

Copper sintering for microelectronics application

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Abstract

In this paper, we report the recent research and development at the Technische Hochschule Ingolstadt (THI) on Cu based sinter pastes and conductive inks for applications in the field of high power electronics packaging and printed electronics. Cu based sinter pastes have been developed for low temperature (250-275°C), rapid (3-5 min) and low pressure (≤ 20 MPa) die-attach bonding process in an open bond chamber under N₂ flow. A simple two-step sintering process similar to industrialized Ag sintering processes is implemented, thereby offering an attractive, cost-effective alternative that can be used on the same equipment currently used for Ag sintering under pressure. The average shear strength of 60 MPa which is comparable to commercial micro-scale Ag sinter pastes under same processing conditions is reported. Based on the development of Cu die-attach materials, also Cu inks for printed electronics were developed by complexing Cu(II) formate salt with an alkanol amine generating in-situ nanoparticles (ranging from 100-500 nm) after decomposition at lower temperatures ($< 160^\circ\text{C}$). Fine Cu traces of ~ 100 μm width are realized through ink-jet printing. The sintered inkjet printed traces gave a bulk resistivity value of 102 $\mu\Omega\text{cm}$ for a trace of thickness 2.5 ± 0.5 μm .

1. Introduction

Solid state sintering has emerged as the preferred die-attach process for high-temperature applications because it produces near-bulk interconnects suitable for high-temperature operation. Ag sintering has been extensively researched and industrialized as a reliable interconnect technology for high temperature ($> 175^\circ\text{C}$) applications. However, due to its high cost and challenges arising due to the susceptibility to electromigration; in the last decade Cu sintering has emerged as low cost alternative for reliable interconnect technology for high temperature application [1,2]. Due to its high electrical conductivity, good oxidation resistance and low sintering temperatures Ag has been extensively used and commercialized as metal based inks/pastes for microelectronics as well as printed electronic applications [3,4,5]. However, the high cost of Ag and challenges arising due to the susceptibility to electromigration have motivated the re-search for alternatives [4]. Cu due to its high electrical conductivity (second to only Ag), low cost (about 1 % the cost of Ag), higher abundance (1000 times more than Ag) and

lower electromigration tendency than Ag has proved to be the most promising alternative to Ag [3,6]. The biggest challenge of using Cu is its high affinity to oxidation especially at elevated temperature which leads to formation and growth of a surface oxide layer – hindering the sintering of Cu particles. Numerous methods such as use of reducing atmosphere (H_2 , formic acid enriched N_2), use of solvents with reducing effects to reduce Cu oxide (Cu_2O) or use of protective/capping agents have been deployed to avoid oxidation [6]. In this paper, the use of Cu based conductive inks/pastes will be discussed further in application of Cu die attach material for microelectronic packaging and printed electronics.

For large-scale adaptation of copper sintering by the industry, it is important to ensure comparable or better results to Ag sintering under the same processing parameters, which are $T \leq 275^\circ C$, $t \leq 5$ min and $p \leq 20$ MPa. With this as focus, three novel approaches are proposed namely:

1. Sintering with microscale brass metal flakes, where Zn is selectively etched from the flakes to create enhanced surface modifications, enabling low temperature, low pressure sintering and rapid sintering returning high shear strength values of 60 MPa [1,2].
2. Cu salt-based sinter pastes, where Cu(II) formate was used as an in-situ source of Cu nanoparticles during sintering, helping to realize a thin (10-12 μm) sintered interconnect with near bulk-like density and a high shear strength of ~ 70 MPa [2].

These approaches have helped in realizing a well-sintered interconnect even at a low solids content of only 60 wt% in the paste formulation, compared to commercially available Ag sintering pastes with ~ 90 wt% solids content. A detailed discussion with results will be presented in the following section.

Metal sintering also plays an important role in printed electronics technology that involves innovative materials such as functional conductive inks that are printed or deposited on a suitable substrate to fabricate electronic devices. In recent years, there has been rapid development and commercialization of metal nanoparticles (NPs) based inks owing to its high metal loading content and good electrical conductivity. However, these inks have a complex synthesis route and requires higher sintering temperature ($>200^\circ C$) to form highly conductive traces by removal of capping agents around nanoparticles [7]. Aside this, they have issues of agglomeration and storage at room temperature. On the other hand, metal particle free inks offer facile synthesis route, good stability and conductive traces can be formed at lower temperature ($<170^\circ C$) which enables fabrication on temperature sensitive substrates such as PET etc. [6]. The metal exists as an ionic form in these inks which prevents the problem of agglomeration and storage [7]. Owing to these advantages, rising interest has been shown in development of Ag and Cu based particle free inks. The Cu particle free inks are formed by mixing Cu salts containing Cu metal precursor, complexing agents that

help in decreasing the decomposition temperature of the Cu salts and solvents that help in improving the properties of the ink related to printing purpose. Compared to conventional Cu nanoparticle inks, there is an in-situ Cu NPs generation after the decomposition of Cu salts. In this paper, a detailed discussion about the synthesis of Cu particle free inks, inkjet printing process and post sintering characterization of printed traces will be presented.

2. Cu Die attach material for microelectronic packaging

Die attach and sintering with copper micro-scaled flakes have shown to be a reliable alternative to silver sintering. Sintering pastes are designed in a way to reduce the oxide layer of the flakes back to metallic copper and avoid further oxidation [8].

A pressure-less copper sintering procedure has still to be developed, despite this the processes with pressure show results comparable with silver but costs fraction of the price. The brass flakes underwent a process of etching in concentrated hydrochloric before being used. This step dissolves the zinc in the alloy leaving a more porous and activated copper surface. The etched flake enables more contact points for sintering but also are more prone to oxidation. Fig. 1 shows SEM of the brass flakes before and after the etching process. The pastes are prepared simply by blending the flakes with a mixture of binders to give good consistency for a good printability, and to prevent oxidation. The sinter process is composed of two major steps: the pre-drying and the sintering. The predrying is performed after the printing simply by heating the paste. Excessive binder is removed by predrying that may cause excessive squeezing out of paste during sintering under pressure.

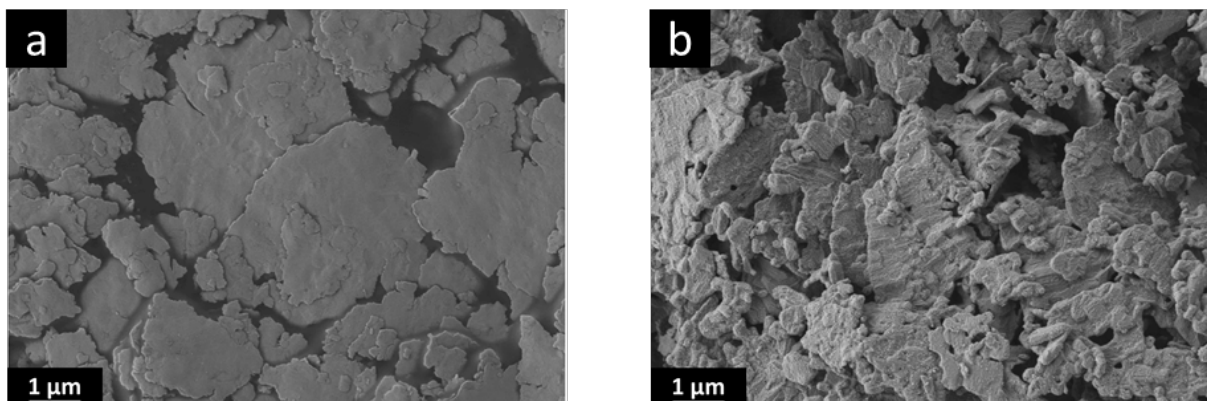


Fig. 1: SEM of brass flakes, (a) before etching and (b) after etching

2.1. Performances of the pastes

Die attach applications of the discussed pastes are very promising in terms of mechanical properties. In Table 1 some results of shear strength of the bonded chips are reported.

The cross section of the interconnection shows a decrease in porosity with the addition of the complex to the paste (keeping the binders combination equal) that also follow the trend of shear strength.

Pastes	Composition		Sintering conditions (pressure, temperature)	Shear strength of bonded chips
	Cu type	Binder		
Paste A	Cu flakes	Alcohol-Glycol based binder	10 MPa, 275°C	34±6 MPa
Paste B	Etched brass flakes	Alcohol-Glycol based binder	10 MPa, 275°C	63±6 MPa
Paste C	Etched brass flakes	Glycol based binder	20 MPa, 250°C	44±26 MPa
Paste D	Hybrid paste	Glycol based binder	20 MPa, 250°C	82±28MPa
Paste E	Cu(II) formate	Alcohol-Glycol based binder	10 MPa, 275°C	50±10 MPa

Tab. 1: Shear strength results for the freshly developed copper sintering pastes

In Fig. 2 SEM of the interconnects made with the five pastes are shown: The use of the etched flakes improved the interconnection in terms of porosity. All pastes are prepared using Cu flakes. Paste D is a hybrid paste.

The predrying step is essential to assure a low porosity, avoiding excessive degassing during sintering.

Another approach is the development of a paste made with only Cu formate dehydrated and the same combination of binders used for the original pure copper flakes. This paste gives shear strengths up to 60 MPa, showing how promising in situ formation of copper nanoparticles may be. Transient thermal analysis of the interconnect indicates a performance improvement by ~ factor 2 compared to traditional SAC305 solder interconnects [9]. A SEM of this interconnect is represented in Fig. 2(e).

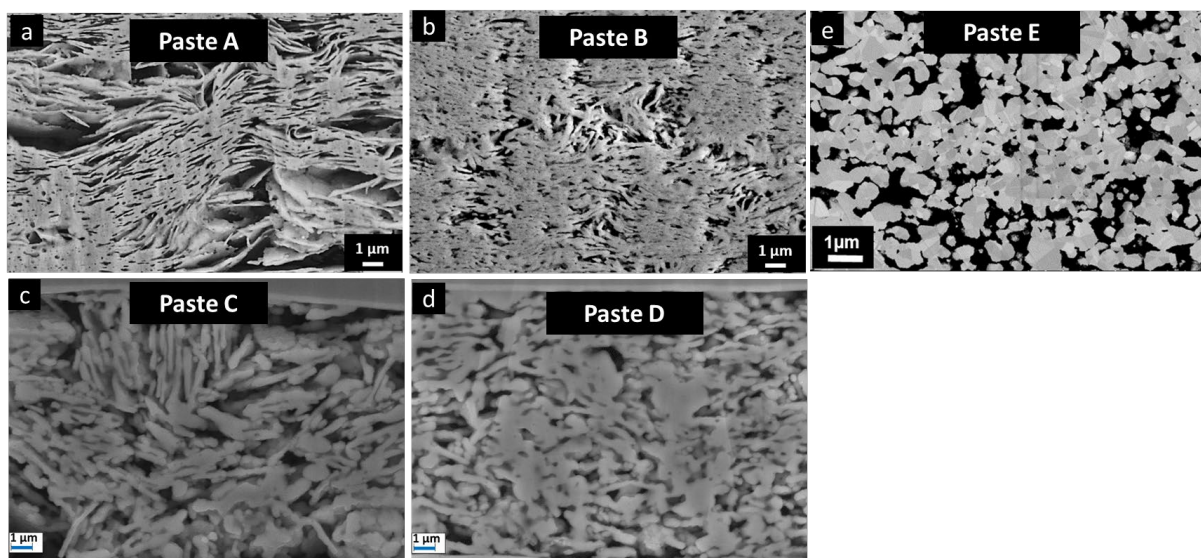


Fig. 2: SEM of the paste interconnect: (a) Paste A: alcohol-glycol based binder and Cu flakes, (b) Paste B: alcohol-glycol based binder and etched brass flakes, (c) Paste C: etched flakes and glycol based binder, (d) Paste D: hybrid paste with in-situ realized Cu nanoparticles and etched flakes and (e) Paste E: Cu(II) formate and alcohol-glycol based binder without any flakes.

In summary these novel copper pastes can give results even >100 MPa with a temperature of only 250°C. The problem to avoid oxidation remains, and sintering under nitrogen is required.

Mild reducing properties from the binder ensure a good sintering of the paste, this may lead to various solutions for low temperature copper sintering materials.

3. Cu particle free inks for printed electronic application

3.1. Synthesis of Cu particle free inks

Cu(II) formate decomposes to metallic Cu, when heated at ~200°C, as shown in the equation below:



However, this decomposition takes place at a higher temperature ($\geq 200^\circ\text{C}$) which is not suitable for many flexible substrates. To lower the decomposition temperature of Cu(II) formate, it is coordinated with organic ligands such as alkylamine, pyridine derivatives and alkanolamines. In this paper, the ink formulation consists of Cu(II) formate salt as the Cu metal precursor and the complexing agent consists of an alkanolamine, which reduces the decomposition temperature of pure Cu(II) formate to less than 170°C or even further.

Cu(II) formate tetrahydrate ($\text{Cu}(\text{HCOO})_2$), CuF is mixed with alkanolamine at a specific molar ratio to prepare a copper complex. In the alkanolamine, the ligand binds with Cu atom through two sites (N and O). Such a ligand is called a bidentate ligand and the corresponding chelating complex is more stable than other monodentate ligands. The complex ink prepared with CuF, and alkanolamine was then drop deposited on a flexible polyimide substrate of thickness $125\ \mu\text{m}$ using a pipette. The prepared sample was then sintered at 160°C for 10 minutes under formic acid enriched nitrogen atmosphere to check the formation of Cu NPs from the complex ink. The microstructure and sheet resistance of the thin metallic Cu film formed on the polyimide (PI) film was examined using a scanning electron microscope and a four point probe respectively. Fig. 3 shows the decomposition of CuF complex ink (Fig. 1(a)) to metallic Cu film (Fig. 1(b)) after the sintering procedure.

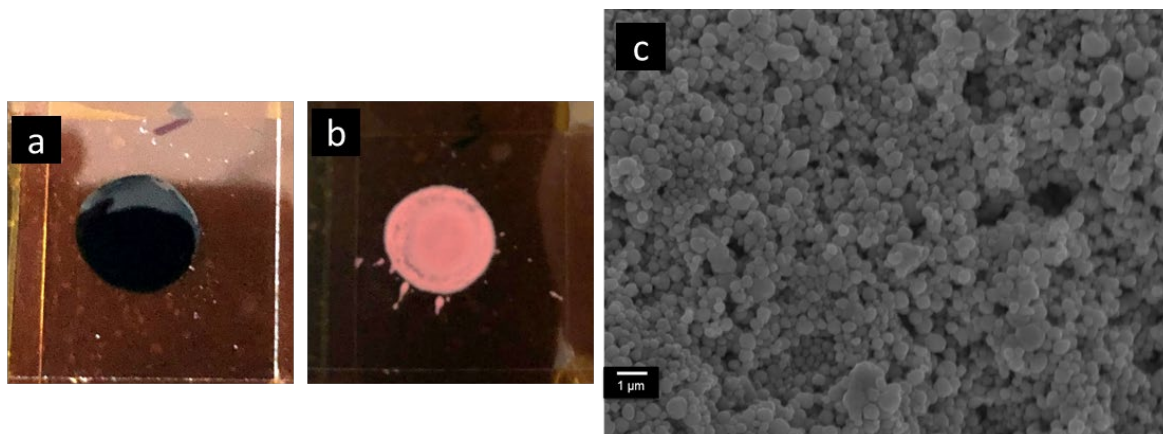


Fig. 3: Cu thin film formed on PI substrate after sintering at 160°C for 10 minutes. (a) shows the drop deposited Cu complex ink, (b) shows the metallic Cu film after decomposition and (c) shows the SEM image of Cu NPs formed after decomposition.

The SEM image (Fig. 1(c)) shows the formation of Cu NPs in the range of 100-500 nm and agglomeration of smaller particles into larger particles during the sintering process. The sheet resistance of the sintered drop deposited trace on PI substrate was measured at $0.096\ \Omega/\text{sq}$.

3.2. Inkjet printing of Cu particle free inks

Inkjet printing involves drop by drop deposition by ejection of conductive ink droplets from printhead nozzle onto a printable substrate. For the printing of Cu complex ink, a piezoelectric drop on demand inkjet printer (DMP-2850, Fujifilm Dimatix Inc., USA) is used. The principle behind inkjet process is creation of pressure pulse in the ink chamber by a piezoelectric actuator to eject ink droplets [10]. To achieve good printability, the properties of the ink such as viscosity and surface tension play an important role in drop formation and drop deposition on the substrate. This requires good tailoring of ink properties using different solvent combination such as ethylene glycol, ethanol, etc.

to achieve ink viscosity and surface tension in range of 25-30 mPa.s and 30-35 mN/m respectively.

Based on the preliminary investigations, the Cu complex consisting of CuF, and alkanol amine is mixed with a solvent mixture of ethanol and ethylene glycol to formulate a low viscosity ink (28 mPa.s) for inkjet printing. Ethanol was added to adjust the viscosity of the ink and ethylene glycol was added to increase the contact angle (from 12° to 50°) of the ink droplet formed on the PI substrate to prevent uneven spreading and formation of irregular pattern after printing. Fig. 4(a) and Fig. 4(b) shows the contact angle of the ink formed without ethylene glycol and with ethylene glycol. Ethylene glycol also acts as a stabilizing solvent which decreases the rate of evaporation of the ink.

A 10 pL drop volume cartridge is used to print 15 layers of the ink on a PI substrate of thickness 125 μm with drop spacing of 15 μm and at a jetting voltage of 40 V using the inkjet printer. The substrate temperature is maintained at 60°C to further improve the printability of the ink and to initiate partial evaporation of ethanol to form denser printed traces after every printing pass using a heating plate built within the printing system. After printing, a two-step fabrication process was designed involving subsequent pre-drying at 110°C for 10 min under a slow ramp rate of 5°C/min followed by faster sintering at 200°C for 30 min under formic acid enriched N₂ atmosphere. The slow pre-drying step helped in controlling the bubbling during the decomposition process of Cu complex to metallic Cu and sintering at 200°C helped in removal of ethylene glycol from the sintered traces. Fig. 4 also shows the inkjet printed Cu particle free inks: (c) after printing, (d) after sintering and (e) SEM image of sintered trace.

From the sintering experiments of inkjet printed traces, it was also found that using the given binder formulation, reduction of the copper complex to Cu begins between 120-130°C. The printed Cu traces after sintering gave a sheet resistance value of 0.408 Ω/sq for a trace of length 20 mm and width 1.2 mm. From the profilometer measurements, the traces showed an average thickness of $2.5 \pm 0.5 \mu\text{m}$ with the bulk resistivity value at 102 $\mu\Omega\text{cm}$ which is 60 times of the bulk resistivity of pure Cu. This is due to the formation of larger spherical Cu particles that are sparsely distributed and hence the bulk resistivity is high (see Fig. 4e).

Thicker traces need to be printed for appropriate conductivity. Further investigations are ongoing with different binder combinations and process setting to control on the one side the particle formation and growth and on the other side to reduce the sintering temperature below 160°C, which would help in fabricating conductive traces onto temperature sensitive flexible substrates such as PET.

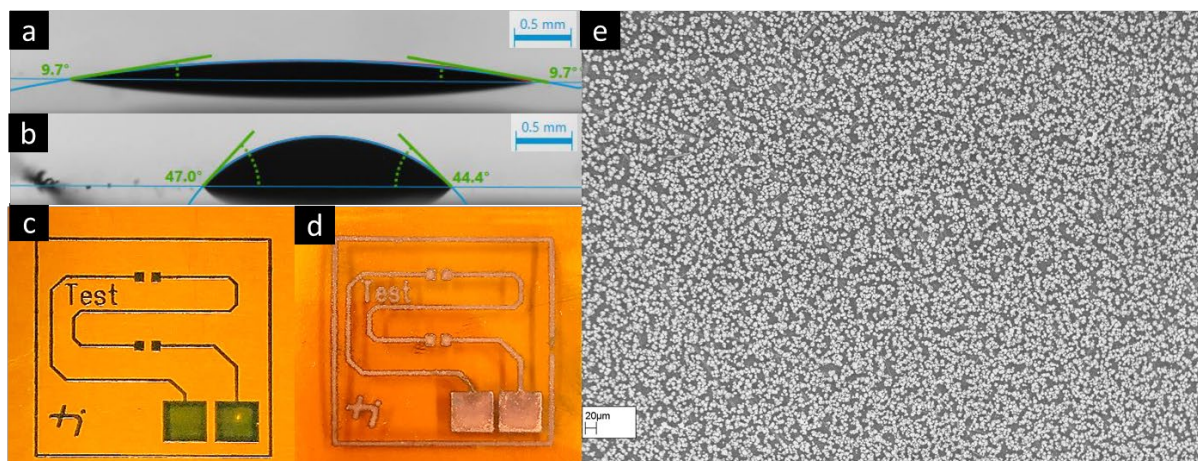


Fig. 4: (a) and (b) shows the contact angle of Cu particle free ink formed on the PI substrate without ethylene glycol and with ethylene glycol, (c) and (d) shows the inkjet printed Cu particle free ink after printing and after sintering respectively. (e) shows the SEM image of the sintered traces after inkjet printing.

4. Conclusion and outlook

Extending the know-how from the die-attach paste development, particle free inks were developed based on a combination of Cu(II) formate as precursor and an alkanol amine as a complexing agent. Fine Cu traces of 100 μm width are realized through ink-jet printing at low temperatures (160°C). However, particle free inks pose the challenge of high volume shrinkage, due to low solids content (<10 wt%). Therefore, slow ramp rates are necessary while using conventional methods to ensure efficient degassing of the organics. Another alternative is to tailor the ink formulation such that a rapid evaporation of the organics is ensured by intense pulse light sintering. The low solids content also poses a challenge in realizing thick traces (>1 μm) with high electrical conductivity due to the sparse population of the in-situ realized nanoparticles. A possible strategy to overcome this, which is of high interest for printing copper traces on 3D parts, is the use of hybrid inks, which are a combination of flakes and Cu salts, ensuring a solid content of at least 50 wt% which in case of Ag inks has shown to be effective in realizing highly conductive traces.

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