**1.Introduction**

Printed Electronics is a technology that produces electronic devices on various substrates (such as glass, paper, polymer, etc.) through various printing techniques (such as drop coating, spin coating, Inkjet Printing, Screen Printing, etc.) The research of printing electronics focuses on the development of new conductive inks, the improvement of printing processes and the expansion of application fields.

Metal organic decomposition (MOD) and nanoparticle (NP) is the two core techniques of producing conductive ink. Due to various shortcomings of NP inks (such as high cost, clogging nozzle, etc.), this project focuses on copper - and silver-based MOD inks. Its basic principle is to let the metal compound and ligand reaction to form a metal ink, through the sintering method to deposit the metal onto the substrate, the rest of the substance through the gaseous phase out of the system.

Key points of this study include determining the optimal solution combination and various parameters in the coating process. The main experimental results of concern include low resistivity, stability of the coating, and adhesion to the substrate. In addition, the sintering temperature used in the experimental process is also an important parameter. Lower temperatures mean compatibility with more substrates and broader application in various fields. Therefore, reducing the sintering temperature is one of the goals of this research.

In this project, copper and silver are selected as coating metals, ethanolamine (EA) and 1-aminopropan-2-ol (AP) is used to prepare a series of inks. They were combined to form four different base inks: Cu-EA, Cu-AP, Ag-EA, and Ag-AP. Then, new inks were obtained by mixing them in pairs. The ratio at which these inks are mixed is also a question discussed in this study. These inks are deposited on glass and polymer respectively.

After coating various substrates, the films were characterized by XRD, SEM, contact angle, etc., in order to obtain further properties of the films.

MOD technology has a very wide range of applications, such as wearable flexible displays (for health monitors, high-end clothing, etc.), radio frequency tags for product tracking, printed bendable solar cells, and more.

Its advantages include lower production costs, more energy saving and environmental protection, flexibility that can be printed on flexible substrates, suitable for mass production, and high flexibility that can be customized on demand. Of course, it also has certain limitations, such as lower electron mobility and long-term stability than traditional silicon-based devices, so it is necessary to continuously develop better inks.

**2.Review**

MOD precursors are composed of metal compounds and ligands. While the selection of metal components may be somewhat limited, there is a vast array of ligands to choose from due to their variety. In this literature review, focus on metals Cu and Ag, and various ligands for each metal will be considered. Synthesizing new MOD precursors can be achieved by combining different ligands with metals from previous studies or by employing ligands that have not yet been explored. When selecting a ligand, it is crucial to consider three primary factors: the decomposition temperature, with a preference for lower temperatures, the electrical resistivity after coating, stability and purity.

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Figure . Schematic depicting the synthetic route of MOD precursors involved in the deposition and sintering process of metal coatings From S.P. Douglas et al. (2021) 9

Knapp group result show the basic principle of forming thin metal layer by Metal organic decomposition. Start with metal salts, usually powders. It is mixed with ligand and reacts, during which a small amount of thickener, dispersant and adhesion accelerator are added. During sintering process, by-products are evaporated and leave the system, forming a thin metal layer.

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Figure . process of synthesis Ag-AP-based MOD precursor. From Ye Zhou et al. (2023)4.

Ye Zhou et al. (2023)4 and their research team have developed an innovative synthetic process for a unique silver-based MOD ink. This novel ink can produce highly conductive silver films on substrates that are sensitive to heat. The MOD precursor was created by forming a complex between silver acetate and 1-aminopropan-2-ol (AP), resulting in a diamminesilver(I) complex. According to TGA analysis, the solubility of the diamminesilver(I) cation was determined to be 12.56 wt.%. The study demonstrated the formulation of a silver MOD ink that can be inkjet-printed and sintered at low temperatures, including room temperature. This ink was tested on various substrates at different sintering temperatures (23, 50, 80, 120, and 150 °C), confirming its suitability for use on thermally sensitive materials.

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Figure . the process to form Gallium oxide thin films. From Pugh et al. (2012)2.

Pugh et al. (2012)2 concentrated on gallium hydride complexes as precursors for thin films of gallium oxide. Specifically, they highlighted the β-ketoiminate gallium hydride compounds ([Ga(L1)H], [Ga(L3)H2]). The ligands employed are bis(β-ketoimine) ligands, represented as [R{N(H)C(Me)-CHC(Me)≈O}2] (L1), and donor-functionalized β-ketoimine ligands L3H and L4H.

Samuel et al. (2020)1 utilized dimethyl ethylamine alane (DMEAA) and trimethylamine alane (TEAA) as precursors to deposit highly conductive aluminum films. These compounds, which serve as ligands for aluminum (III), enable deposition at low temperatures of 100 and 120 °C. Specifically, they employed AlH3{N(CH3)3} for storing AlH3. Notably, aluminum (III) can decompose into pure aluminum and hydrogen gas at approximately 60 °C, demonstrating its efficiency at low thermal thresholds.

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Figure . structure of DMEAA and TEAA. From Samuel et al. (2020)1.

In these three literatures, we can find a common denominator, in terms of chemical structure, metal ions are more inclined to bond with one oxygen atom and one nitrogen atom to form a stable structure. So, the choice of ligand became clear, an hydroxyl group, an amine group plus the underlying carbon chain, and the question became how do they fit together.

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Figure . the Synthetic routes compounds 1–3. From Shreya Mrig et al. (2023)10

Therefore, I noticed Shreya Mrig article: She presented an important point that the coordination number and spatial structure of metal atoms can significantly influence the stability of the precursor. Generally, the less stable the prepared precursor, the lower its thermal decomposition temperature. It was observed that the coordination number of the copper ion decreased with increasing steric bulk of the ligands. Specifically, compound 1 exhibited a hexacoordinate copper, compound 2 was pentacoordinate, and compound 3 was tetracoordinate. Notably, in all instances, the formate was never bound to Cu2+. In compound 1, all three ligands coordinated to the central copper ion in a bidentate manner. Due to steric constraints, the O2 and O3 atoms only weakly coordinated to the copper, which was evident from the interatomic distances (Cu–O1: 1.9387(11) Å, Cu–O2: 2.4734(14) Å, and Cu–O3: 2.5297(15) Å). The Cu–O1 bond length was significantly shorter than that found in a triflate analogue (Cu–O1: 1.960(2) Å), highlighting the critical role of both the ligand and counterion in determining the coordination environment.

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Figure . Summary of possible combinations of literature review

**3.Methodology**

3.1 Sintering process

At high temperature, the solid particles are bonded to each other, the grains grow, the voids (pores) and the grain boundaries gradually decrease, and through the transfer of materials, the total volume shrinks, the density increases, and finally becomes a dense polycrystalline sintered body with a certain microstructure, which is called sintering.

3.2 X-Ray Diffraction

XRD is one of the characterization methods used in this study. By emitting X-rays, different phases in the material are identified, lattice parameters are calculated, and the spacing between atomic layers is calculated.

3.3 Contact angle

The contact angle is the angle formed at the junction of a solid, liquid, and gas interface, specifically at the liquid-solid interface and the gas-liquid interface. A small contact angle between the ink droplet and the substrate is crucial for printing clear conductive patterns. The contact angle depends on the surface energies of the droplet and the substrate, as well as the substrate's surface roughness. The closer the surface energies of the droplet and substrate and the smoother the substrate surface, the smaller the contact angle. Surfactants can also reduce the contact angle.

3.4 Scanning Electron Microscopy (SEM)

SEM operates by focusing a beam of electrons, generated by an electron gun, onto the sample. Condenser lenses are used to narrow and control this beam. Scanning coils then direct the electron beam to scan across the sample's surface in a raster pattern. As the focused electron beam interacts with the sample, it produces various signals. These signals are detected and processed to form an image, which is displayed on a screen, allowing for detailed analysis of the sample's surface structure and composition.

3.5 Drop coating

Drop coating is a deposition technique in which a small liquid solution is dropped onto the substrate. The solution diffuses outward under the action of surface tension and gravity, forming a uniform film as the solvent evaporates. It is commonly used to prepare films or coatings in a laboratory environment. It is particularly useful for depositing materials over small areas and is often used in applications such as sensors, organic electronics and nanomaterials.

3.6 Spin coating

In the spin-coating process, an initial ink droplet is placed onto the substrate. The substrate is then spun at high speed, causing the ink to spread evenly into a thin liquid film due to the centrifugal force generated by the rotation.

3.7 Coffee ring effect

Potential conductive particles undergo decomposition at temperatures well below the actual melting point of the metal, precipitating and forming a continuous conductive pattern. During this process, the contact area between the ink and the substrate changes due to the diffusion of precursors and uneven solvent evaporation, which can degrade the quality of the printed pattern. For instance, some printed conductive films may form a coffee ring pattern because the evaporation rate is higher at the edges. In such cases, particles in the conductive ink are drawn to the perimeter of the droplet by capillary action, resulting in poor conductivity.

To avoid the coffee ring effect, increasing the ink's saturation can reduce particle mobility and prevent accumulation at the edges. However, high-viscosity ink can cause nozzle clogging during inkjet printing and lead to large holes and uneven surfaces during printing and decomposition. Uno et al. found that higher evaporation rates at the droplet edges are a primary cause of the coffee ring effect11. To counteract this uneven evaporation, surfactants can be added to the base fluid to influence internal flow and control droplet geometry.

In 2012, Still et al. discovered that adding sodium dodecyl sulfate (SDS) led to more uniform deposition of colloidal particles after evaporation12. SDS induces Marangoni flow, causing particles to flow back toward the center of the droplet due to surface tension, preventing deposition at the droplet edges. Later, Titkov et al. investigated the interaction between polymeric surfactants and organic silver salts in Ag NP ink, finding that it enhanced the dispersion of silver nanoparticles in the solvent, providing the low viscosity required for inkjet printing and better pattern quality. However, the addition of surfactants typically results in higher sintering temperatures and lower conductivity, so careful consideration is needed when choosing surfactants for conductive inks.

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Figure . Coffee ring effect of Cu and Ag films deposited on glass

Drop coating, respectively at 150 °C

**4. Experimental**

4.1 Materials:

Silver (I) acetate (anhydrous) (99 wt. %)

copper (Il) formate tetrahydrate (97% purity)

1-aminopropan-2-ol (AP) (93 vol.%)

2-aminoethan-1-ol (EA) (>99 vol. %)

Formic acid (395 vol.%)

4.2 Synthesis of MOD Precursor

All the process followed the method from Knapp’s group.

4.2.1 Synthesis of Cu-EA MOD Precursor

Copper (Il) formate tetrahydrate (1 g, 6.5 mmol) was vortex-mixed with ethanol (1 mL, 0.8 g) for 30s and formed a blue slurry. 2-Aminoethan-1-ol (4 mL, 4.04g, 65 mmol) was vortex-mixed with the slurry. The solution was kept at room temperature overnight with continuous stirring. After that, it was filtered through a 200 nm syringe filter to produce a clear blue Cu-EA precursor ink.

All mixing process was operated in an ice bath with a temperature of 0 to 3 °C.

4.2.2 Synthesis of Cu-AP MOD Precursor

copper (Il) formate tetrahydrate (1 g, 6.5 mmol) was vortex-mixed with ethanol (1 mL, 0.8 g) for 30 s and formed a blue slurry. 1-Aminopropan-2-ol (4 mL, 3.89 g, 52.4 mmol) was vortex-mixed with the slurry. Additional ethanol (1 mL, 0.8 g) added to the solution, and vial containing the solution sealed and wrapped using aluminiun. The solution was kept at room temperature overnight with continuous stirring. After that, filtered through a 200 nm syringe filter to produce a clear Cu-AP precursors.

All mixing process was operated in an ice bath with a temperature of 0 to 3 °C.

4.2.3 Synthesis of Ag-EA MOD Precursor

Silver (I) acetate (0.5 g, 2.96mmol) was vortex mixed with ethanol) (1 mL, 0,8 g) for 30 s and formed a white homogeneous suspension.

2-Aminoethan-1-ol (1 mL, 0.973 g, 16.6 mmol) was vortex-mixed with the suspension for 120 s, resulting in a translucent light brown solution with a small amount of black precipitate. Formic acid (0.05 ml, 0.061g, 1.3 mmol) was added dropwise, and the solution was vortex-mixed after each dropwise. The vial containing the solution was sealed and wrapped using aluminium foil. The solution was kept at room temperature overnight with continuous stirring. After that, filtered through a 200 nm syringe filter to produce a clear and

transparent Ag-EA precursor.

All mixing process was operated in an ice bath with a temperature of 0 to 3 °C.

4.2.4 Synthesis of Ag-EA MOD Precursor

Silver (I) acetate (0.5 g, 2.96 mmol) was vortex-mixed with ethanol (1 mL, 0,8 g) for 30 s and formed a white homogeneous suspension. 1-aminopropan-2-ol (1 mL, 0.751 g, 13.1 mmol) was vortex-mixed with the suspension for 120 s, resulting in a translucent light brown solution with a small amount of black precipitate. Formic acid (0.05 mL, 0.061g, 1.3 mmol was dropwise added, and the solution was vortex-mixed after each dropwise. The vial containing the solution was sealed and wrapped using aluminium foil. The solution was kept at room temperature overnight with continuous stirring. After that, it was filtered through a 200 nm syringe filter to produce a clear and transparent Ag-AP precursor.

All mixing process was operated in an ice bath with a temperature of 0 to 3 °C.

4.2.5 Synthesis of Ag-Cu Hybird MOD inks

Formulation of Ag-Cu Hybrid MOD inks: Four Ag-Cu Hybrid MOD inks were synthesized and evaluated in this study: Cu-EA precursor with Ag-AP precursor, Cu-EA with Ag-EA, Cu-AP with Ag-EA, and Cu-AP with Ag-AP. The calculated mole ratio of Cu and Ag content in the synthesized Ag-Cu hybrid MOD ink was 1.05:1.

Except for Cu-AP with Ag-EA, 1 mL of Cu MOD precursor was vortex-mixed with I mL of Ag MOD precursor in all Ag-Cu Hybrid MOD inks. The vial containing the mixture was sealed and wrapped using aluminium foil. The solution was kept at room temperature overnight with continuous stirring. After that, it was filtered through a 200 nm syringe filter to produce a clear g-Cu ink. For Cu-AP with Ag-EA, the addition of ethanol (1 mL, 0.8 g) was required for stirring.

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