating a small amount of nano-silver ink into micro/nano-copper ink can effectively reduce resistance and enhance conductive performance. The addition of 25% nano-silver was shown to decrease sheet and line resistance by up to three times, all while maintaining strong adhesion on FTO-coated glass substrates. This finding offers a cost-effective solution for improving conductivity. Moreover, the study suggests that further optimization of the silver–copper ratio could potentially achieve an even better balance between conductivity and cost. Initial cost estimates suggest an approximately three- to fourfold reduction in the bill of materials. Any such cost analysis would need to examine the additional costs of producing a controlled reducing environment. The blending of silver with copper ink had a positive impact on electrical performance, which was more

than could be explained by the lower resistivity of silver alone. It is postulated that the silver improved the conductive structure and pathways of the film, enabling the large copper particles to be the primary backbone of conduction with inter-micro-copper particle junctions being filled with fully sintered silver nanoparticles. The lack of visible nano-copper sintering (Fig. 3a) suggests that the presence of microparticles prevents visible sintering of the copper nanoparticles. However, this phenomenon is not observed with the silver ink (Fig. 3c), and the study proposes that the presence of silver may help prevent copper oxidation during the sintering process. It is also plausible that silver particles react preferentially with any available oxygen, thereby inhibiting the formation of copper oxide.

Conclusion

The work conducted in this study has demonstrated the potential of copper/silver mixtures as a viable method for producing highly conductive and physically durable structures on FTO-coated glass. The study achieved success by formulating a blended ink in which the addition of 25% nano-silver achieved a significant fivefold reduction in conductivity ($4.21\text{--}0.93\ \Omega$) while still leveraging the potentially

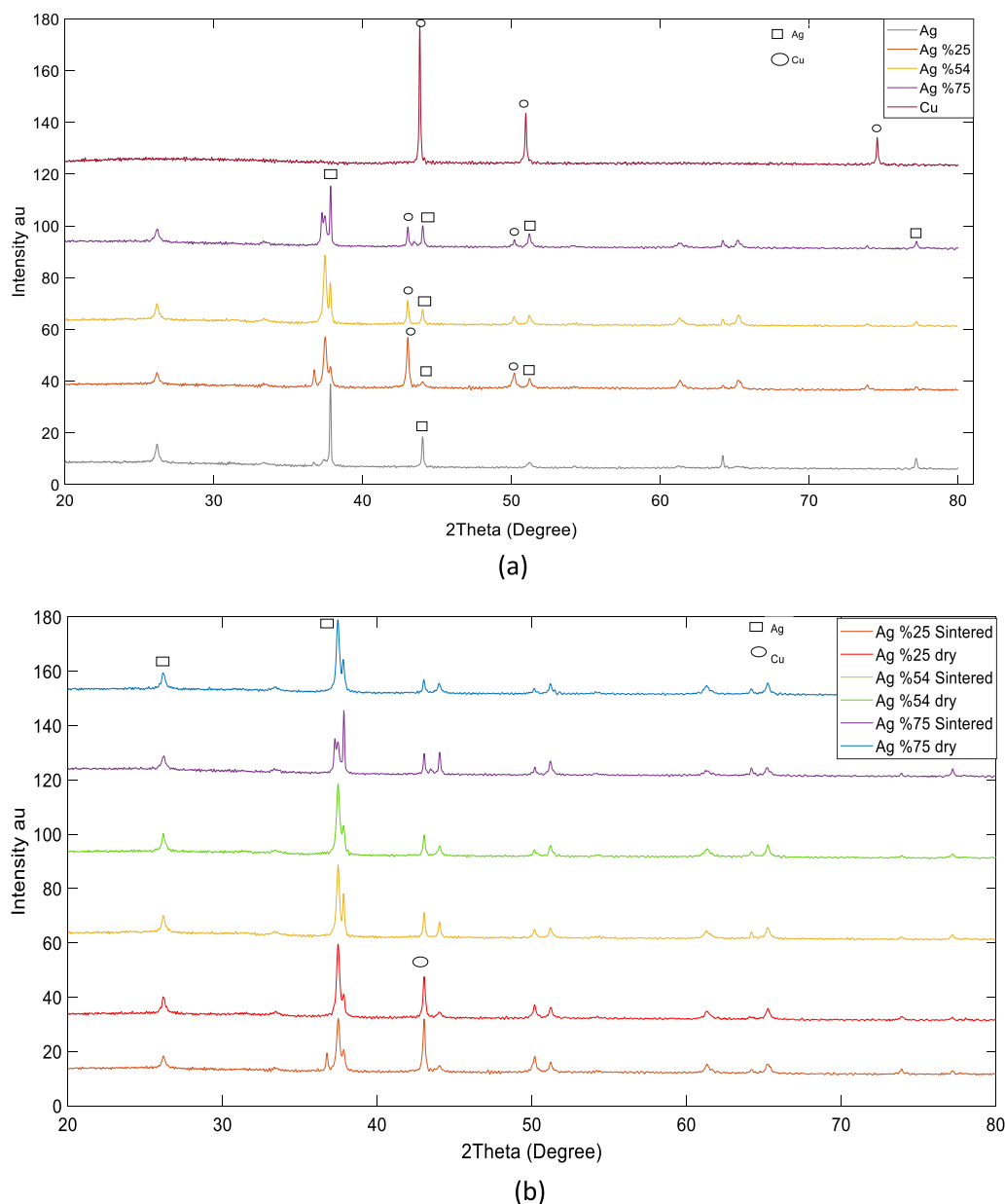


Fig. 4 (a) X-ray diffraction of the mixed ink: (a) XRD comparison for each film sintered at 5% H_2/N_2 for 30 min at 250°C in comparison to the unmixed material, (b) XRD response of each mixed metal

ink before (dry) and after the sintering process for 30 min in a H_2/N_2 environment for 250°C.

lower cost of copper, the essential conductive material. The blending of copper nano/micro-inks with silver nanoparticles offers the advantage of preserving adhesion on FTO substrates while simultaneously enhancing material conductivity. A significant consideration is that achieving precision and uniformity in the deposition of materials at larger scale can be challenging.

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Data availability Data will be made available on request.

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