

Abstract

Metal Nanoparticles in Additive Manufacturing of Conductive Features at the Micrometer Scale by Precise Deposition Method

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Printed electronics represents a transformative approach to manufacturing functional electronic components through additive techniques, enabling the deposition of conductive, semiconductive, or dielectric inks onto diverse substrates. This doctoral thesis explores the integration of metal nanoparticles (NPs) into additive manufacturing, with a focus on developing high-performance conductive inks and pastes tailored for the Ultra-Precise Dispensing (UPD) technology pioneered by XTPL S.A. The UPD method facilitates the creation of micrometer-scale conductive features—such as lines with widths of 1–30 μm and single drops of similar diameters—on flat or topographically complex surfaces, including rigid and flexible substrates like glass, silicon, polymers, and fabrics. This technology addresses key limitations in traditional electronics fabrication, such as achieving printouts high resolution, the environmental impact and high costs associated with etching or lithography in printed circuit boards (PCBs), by offering a more sustainable, cost-effective alternative.

The primary motivation for this research stems from the challenges encountered during the early development of XTPL's UPD system. Commercial conductive inks and pastes often exhibited poor compatibility, leading to issues like nozzle clogging due to nanoparticle agglomeration under high shear stress or rapid solvent evaporation forming dried plugs. These problems compromised printability—defined as the ability to produce homogeneous, reproducible structures without altering printing parameters. To overcome this, the thesis outlines a comprehensive methodology for in-house ink development, emphasizing synergy among dedicated inks, specialized printheads with nozzles of 0.5–10 μm diameters, and precise mechanical control systems. The research milestones include: (1) synthesizing metal NPs; (2) characterizing nanomaterials; (3) initial printhead compatibility tests; (4) formulating and evaluating inks' physicochemical and rheological properties; (5) advanced printing tests; (6) iterative composition modifications; (7) parameter optimization for submicron structures; (8) post-treatment and morphological analysis; (9) electrical, adhesion, and mechanical characterization; and (10) commercial application in microelectronics projects.

The review section provides a foundational overview of printed electronics, direct deposition methods (e.g., inkjet, aerosol jet, extrusion printing), and additive manufacturing techniques for micrometer-scale metal structures, including direct ink writing (DIW), electrohydrodynamic printing, and laser-induced forward transfer. It delves into nanomaterials, particularly silver (Ag) and copper (Cu) NPs, covering synthesis mechanisms (nucleation, growth, stabilization, and oxidation protection) and liquid-phase methods like polyol synthesis. Conductive ink technology is examined in detail, including composition (metal precursors, reducing agents, solvents, stabilizers), key properties (viscosity, wetting, drying), rheology (non-Newtonian behavior), and post-treatment sintering methods (thermal, photonic, microwave, plasma, electrical, chemical).

In the experimental section, AgNPs and CuNPs were synthesized using the polyol method, yielding particles in the 20–100 nm average size range with controlled parameters such as temperature, reagent ratios, and injection rates. AgNPs exhibited uniform spherical morphology (~45 nm average size), while CuNPs showed higher polydispersity. A novel wet transfer formulation technique was developed, concentrating NP dispersions from low- to high-boiling-point solvents under vacuum to prevent aggregation and oxidation, incorporating additives like dispersants, plasticizers, and adhesion promoters for enhanced compatibility with UPD and other printing methods.

Quality control (QC) protocols were established for raw materials and final products by UV-Vis spectroscopy, dynamic light scattering (DLS), transmission electron microscopy (TEM), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), inductively coupled plasma optical emission spectrometry (ICP-OES), X-ray diffraction (XRD), and rheometry. QC assessed solid and metal content, UV-Vis spectra, NP size/morphology/aggregation, rheology, electrical properties, adherence (scotch-tape tests), printing performance, and stability. Rheological studies revealed non-Newtonian behavior in highly concentrated inks (>60 wt.%), with shear-thinning facilitating flow through micronozzles (1.5–5.0 μm). Printing tests using the UPD system evaluated nozzle clogging, geometrical uniformity, and repeatability, achieving excellent results with formulations like CL85 (Ag-based) and CuEX (Cu-based). These enabled depositions of conductive lines as narrow as 1–2 μm with high aspect ratios in a single pass, multi-layer structures for 3D features, and complex patterns like micro meshes.

Sintering optimization (thermal and photonic) yielded conductivities up to 50% of bulk metal values for both Ag and Cu compositions, with CuEX requiring protection against oxidation for thermal sintering. Printed structures demonstrated strong adhesion across substrates and competitive electrical performance compared to market alternatives, as benchmarked in comparative analyses. Applications in microelectronics, including integration with XTPL's business partners, highlight the inks' utility in flexible electronics, displays, microLEDs, organic field-effect transistors (OFETs), RFID tags, and sensors.

In conclusion, this thesis establishes a scalable production framework for high-performance conductive inks, advancing UPD technology for micrometer-scale electronics. The developed inks overcome traditional limitations, enabling precise, reliable additive manufacturing with implications for sustainable electronics fabrication.