

Electrical and Morphological Properties of Tollens-Deposited Silver on Photopolymer Resin Relevant to 3D-Printed Microwave Components

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ABSTRACT This work presents the first systematic investigation of the fundamental electrical and morphological properties of Tollens-deposited silver on stereolithography (SLA) 3D-printed polymers. Instead of examining specific waveguides or components, the goal is to establish reliable superordinate process-property relationships for the Tollens-based metallization. Therefore, planar specimens were fabricated to allow quantitative characterization of the metallization. Fundamental process parameters: immersion time, temperature, surface cleaning, and surface pretreatment were systematically varied, and additional influencing factors including ultrasonic assistance, water purity, surface contamination, and repeated metallization were assessed. The characterization included measurements of layer thickness, electrical conductivity, sheet resistance, surface roughness, as well as morphological analysis by scanning electron microscopy and optical microscopy. Depending on the combination of process parameters, the conductivity and layer thickness show significant variations from 27.9 to 6.6 MS/m and 164 to 77 nm, respectively. The best result for a single metallization, 27.9 MS/m and 164 nm, was achieved using deionized water and ultrasonic assistance. The deposited silver thickness is markedly smaller than the surface roughness, and the silver layer is overlain by an island-like layer of irregular silver agglomerates, resulting in an atypical multilayer structure. The findings of this work establish a quantitative basis for the future assessment and optimization of loss and propagation characteristics in microwave components based on 3D-printed, Tollens-metallized photopolymers.

INDEX TERMS 3D printing, additive manufacturing, electroless plating, silver thin films, stereolithography (SLA), Tollens' reagent.

I. INTRODUCTION

Additive manufacturing has evolved into a mature technology for realizing complex radio-frequency (RF) components. Companies such as *Optisys INC* [1] and *SWIS-Sto12 SA* [2] demonstrate this maturity by commercializing aerospace- and space-qualified product lines that exploit additive manufacturing-enabled functional integration. Despite these advances, the full potential of additive manufacturing for high-performance RF devices has not yet been fully exploited

and remains an active area of research, particularly with respect to integration density, process repeatability, and surface quality. Representative systems [3], [4], [5] combine horn antennas, feed networks, polarizers, and power dividers into monolithic metal assemblies fabricated via powder-bed selective laser melting (SLM). With typical layer thicknesses of 20–40 μm and feature resolutions in the order of 100 μm [6], SLM enables the direct fabrication of metal RF components. However, the entry barriers associated with metal additive

manufacturing remain substantial, primarily due to high capital investment and demanding infrastructure requirements. Vat photopolymerization, in particular stereolithography (SLA), offers comparable geometric resolution and surface quality to SLM [7] at a significantly lower investment cost. Since SLA cannot produce conductive structures directly, the achievable RF performance critically depends on the quality and reliability of the subsequent metallization process.

Metallization methods such as copper foil lamination [8] or the application of conductive polymer dispersions [9] do not achieve the RF performance of fully metallic structures. These approaches are particularly limited in their ability to coat internal surfaces of monolithic waveguides, which is particularly problematic for highly integrated components based on complex-shaped monolithic architectures. Electroplating provides high-quality metal layers but requires a conductive seed layer [10]. Since the deposition rate is proportional to the local current density, only electrically accessible surfaces are metallized. Internal features of monolithic conductive structures (e.g., the inner wall of a waveguide) are self-shielded and therefore exhibit strongly reduced metal growth. Vacuum-based techniques such as chemical vapor deposition and physical vapor deposition offer uniform, high-purity coatings, yet demand substantial infrastructure and are generally unsuitable for enclosed geometries [11]. Electroless deposition (ED) represents a more flexible alternative, enabling metal deposition via chemical reduction without an external current source. A key advantage is the capability to circulate plating solutions through complex internal channels in monolithically integrated RF components. However, standard ED chemistries for nickel, copper, or gold often employ cyanide-containing complexes, palladium catalysts, or formaldehyde-based reducing agents [12], [13]. Safe handling of these compounds requires considerable chemical expertise and dedicated laboratory infrastructure, which results in considerable overhead efforts.

The Tollens' process [14], originally developed as a qualitative test for aldehydes, enables the deposition of silver through a reduction reaction. Its low toxicity, straightforward preparation, and compatibility with dielectric materials make it an attractive and cost-effective alternative to conventional electroless chemistries. The feasibility of Tollens-based metallization for RF components was first demonstrated in 2016 with the silver coating of rectangular waveguides [15]. Since then, numerous application-oriented studies have applied this process to a wide range of RF components, resulting in a broad yet heterogeneous body of experimental results [11], [16], [17], [18], [19], [20]. Although these works provide qualitative indications of process-parameter sensitivity, they do not focus on a systematic characterization of the resulting silver layers.

In [16] and [17], a modified Tollens' procedure employing a palladium-based activation bath was introduced. To increase coating thickness, four successive silvering cycles were applied to achieve approximately a thickness of 5 μm . However, the measurement method used to determine this thickness is

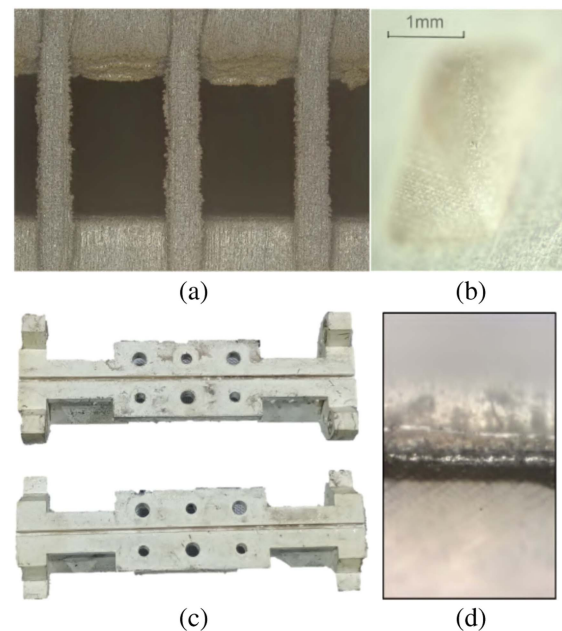


FIGURE 1. Heterogeneous Tollens-deposited silver layers reported in application-oriented studies: (a) rough surface with crystalline protrusions [16, Fig. 4], (b) homogeneous and highly reflective silver layer [18, Fig. 6], (c) matte silver layer with pronounced discoloration [19, Fig. 5], and (d) severe black discoloration [20, Fig. 10].

not reported. The close-up in Fig. 1(a) (extracted from [16, Fig. 4]) reveals a rough surface with crystalline-like protrusions, yet no further analysis of this distinctive morphology is provided.

In [18], a Tollens-derived silver layer is used as a seed layer for subsequent electroless copper deposition. The silver surface presented in [18, Fig. 6], shown in Fig. 1(b), exhibits a clean, homogeneous, and highly reflective appearance. The study states that this single silvering step produces a layer thinner than 200 nm, but no details on the measurement method are specified.

To further advance the metallization process, [19] systematically investigated surface preparation techniques for SLA-fabricated waveguides. The best-case split-block specimen reported in [19, Fig. 5], shown in Fig. 1(c), exhibits a matte silver layer with a pronounced discoloration. Layer thickness was inferred from sheet-resistance measurements by assuming a conductivity of 75 % of bulk silver. Based on these observations, Quint et al. concluded in [11] that the Tollens' process is unsuitable for monolithic components and that electroless copper plating is a more viable alternative. This assessment contrasts with the conclusions reported in [16], [17].

A first comprehensive evaluation of Tollens-based metallization for SLA components was presented in [20], addressing optical surface imperfections, coating thickness, and RF performance parameters at Ka-band. The study provides an experimental baseline for assessing the applicability of Tollens' metallization to additively manufactured waveguides. Some reported observations, however, differ from results

described in other studies and are discussed here in a comparative context. Black discolorations at waveguide edges from [20, Fig. 10] shown in Fig. 1(d) were attributed to local oxidation, whereas [21] and [22] suggest that silver oxidation is typically associated with ozone exposure. Moreover, the initially deposited silver layer was described as highly inhomogeneous, requiring multiple deposition cycles. By comparison [18] reports uniform single-cycle coatings without visible discoloration. In addition, different conclusions have been reported regarding the suitability of some resins for Tollens' metallization. For example, [20] states that *Formlabs Clear Resin* is unsuitable for Tollens' metallization, whereas [23] demonstrates homogeneous coatings on the same resin type after a single cycle.

The heterogeneous results reported across application-driven demonstrations and visualized in Fig. 1 indicate that process parameters critically determine the silver layer's morphology and properties. However, existing studies provide only fragmentary analyses and rarely specify how key quantities such as layer thickness were determined. As a consequence, parameters including coating uniformity, electrical conductivity, surface roughness, and compatibility with SLA-fabricated substrates remain insufficiently understood and inconsistently reported. To address these gaps, this article presents, to the best of the authors' knowledge, the first systematic investigation of process- and material-level electrical and morphological properties of Tollens-based metallization in the context of microwave applications. The study includes a detailed analysis of the relationship between layer thickness, surface roughness, and the formation of porous silver agglomerates on the substrate surface. The fundamental process parameters: immersion time, temperature, surface cleaning, and surface pretreatment are systematically investigated in this study to analyze process-induced effects and to deepen the understanding of the underlying chemical mechanisms. Moreover, additional process-influencing factors such as ultrasonic assistance, water purity, surface contamination, and repeated metallization are examined. Rather than investigating exemplary RF components, which would inherently limit generality, dedicated planar specimens are fabricated to isolate and quantitatively assess the key properties of the silver layer. These include layer thickness, electrical conductivity, sheet resistance, and surface roughness, which characterize the coating itself and serve as surrogate parameters for RF performance. The layer morphology is assessed using scanning electron microscopy (SEM) and optical microscopy. In addition, a WR-15 rectangular waveguide is fabricated as a component-level demonstrator to assess the transfer of the selected metallization process to a typical microwave component. A preliminary investigation is further conducted to evaluate whether functional additives can be incorporated into SLA resins to tailor the surface energy, thereby improving silver deposition.

The article is organized as follows. Section II summarizes the fundamentals of the Tollens' reaction relevant to metallization. Section III details the methodology used to

characterize the silver layer. The results and discussion of the individual experiments are presented in Section IV, whereas Section V provides a cross-experimental discussion. Section VI analyzes the silver film morphology in the context of microwave applications. A component-level proof of concept for applying the metallization process to a microwave structure is provided in Section VII. Section VIII concludes this article.

II. FUNDAMENTALS

This section establishes the foundations of vat-photopolymerization-based additive manufacturing, the chemistry of the Tollens' reaction, and the electroless deposition of metal layers, which form the basis for interpreting the experimental results. It first outlines the fabrication of polymer components by vat photopolymerization, then introduces the Tollens' reaction mechanism, and finally discusses electroless silver deposition.

A. VAT PHOTOPOLYMERIZATION

Vat photopolymerization (VP) is the oldest additive manufacturing process, first mentioned in a patent by Hideo Kodama in 1980 [24] and detailed in a publication in 1981 [25]. VP selectively cures a photosensitive resin within a vat using an ultraviolet light (UV) source. The 3D object is created by curing layer by layer to a build platform. SLA represents the original form of VP and employs a UV-laser that scans the resin surface to cure each layer. Later developments such as digital light processing (DLP) and masked stereolithography (LCD) expose entire layer images instead of relying on laser scanning.

The basic building blocks of photosensitive resins for VP are monomers, oligomers, crosslinkers, photo-initiators, and fillers. Monomers and oligomers are individual molecules and short polymer chains, which can polymerize into long polymer chains. Crosslinkers connect these chains, determining the mechanical properties of the printed part [26]. Polymerization is triggered by photo-initiators, which can be split by UV light, resulting in a highly reactive radical pair. If a radical meets a monomer or a crosslinker, the chance of them forming a bond is high. The polymerization results in numerous polymer chains consisting of hundreds to thousands of monomers and oligomers, which are connected by crosslinkers and, thus, form a solid.

Fillers such as plasticizers or color pigments are not covalently bound but embedded between polymer chains [26]. By exploiting this property, users can incorporate custom fillers into the resin to tailor surface characteristics or mechanical properties. The exact composition of the photosensitive resins for VP is generally not publicly available, but all manufacturers rely on the same building blocks.

After printing, residual uncured resin is removed in a solvent bath, followed by UV post-curing. During printing, each layer is exposed only until the part is dimensionally stable. The subsequent post-curing step completes the polymerization and cross-linking at the surface, thereby achieving the

final mechanical strength while leaving a relatively unreactive and poorly wettable surface.

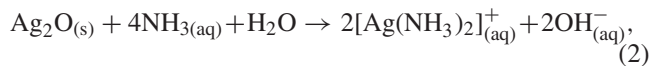
B. TOLLENS REAGENT

Tollens' reagent is a qualitative test for aldehydes, first described in 1881 by the chemist Bernhard Christian Gottfried Tollens [14].

To prepare Tollens' reagent, silver nitrate (AgNO_3) is first dissolved in water and is present in ionic form. The aqueous ammonia solution that is subsequently added contains, due to the acid-base reaction between ammonia (NH_3) and water, ammonium (NH_4^+) and hydroxide ions (OH^-). The hydroxide ions react with the silver ions, forming the intermediate silver hydroxide (AgOH), which subsequently produces the sparingly soluble silver(I)-oxide (Ag_2O) [27] and water:



The silver(I)-oxide precipitates out of the solution as a brown solid. With further addition of ammonia



the silver(I)-oxide dissolves again, forming a diamine-silver complex $[\text{Ag}(\text{NH}_3)_2]^+$. This complex is now susceptible to reducing agents and can be employed in the Tollens' test [27].

The addition of aldehydes or other reducing groups initiates a redox reaction. In the alkaline conditions of Tollens' reagent, the aldehyde is oxidized, yielding the corresponding carboxylate. During the reduction, the diamine-silver complex is reduced to metallic silver (Ag). The formation of a metallic silver layer on the reaction vessel is the characteristic outcome of the Tollens' test and confirms the presence of aldehydes.

C. ELECTROLESS DEPOSITION OF METAL LAYERS

Electroless plating is a metal deposition process that proceeds without an external electric current source, in contrast to electroplating. The process relies on the reduction of metal ions from a metal complex in solution by a chemical reducing agent. A key advantage of electroless deposition is that the substrate surface must only be chemically functionalized. Electrical conductivity is not required for uniform metal growth.

Electroless deposition corresponds to a redox reaction where the reducing agent is oxidized, while metal ions in the complex are reduced and deposit as neutral atoms. After addition of the reducing agent, the bath is often in a metastable state and, therefore, metal only deposits once a nucleation barrier is overcome. Deposition starts at sites where this barrier is lowered, e.g., on activated surfaces or suspended particles. Qualitatively, three nucleation modes can be distinguished [28]:

1) Homogeneous nucleation

The metal ions are reduced within the bulk solution, forming clusters that grow into agglomerates. This happens once the bath is driven strongly enough with, e.g.,

elevated temperature, high driving force, strong or concentrated reductant to overcome the volume nucleation barrier.

2) Non-selective heterogeneous nucleation

If the volume nucleation barrier is not exceeded, metal forms preferably on interfaces with reduced nucleation barrier. In this mode, virtually all sufficiently polar or high-surface-energy interfaces get coated.

3) Catalytic heterogeneous nucleation

In a more stable bath, only surfaces that catalyze the reducing reaction exhibit sufficiently low nucleation barriers. As a result, metal deposition is confined to these catalytic substrates, enabling selective metallization.

To promote metal deposition on the target substrate, homogeneous nucleation in the bulk must be suppressed such that heterogeneous nucleation dominates at the substrate-solution interface. This requires chemical activation of most substrate surfaces to lower the interfacial nucleation barrier and thereby initiate deposition at the intended sites [28]. Implantation of copper (Cu^{2+}) or tin (Sn^{2+}) ions into the near-surface region enables metal nanoparticle formation directly on the surface when exposed to metal-ion solutions. A dense, uniform seed distribution is essential, as the silver film subsequently forms by Volmer–Weber [29] island growth: isolated nanoparticle islands nucleate and grow until they coalesce into a continuous layer. When the ratio of metal ions, reducing agent, pH value, and complexing agent shifts to the point that the effective redox potential is no longer sufficient or a component is depleted, the metal deposition process stops.

III. METHODOLOGY

This section presents the methodology developed to investigate the influence of surface treatment and deposition parameters on the thickness, electrical conductivity, and morphology of silver layers deposited on SLA-printed samples by the Tollens' reagent. For this purpose, dedicated test samples were fabricated, and a custom probe head was manufactured to enable sheet resistance measurements. The following subsections describe the fabrication of test samples, the metallization process, the conducted experiments, and the employed characterization methods.

A. TEST SAMPLES

The samples and holders used in this study, shown in Fig. 2, were fabricated using a *Formlabs Form3+* printer with *Formlabs Grey Resin V4* at a layer height of 50 μm . Hereafter, this resin is referred to as *Grey Resin*. Curing and cleaning followed the manufacturer's specifications unless stated otherwise [30], [31].

For the investigation of process parameters and surface treatments, the circular discs from Fig. 2(a) with a diameter of 30 mm and a thickness of 2 mm were used. Accurate measurements of silver layer thickness and added surface roughness require the sample surface to be substantially

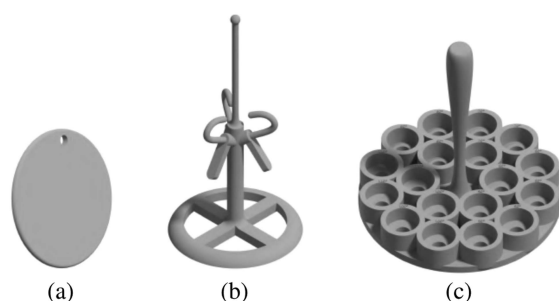


FIGURE 2. (a) Planarized test sample, (b) holder used during metallization, and (c) complex-geometry sample employed for the cleaning study.

smoother than the expected film thickness. However, our preliminary measurements indicate that the SLA-printed parts exhibit a comparatively high surface roughness, with a root mean square (RMS) height $R_q = 1.5 \mu\text{m}$ and a maximum height $R_z = 7.7 \mu\text{m}$, whereas the nominal layer thickness is expected to be approximately one order of magnitude smaller. To enable reliable measurements, the printed samples were planarized by stamping with a polished Pyrex glass wafer with $R_q < 1.5 \text{ nm}$ [32]. For this, after cleaning and curing, a thin layer of *Grey Resin* was first applied by pipette and then spread uniformly by pressing the wafer onto the sample. Subsequently, the assembly was cured again according to the manufacturer's specifications. This stamping process imprints the wafer's smooth surface onto the 3D printed part and ensures material consistency with SLA 3D printed RF components.

The holder in Fig. 2(b) was designed to ensure uniform conditions during silver deposition. It accommodates three of the circular samples from Fig. 2(a) inclined at 30° to the central axis. The extended handle enables immersion and agitation of the specimen while avoiding direct contact with the silver solution.

To evaluate the cleaning process, the test sample shown in Fig. 2(c) was designed. This complex-geometry sample includes 15 open right circular cylindrical cavities where the bottom base of each is inclined by a different angle ranging from 60° to 110° . Their geometry introduces narrow gaps and deep recesses with high aspect ratios, making the structure challenging to clean.

B. METALLIZATION USING TOLLENS' REAGENT

When interpreted as an electroless metallization process, the Tollens' reaction initially proceeds via non-selective heterogeneous nucleation on all sufficiently active surfaces. A low contact angle is critical because it implies good wettability of the substrate by the plating solution, which suppresses air entrapment at surface asperities and, thus, enables the formation of a dense, continuous silver layer. As the reaction progresses, silver clusters formed in solution act as additional catalytic sites and progressively lower the barrier for further reduction. This can shift the process toward homogeneous nucleation mode. To achieve high deposition rates on SLA components

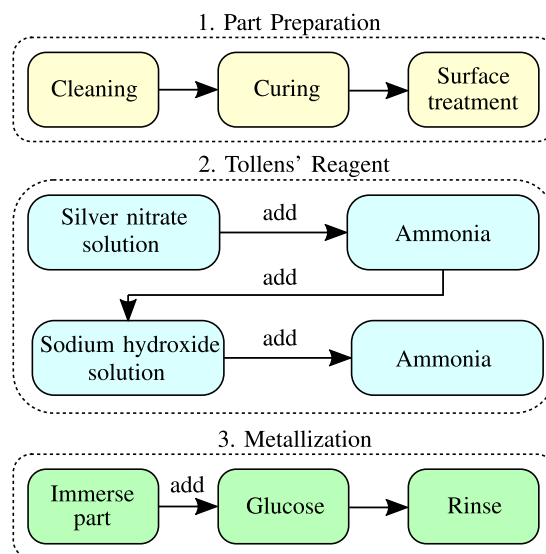


FIGURE 3. Flowchart illustrating the metallization process for components manufactured by the SLA additive process.

before this transition, the substrate must be clean, fully cured, and functionalized. As printed SLA surfaces are typically non-polar, hydrophobic, and not sufficiently catalytic, seeds must be introduced.

The Tollens' metallization process, based on [15], comprises three sequential steps, as illustrated in Fig. 3: 1. part preparation, 2. Tollens' reagent preparation and 3. the metallization. Throughout all processing steps, every item in contact with the samples or the Tollens' reagent was thoroughly cleaned to eliminate any contamination. The part preparation ensured complete removal of residual resin and full curing of the printed samples. To avoid additional cleaning steps, the samples were handled exclusively with clean gloves. The surface treatment consisted of immersing the sample in an aqueous acidified stannous chloride (SnCl_2) solution for 10 min. To prepare 100 ml of this solution, 87.5 ml of deionized (DI) water, 12.5 ml hydrochloric acid (HCl) and 6 g of SnCl_2 were mixed. This sensitizing step implants tin(II) ions (Sn^{2+}) into the surface, providing nucleation sites for silver deposition. Because the SnCl_2 solution is a strong reducing agent, any residue must be completely removed by rinsing the sample thoroughly with DI water. Incomplete rinsing leads to local homogeneous nucleation of silver particles visible as a brown precipitate upon immersion in the Tollens' reagent, rendering the reagent unusable.

The Tollens' reagent for metallization was prepared by dissolving 1 g of silver nitrate in 50 ml DI water. Approximately 1 ml ammonia (NH_3) with a concentration of 30–33 % was added dropwise until the solution turned brown and then cleared, indicating the formation of the $[\text{Ag}(\text{NH}_3)_2]_{(aq)}^+$ complex. In addition to the procedure described in Section II-B, 50 ml of a sodium hydroxide (NaOH) solution consisting of 0.2 g NaOH and 50 ml DI water was added. The increased pH value of the reagent accelerates the reaction rate, as higher

pH values increase the sensitivity of the reagent [33]. Upon adding sodium hydroxide, the solution darkens. It returns to a clear state after adding approximately 0.46 ml of ammonia. The resulting clear solution served as the Tollens' reagent and was used directly for metallization. After immersing the part, silver deposition was initiated by adding a glucose solution prepared by dissolving 1 g glucose in 20 ml DI water. Following the metallization, the samples were rinsed with DI water and dried using compressed air. Any clouding of the reagent or discoloration on the sample indicates that contamination is present, hence the solution is unusable.

C. EXPERIMENTS

The aim of the study was to identify the influence of fundamental process parameters, evaluate possible optimizations, and assess the feasibility of resin modification through additives. The investigated fundamental parameters included temperature, reaction time, surface cleaning, and surface treatment. Process optimization was examined by adding an additive to the Tollens' reagent, applying ultrasonic agitation and varying the water purity. In addition, the additive was incorporated into the resin to verify whether modifications of the resin properties are feasible and could improve compatibility with the Tollens' reagent. Polysorbate 20, commercially known as *Tween 20*, is used as an additive in this work. It is a nonionic surfactant commonly employed as a wetting agent. To assess the effect of the additive, contact angle measurements were conducted to evaluate its wetting performance.

To ensure comparability, all experiments, unless stated otherwise, were performed using 100 ml of Tollens' reagent, prepared according to Section III-B, in a 150-ml beaker at a temperature of 17 °C. For each test series, a holder [Fig. 2(b)] equipped with three planarized samples [Fig. 2(a)] was used. The samples were removed from the solution after a reaction time of 4 min. The following studies were conducted:

- 1) *Contact Angle*: The wettability of the *Grey Resin* was compared with and without *Tween 20* as an additive. *Tween 20* was added to the silver solution and the resin in a volume ratio of 1:1000 and 1:10, respectively.
- 2) *Surface Cleaning*: In addition to the standard cleaning procedure described by *Formlabs* [30], [31], an extended three-step ultrasonic-assisted cleaning method was used prior to metallization. The complex-geometry samples were placed in a beaker filled with 2-propanol (isopropanol) for 10 min, with the 2-propanol being replaced after 5 min. Subsequently, the samples were cleaned for 3 min in 2-propanone (acetone). The beaker was placed in a *Bandelin Sonorex RK255H* ultrasonic bath operating at a frequency of 35 kHz and a power of 160/320 W (RMS/Peak) during each step. Subsequently, the samples were dried using compressed air.
- 3) *Surface Pretreatment*: The necessity of the SnCl_2 sensitization was investigated using pretreated and untreated planarized samples. In addition, it was examined whether adding *Tween 20* to the resin can eliminate the

SnCl_2 pretreatment by improving the surface properties, in particular the wettability.

- 4) *Effect of Time*: The planarized samples were silvered for different durations ranging from 1 to 7 min in increments of 1 min. The silver solution was prepared once and divided into seven beakers.
- 5) *Effect of Temperature*: The silver solutions were temperature-controlled using a heated water bath. The beaker containing the reagents was placed in the bath and brought to the target temperature. Once steady-state conditions were reached, the metallization of the planarized samples was initiated. The tested temperatures were 5 °C, 17 °C, 40 °C, 60 °C, and 80 °C. Based on the assumption that the reaction rate follows the Van't Hoff rule [34], the process time for the 5 °C sample was increased by a factor of 2.4 to 10 min to ensure complete reaction.
- 6) *Effect of Ultrasonic Assistance*: For this test, the beaker containing the reagent was placed in the *Bandelin Sonorex RK255H* ultrasonic bath. Ultrasound was activated prior to the addition of the glucose solution.
- 7) *Water Purity*: The influence of water purity was examined by preparing the Tollens' reagent entirely with either tap water, having an average conductivity of 296 $\mu\text{S/cm}$ [35], or with DI water obtained from a *LAB-IO* deionization system with a conductivity of 0.1 $\mu\text{S/cm}$.
- 8) *Contamination*: To investigate contamination effects, the specimens were suspended using short copper wires instead of a dedicated sample holder. During the sensitization step, a brittle black crust formed at the interface between the SnCl_2 solution and air. Upon subsequent immersion in the Tollens' reagent, this crust detached and dispersed into the bath as fine particles, leading to unintended contamination of the metallization process.
- 9) *Sequential Silver Deposition*: After the first silvering step, the samples were rinsed with DI water and immediately immersed into a fresh Tollens' reagent for another silvering process. Because the process is autocatalytic, no additional pretreatment steps are required between cycles.

D. CHARACTERIZATION METHODS

The characterization of the deposited silver films was carried out using a combination of optical, electrical, and microscopic measurement techniques to qualitatively and quantitatively assess their structural and functional properties. The investigated parameters are the contact angle, layer thickness, sheet resistance, electrical conductivity, surface roughness, and morphology. Each parameter provides information on the film quality and uniformity. The thickness determines the amount of deposited silver, the conductivity reflects the electrical performance of the metallized surface, the roughness describes the topographical properties, the contact angle characterizes the surface energy and hydrophilicity, and the morphology reveals microstructural features such as porosity

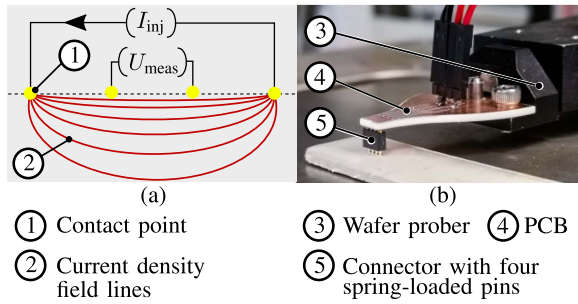


FIGURE 4. (a) Schematic illustration of the four-probe measurement in top view; for clarity, the upper half of the current density field lines is omitted. (b) Photograph of the measurement setup.

and grain formation. All measurements were performed on representative areas of multiple samples to ensure statistical reliability and comparability across different process variations.

1) SILVER LAYER THICKNESS

After metallization, one half of the silver layer on the planarized samples was removed using adhesive tape. This partial removal created a distinct step between the resin surface and the remaining silver layer, allowing the layer thickness to be determined as the height difference between both surfaces. Since tearing off the silver layer may cause local deformations near the edge, the height difference was not evaluated directly at the transition region. The measurements were performed using a *Keyence VK-X3050* confocal laser scanning microscope equipped with a 50× objective lens. The instrument provides a field of view of $213 \mu\text{m} \times 284 \mu\text{m}$ with 1024×768 data points containing height information.

For each experiment, three samples were prepared. On each sample, three measurement areas were recorded. Within each area, three independent measurements of the height difference between resin and silver surface were conducted. Each measurement corresponds to an averaged surface profile obtained by averaging 20 parallel line scans with 278 nm (one data point) offsets. Consequently, each thickness value results from averaging a total of 27 individual measurements.

2) ELECTRICAL CONDUCTIVITY

To determine the electrical conductivity σ of the silver layer deposited on the nonconductive substrate, the sheet resistance R_s was first measured using the four-point probe method [36] and converted according to

$$\sigma = \frac{1}{R_s d} \quad (3)$$

with the known layer thickness d .

The four-point probe method determines the sheet resistance R_s of thin films using four collinearly aligned probes with equal spacing, assuming that contact and lead resistances are negligible [36]. The measurement principle is schematically illustrated in Fig. 4(a). A defined current is injected through the two outer probes, while the voltage drop between

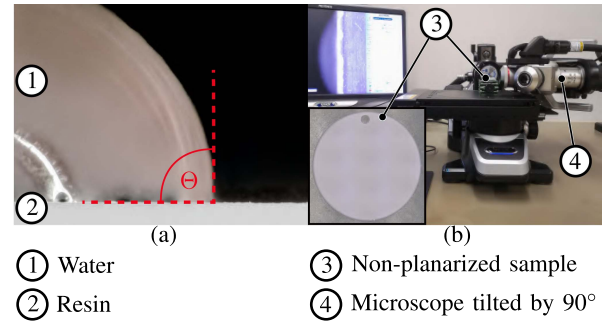


FIGURE 5. (a) Lateral view of a water droplet on the Grey Resin surface with the contact angle Θ indicated, and (b) the measurement setup.

the two inner probes is measured. The sheet resistance is obtained from

$$R_s = \frac{\pi}{\ln(2)} \frac{U_{\text{meas}}}{I_{\text{inj}}} C, \quad (4)$$

where C denotes a geometric correction factor ranging from $0 < C < 1$. For finite sample geometries, a correction must be applied to account for boundary effects [37]. For the circular samples used, the resulting correction factor is $C = 0.985$.

The experimental setup shown in Fig. 4(b) is based on a *Cascade Microtech Summit 9000* wafer probe, which enables precise positioning of the probe head at the sample center. The probe head consists of a *Mill-Max 854* [38] connector equipped with four spring-loaded pins providing uniform surface contact. The pins are spaced 1.27 mm apart and have rounded tips. Measurements were conducted using a *Hewlett Packard 34401A* digital multimeter.

For each process variation, three samples were measured at three positions near the sample center. The mean of the nine measurements was used as the representative sheet resistance. The corresponding layer thickness values used to calculate the conductivity were obtained as in Section III-D1.

3) SURFACE ROUGHNESS

The two line roughness parameters R_q and R_z , were determined using a *Keyence VK-X3050* confocal laser scanning microscope equipped with a 50× objective lens. For each measurement, the full field of view of $213 \mu\text{m} \times 284 \mu\text{m}$ with 1024×768 data points containing height information was utilized. No cutoff filters were applied for the parameter evaluation, only a surface form correction was performed to minimize waviness. Each roughness value represents the average of 20 parallel line profiles recorded at $1.66 \mu\text{m}$ (six data points) lateral offsets.

4) CONTACT ANGLE

Six droplets of approximately $250 \mu\text{l}$ each were applied with a pipette to non-planarized samples. The droplet contour shown in Fig. 5(a) was recorded using a *Keyence VHX-6000* digital microscope. To obtain a lateral view of the droplet, the microscope head was tilted by 90° , as illustrated in Fig. 5(b), enabling the determination of the contact angle Θ . Contact

TABLE 1. Results of the Contact Angle Measurements

Material	DI Water	DI Water + <i>Tween 20</i>	SnCl ₂	SnCl ₂ + <i>Tween 20</i>
<i>Grey Resin</i>	90.7°	50.3°	88.7°	48.8°
<i>Grey Resin</i> + <i>Tween 20</i>	68.1°	39.4°	62.6°	n.a.

angle measurements were performed on the *Grey Resin* samples using DI water as well as the SnCl₂ sensitization solution. Furthermore, the addition of *Tween 20* to both the resin and the processing liquids was investigated with respect to its influence on the contact angle. For each condition, three independent droplets were measured, and the results were averaged.

5) MORPHOLOGY

The morphology and structural details of the silver layer were examined using a *Zeiss Leo 1530 SEM*. Except for one detailed micrograph, the samples were not additionally sputter-coated with gold, as the conductivity of the silver layer was sufficient to prevent charging. The analysis focused on porosity, agglomerate size, and film continuity. Larger-scale surface features were investigated using a *Keyence VK-X3050* confocal laser scanning microscope and a *Keyence VHX-6000* digital microscope.

IV. RESULTS AND DISCUSSION

This section presents the measurement results of the experimental studies and discusses their implications to reliably forming conductive silver layers on SLA-printed resin samples. Reported variations refer to changes in the corresponding mean values, calculated according to the procedure outlined in Section III-D.

A. CONTACT ANGLE

The results of the contact angle Θ measurements are summarized in Table 1. DI water exhibits a contact angle of 90.7° on *Grey Resin*, classifying it as a hydrophobic material. The SnCl₂ sensitization solution shows a similar value of 88.7°. The addition of 0.1 vol% *Tween 20* to the liquids decreases the contact angle by 40.4° for DI water and by 39.9° for the SnCl₂ solution. Incorporating 10 vol% *Tween 20* into the resin as an additive reduces the contact angle by 22.6° for DI water and by 26.1° for the SnCl₂ solution. When both the resin and the liquid contain *Tween 20*, the contact angle of DI water decreases by 51.3° to 39.3°. In this combined case, the SnCl₂ droplet spread completely across the surface, preventing an accurate determination of the initial contact angle. Fig. 6 shows the spread of the SnCl₂ droplet over 5 min.

Since the Tollens' reagent is an aqueous coating method, surfaces with contact angles exceeding 90° are considered poorly wettable and prone to incomplete coating. For reference, polytetrafluoroethylene (PTFE) exhibits a contact angle of approximately 111° [39]. The strong reduction in contact angle induced by *Tween 20* confirms its effectiveness as a

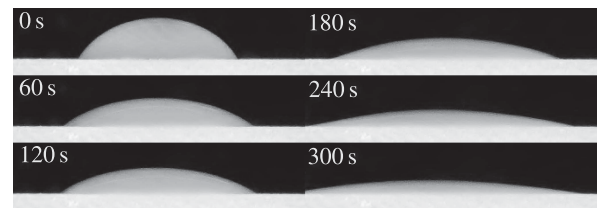


FIGURE 6. Sequence of six images showing the evolution of a SnCl₂ droplet on the *Grey Resin* containing *Tween 20* as an additive, captured at 60 s intervals.

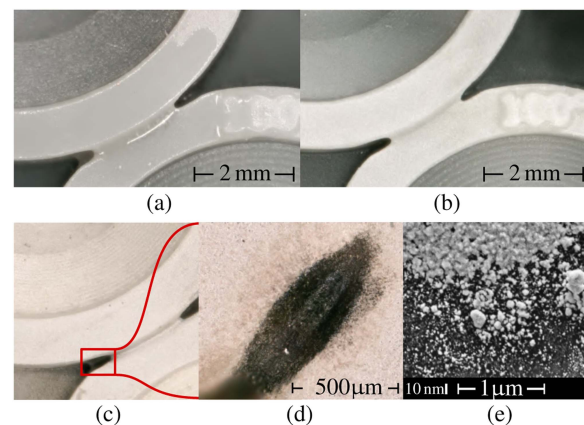


FIGURE 7. Results of the cleaning study using the complex-geometry samples from Fig. 2(c). (a) after the standard procedure recommended by *Formlabs* and (b) after the extended cleaning protocol. (c) Metallization result obtained after the standard cleaning procedure, showing discolorations which are detailed in (d). (e) SEM image of a residue-covered area on a planarized test sample.

wetting agent and demonstrates its potential for improving the coating behavior of the *Grey Resin*. Furthermore, the results indicate that, for the investigated resin system, direct incorporation of custom fillers into the resin vat can be used to modify surface properties. Since this approach is resin-system-specific, its effectiveness must be verified separately for each resin formulation. Potential trade-offs associated with *Tween 20* addition are evaluated in the following sections.

B. CLEANING PROCEDURE

The detailed views in Fig. 7 show the impact of the cleaning procedure on the complex-geometry samples from Fig. 2(c). The sample in Fig. 7(a) was cleaned according to the procedure recommended by *Formlabs*. During drying with compressed air, residual resin was expelled from the narrow gaps, as illustrated in Fig. 7(a). Due to the mixing of resin and 2-propanol during cleaning, these residues only partially cured and were difficult to remove.

For the sample shown in Fig. 7(b), the extended cleaning protocol was applied, followed by compressed air drying. No resin residues were observed on the surfaces, which was verified by inspection using an optical microscope. Fig. 7(c) presents the metallized result obtained after using the standard cleaning protocol but drying with compressed air was omitted.

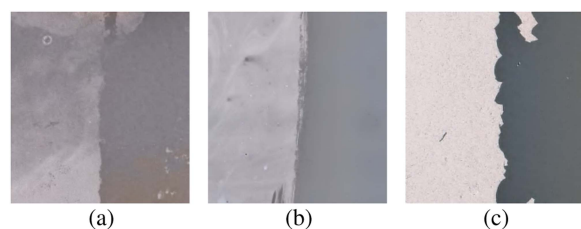


FIGURE 8. Surface of the *Grey Resin* after metallization (a) and (b) without SnCl_2 pretreatment: (a) without and (b) with the additive *Tween 20*. For comparison, (c) Reference sample fabricated using the standard process sequence, including SnCl_2 pretreatment. The right half of the metallized area was removed using adhesive tape.

Dark discolorations are visible in the narrow gaps, which are detailed in the magnified view shown in Fig. 7(d).

These observations demonstrate that the standard *Formlabs* cleaning procedure is insufficient for complex features, therefore an extended protocol is required. Moreover, it was observed that residual resin–2-propanol mixtures remaining on the surface cause a black discoloration after silver deposition. Organic residues on the incompletely cured resin surface, such as residual 2-propanol and trace amounts of unreacted photoinitiator components, can act as weak local reducing agents during the Tollens' reaction. These species reduce the $[\text{Ag}(\text{NH}_3)_2]^+$ complex to metallic silver only at discrete sites. The resulting silver particles are in the size of 10 nm or smaller, which do not coalesce into a continuous metallic layer but remain as colloidal silver particles. These nanoparticles scatter light incoherently at a low overall reflection coefficient and additionally absorb visible light through plasmonic effects, resulting in a dark grey to black surface appearance [40]. The SEM image in Fig. 7(e), recorded on a residue-covered planarized sample, supports this finding by showing the transition from a continuous layer (top) to discrete nanoparticles (bottom). When the silver coverage remains below the percolation threshold and, thus, consists only of discrete, non-connected particles, charge transport is limited to hopping and tunneling mechanisms. Consequently, the electrical conductivity is expected to drop by several orders of magnitude [41].

C. SURFACE PRETREATMENT

The experimental study evaluating the necessity of SnCl_2 sensitization revealed that, although a silver layer can form without prior sensitization, the underlying resin remains optically visible, indicating the formation of a thin and porous layer. Fig. 8(a) shows the silver layer achieved without sensitization and Fig. 8(b) shows the silver layer on an untreated sample which contains *Tween 20*. The modified resin allows for a denser but still transparent layer when compared to the reference sample in Fig. 8(c). Due to the insufficient layer thickness, the sheet resistance and therefore the conductivity of the silver layer could not be determined, nor could the film thickness be quantified.

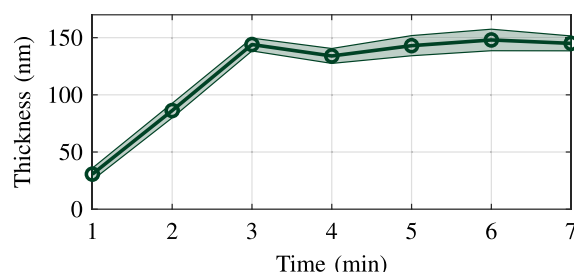


FIGURE 9. Measured results of layer thickness as a function of immersion time in the silver solution. The circles indicate the calculated mean values, while the shaded areas represent the corresponding standard deviations.

Hence, without SnCl_2 pretreatment, silver deposition with sufficient layer thickness cannot be achieved on the *Grey Resin*. This indicates a weak silver-substrate interaction relative to silver-silver interaction, promoting homogeneous nucleation in the solution. Surface functionalization shifts the interaction balance toward silver-substrate binding [28].

D. IMMERSION TIME

Fig. 9 shows the silver layer thickness as a function of the immersion time in the silver solution at 17 °C. During the first 3 min, the layer thickness increases nearly linearly with the immersion time at an average plating rate of 48 nm/min. Beyond this duration, the thickness saturates and remains approximately constant. Consequently, an immersion time of 4 min at 17 °C was selected to ensure a maximum and stable layer thickness.

From the temporal correlation with the onset of reagent turbidity, it can be inferred that homogeneous nucleation of silver particles in the bulk dominates from this point onward, while heterogeneous nucleation at the surface is largely suppressed.

E. PROCESS TEMPERATURE

Fig. 10 summarizes the temperature dependence of layer thickness, electrical conductivity, sheet resistance, and surface roughness. Above 17 °C the thickness has a decreasing trend with increasing temperature. The reduced thickness at 5 °C could be attributed to an insufficient immersion-time extension. Electrical conductivity increases with temperature, except for an outlier at 17 °C. The sheet resistance data indicate that the thickness reduction at elevated temperatures is not compensated by the conductivity increase. Surface roughness increases monotonically with temperature. The RMS height is 23 nm at 5 °C and increases to 572 nm at 80 °C. Likewise, the standard deviation increases monotonically with temperature, rising from 6 nm at 5 °C to 411 nm at 80 °C, indicating a highly non-uniform increase in surface roughness with strong local variations. Fig. 11 compares silver-coated planarized samples processed at 5 °C (a) and 80 °C (b). In both cases, silver agglomerates are visible. The agglomerates grow irregularly after homogeneous nucleation becomes dominant. This behavior can emerge as the autocatalytic Tollens' process progressively shifts from initially non-selective heterogeneous nucleation toward a homogeneous nucleation

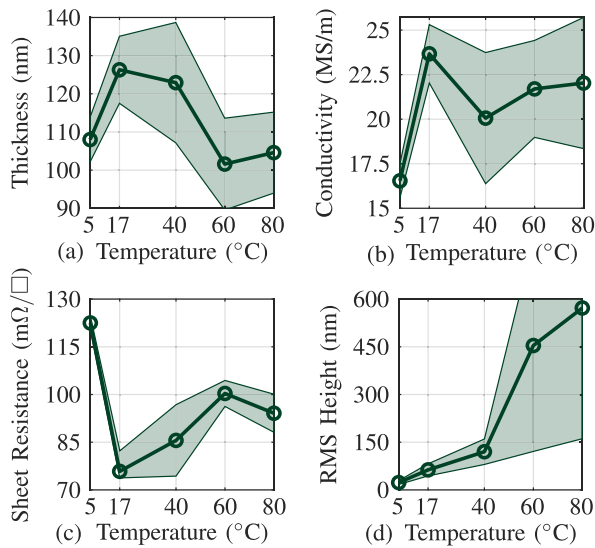


FIGURE 10. Measurement results of (a) layer thickness, (b) electrical conductivity, (c) sheet resistance, and (d) RMS height of the silver layer as a function of temperature. The circles indicate the calculated mean values, while the shaded areas represent the corresponding standard deviations.

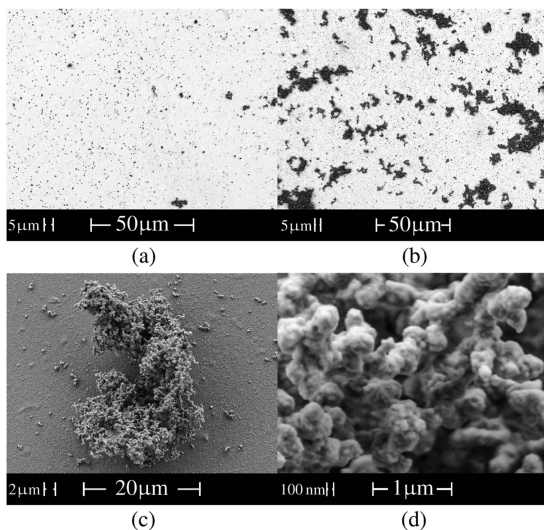


FIGURE 11. Overview images of the silver surface processed at (a) 5 °C and (b) 80 °C captured with the Keyence VK-X3050 optical microscope. SEM detailed views of (c) an agglomerate and (d) its internal structure.

mode, which is reflected in the porous, randomly interconnected structure observed in the SEM images shown in Fig. 11(c) and (d). At 80 °C, agglomerates (dark regions) reach up to 70 μm in lateral extent and 15 μm in height, whereas at 5 °C they remain below 5 μm in size.

These observations suggest that, when the immersion time becomes long relative to the reaction rate, surface roughness increases due to the formation of large agglomerates. This result is consistent with the conclusion drawn in Section IV-D, where it was shown that homogeneous nucleation becomes the dominant mechanism after approximately 3 min. Beyond this point, the agglomerates grow rapidly and subsequently sediment onto the surface, thereby increasing the roughness.

TABLE 2. Results of the Process Optimization Study

Experiment	Thickness (nm)	Conductivity (MS/m)	Sheet Resistance (mΩ/□)
Reference	126.3 ± 8.79	23.0 ± 1.64	75.8 ± 2.06
Ultrasonic Assistance	164.0 ± 11.94	27.9 ± 3.11	53.0 ± 4.47
<i>Tween 20</i> in Resin & Reagent	122.9 ± 6.92	19.51 ± 1.47	92.22 ± 4.47
<i>Tween 20</i> in Resin	110.9 ± 7.50	18.5 ± 1.56	107.5 ± 5.17
Tap Water	127.8 ± 19.38	8.8 ± 1.39	200.2 ± 9.08
Contamination	77.0 ± 14.10	6.6 ± 4.72	942 ± 647.28

The observed increase in conductivity is likely associated with enhanced particle mobility at elevated temperatures. Increased Brownian motion facilitates improved interconnection of the initially deposited silver particles, resulting in a denser and less porous film. However, because the solution reaction proceeds faster at higher temperatures, the plating bath drifts subsequently earlier into the homogeneous nucleation deposition mode, leading to a net reduction in overall thickness.

F. PROCESS OPTIMIZATION

Table 2 summarizes the results of the process optimization study. Fig. 12 reports the relative changes, normalized to the standard procedure outlined in Section III-B. Using the standard procedure, a layer thickness of 126.3 nm and an electrical conductivity of 23 MS/m were achieved. Introducing contaminants, or using tap water, reduced the conductivity by 71.3 % and 61.7 %, respectively. The layer thickness decreased by 39.0 % in the presence of contaminants but increased minimally by 1.2 % when tap water was used. However, the observed increase in layer thickness remains within the standard deviation. A pronounced increase in the standard deviation of the sheet resistance is observed in the presence of solution contamination, reaching 647.28 mΩ/□, while all other measurements exhibit values below 10 mΩ/□. Adding *Tween 20* had little effect on the layer thickness, however, the conductivity decreased by 19.5 % when *Tween 20* was added only to the resin and by 15.2 % when it was added to both the reagent and the resin. In the ultrasonic assistance study, the application of ultrasound increased the layer thickness by 29.8 % while simultaneously increasing the conductivity by 21.3 %. The sheet resistance provides a clear basis for comparison: the stronger the contamination of the Tollens' reagent, the higher the sheet resistance. Only the use of ultrasonic agitation results in a reduction of the sheet resistance.

Fig. 13 shows SEM micrographs of silver films produced with (a) *Tween 20*, (b) tap water, (c) ultrasound assistance, and (d) the standard process. To enable higher magnification, sample (d) was sputter-coated with gold. Compared to Fig. 13(c), the images (a) and (b) display increased film heterogeneity with larger pores, consistent with reduced conductivity. The ultrasound-assisted film in (c) exhibits smaller grain size

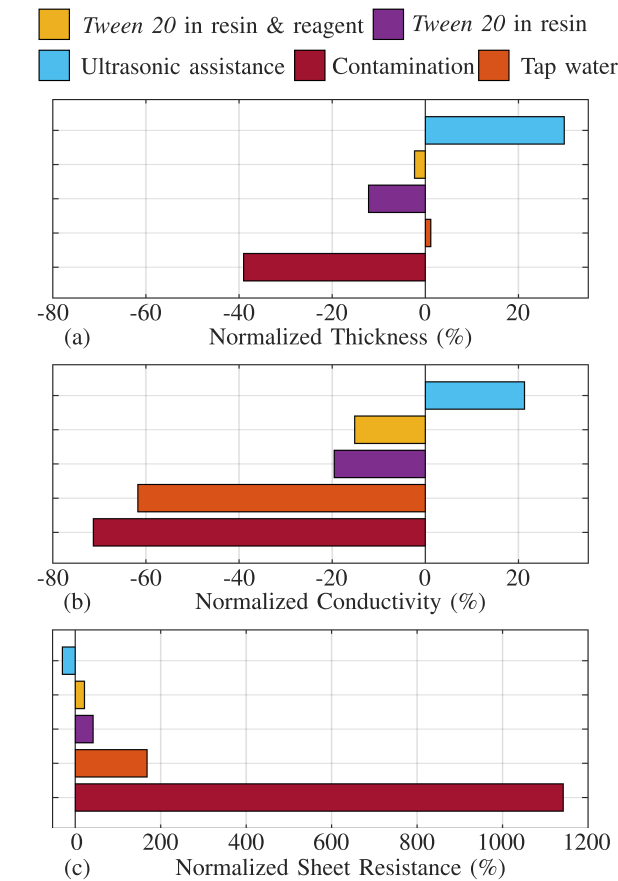


FIGURE 12. Results of the process optimization study. Relative change of the mean values of (a) layer thickness, (b) electrical conductivity, and (c) sheet resistance, each normalized to the reference process.

TABLE 3. Results of Repeated Silver Deposition

Number of depositions	Thickness (nm)	Conductivity (MS/m)	Sheet Resistance (mΩ/□)
1	115.5 ± 9.88	18.0 ± 1.83	108.0 ± 5.92
2	196.4 ± 17.16	21.4 ± 2.74	53.7 ± 5.02
3	270.5 ± 22.66	22.0 ± 1.91	37.7 ± 0.87

and a dense, well-connected microstructure. These results align with reports for other electroless plating processes [42], where enhanced mass transport and degassing at the substrate surface are identified as the primary mechanisms. The high-magnification view in (d) reveals that even high-quality silver layers retain pores. The pore size ranges from the elongated pores with an extent of approximately 200 nm in (a) to approximately 10 nm in (d). Despite the reductions in conductivity and film uniformity, the addition of *Tween 20* can be beneficial for components that exhibit pronounced bubble formation during the metallization or surface sensitization process as a consequence of their geometrical features.

G. REPEATED SILVER DEPOSITION

Table 3 summarizes the results of repeated silver depositions. A second deposition increases the layer thickness by 70.0 %

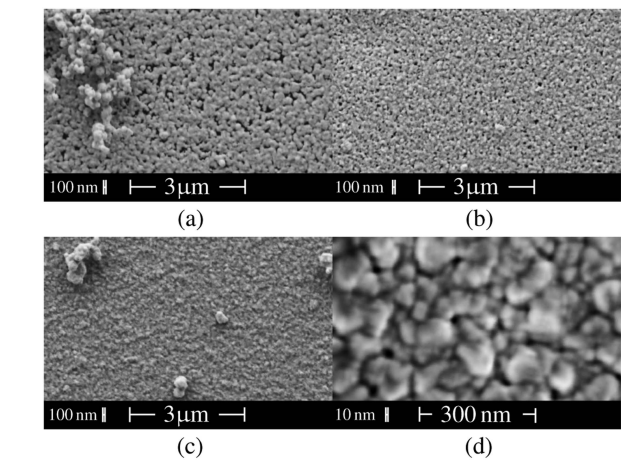


FIGURE 13. SEM detail images of the silver layer morphology with isolated agglomerates. In (a), *Tween 20* was added to both the resin and the reagent. In (b), tap water was used to prepare the reagent. (c) Results obtained with ultrasonic assistance. (d) Magnified view on the morphology obtained by the standard process.

relative to the first; a third deposition adds a further increase of 37.7 %, yielding a final thickness of 270.5 nm. The electrical conductivity rises from 18 MS/m after one deposition to 22.0 MS/m after three depositions, i.e., an increase of 22.2 %. The absolute thickness variation scales with the mean thickness, whereas the relative variation remains approximately constant at 8 %–9 % across one to three silvering cycles. In contrast, the relative variation of conductivity and sheet resistance does not follow a monotonic trend with cycle number. Thus, repeating the deposition process is an effective procedure to increase thickness. The observed conductivity increase can be attributed to filling of voids but cannot be fully explained.

V. CROSS-EXPERIMENTAL DISCUSSION

The results in Section IV show that the silver deposition process is sensitive to external influences and that sample-to-sample variations within one process condition are strongly affected by local factors. The temperature study in Section IV-E indicates that a constant process temperature is required for reproducible results. The comparison of cleaning procedures, as well as the results obtained with tap water and deliberately contaminated samples, further show that impurities markedly increase sample-to-sample variation. When tap water is used instead of deionized water, the standard deviations of conductivity and film thickness increase from approximately 7 % of the mean value to more than 15 %. For the contaminated samples, the standard deviation increases to 18.3 % for film thickness and 71.5 % for conductivity, relative to the corresponding mean values.

The particle-based contamination introduces additional nucleation sites into the reaction solution. This can promote an earlier transition from heterogeneous nucleation on the substrate to homogeneous nucleation in the solution, increasing process variability. Local substrate contamination can also

prevent complete film coalescence, as shown in Fig. 7, resulting in pronounced local conductivity variations.

Consequently, the yield of microwave components fabricated using this metallization process depends strongly on process stability and cleanliness. However, a quantitative yield assessment must be performed for each component geometry individually and should also include mechanical reliability.

The most conductive silver layer obtained in Table 2 exhibits a conductivity of 27.9 MS/m, corresponding to approximately 45% of the bulk conductivity of silver. This reduction is consistent with thin, chemically deposited silver films, where the measured conductivity is not only governed by the intrinsic conductivity of silver but also by size- and microstructure-dependent scattering mechanisms. In the Drude–Sommerfeld [43], [44] description, metallic conductivity is determined by the motion of conduction electrons between scattering events. If the film thickness becomes comparable to the electron mean free path, additional scattering at film surfaces and interfaces increases the electrical resistivity. This size effect is described by the Fuchs–Sondheimer model [45], [46]. For silver at room temperature, the electron mean free path is on the order of 50–60 nm [47]. Surface and interface scattering may therefore remain relevant for the film thicknesses investigated here. Consequently, an increasing film thickness can contribute to higher conductivity not only through improved coalescence and reduced porosity, but also through the reduced relative importance of interface scattering. In addition, grain-boundary scattering can reduce the conductivity of polycrystalline metal films, as described by the Mayadas–Shatzkes model [48]. Impurities, porosity, and nonmetallic voids can further decrease the measured conductivity by introducing additional scattering centers and by reducing the effective metallic cross section available for charge transport.

For incompletely coalesced films, much stronger conductivity reductions can occur and are commonly described within a percolation framework [49]. Below the percolation threshold, no continuous metallic transport path exists, and charge transport is instead dominated by hopping or tunneling processes between isolated metal islands.

VI. SILVER FILM MORPHOLOGY IN THE CONTEXT OF MICROWAVE APPLICATIONS

The results presented in Section IV enable an assessment of the morphology of the Tollens-deposited silver layers. The coating exhibits a distinct bilayer structure with an atypical thickness-to-roughness ratio, as visualized in Fig. 14.

A continuous silver layer with a thickness of approximately 125 nm forms directly on the resin surface. Depending on the process purity, this layer may contain voids with characteristic sizes ranging from 10 to 200 nm, as illustrated in Fig. 13. On top of this first layer, silver agglomerates are deposited by sedimentation, as shown in Fig. 14. Their characteristic size strongly depends on the process time and temperature and ranges from several hundred nanometers up to approximately

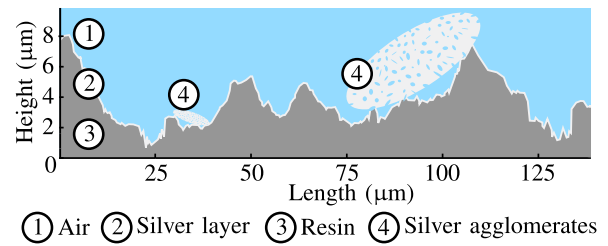


FIGURE 14. Height profile of an SLA-printed surface measured with the Keyence VK-X3050. The vertical axis is magnified by a factor of four to improve the visualization of the surface topology. The white line corresponds to the silver layer on the Grey Resin substrate.

100 μm . Fig. 11 highlights these size variations and demonstrates that this bilayer structure is highly heterogeneous, as both the thickness and spatial distribution of the agglomerate layer vary locally. The agglomerate layer is generally non-continuous, exhibiting an island-like morphology. At extended process durations or elevated temperatures, however, the agglomerates may coalesce, forming an almost continuous upper layer. Including the agglomerate layer in the thickness evaluation can substantially overestimate the thickness of the underlying continuous silver film.

When considering the electrical conductivity, the two layers exhibit different properties. The continuous silver film achieves an electrical conductivity of approximately 18–27.9 MS/m. In contrast, the island-like agglomerate layer can reach thicknesses of several μm but exhibits a lower effective conductivity. The electrical conductivity of porous, foam-like materials decreases approximately linearly with decreasing material density [50] and is therefore lower than that of the corresponding dense bulk material.

Surface roughness is a critical parameter in mmWave applications, as it directly affects conductor losses and alters the propagation constant. For Tollens’ silver-coated microwave components, the overall surface roughness arises from three primary contributions: the intrinsic roughness of the underlying resin substrate, the roughness introduced by the compact silver film, and the additional roughness caused by silver agglomerates. A planarized, silver-coated sample from Section IV-E, measured at a location free of agglomerates, exhibits a compact-film roughness of $R_q = 23\text{ nm}$. Since the roughness of the planarized resin substrate is on the order of $R_q = 1.5\text{ nm}$, the additional roughness introduced by the compact silver film is small. In contrast, the agglomerates introduce a pronounced roughness contribution. As shown in Fig. 10(d), the agglomerate-induced roughness increases with process temperature and reaches up to $R_q = 572\text{ nm}$ at 80°C . The third component is the surface roughness of the SLA-printed substrate, which is approximately $R_q = 1.5\text{ }\mu\text{m}$. Consequently, the overall surface roughness is dominated by the base-material topography and the presence of agglomerates, whereas the roughness contribution of the compact silver layer is negligible.

A comparison between conventional technologies highlights the atypical thickness-to-roughness ratio of the silver

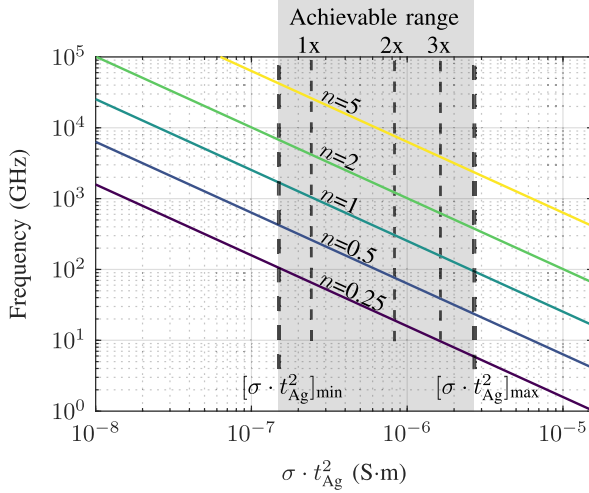


FIGURE 15. Ratio of layer thickness to skin depth $n = t_{Ag}/\delta$ as a function of frequency and the product of electrical conductivity and layer thickness squared ($\sigma \cdot t_{Ag}^2$). The dashed lines in the grey shaded area represent the results listed in Table 3.

coating. Copper foils used in conventional microwave printed circuit board (PCB) processes typically have a thickness of $18 \mu\text{m}$ (1/2 oz). Their RMS surface roughness ranges from approximately 0.4 to $2.0 \mu\text{m}$ on the dielectric-facing side and is about $0.4 \mu\text{m}$ on the top side [51]. Consequently, the copper layer thickness exceeds the surface roughness by roughly one order of magnitude.

For the silver coating, this ratio is effectively inverted: the RMS surface roughness is approximately one order of magnitude larger than the layer thickness. Fig. 15 illustrates the ratio of the silver layer thickness to the skin depth, defined as

$$n = \frac{t_{Ag}}{\delta}, \quad (5)$$

where t_{Ag} denotes the thickness of the deposited silver layer. The skin depth is given by [52]

$$\delta = \sqrt{\frac{1}{\pi f \sigma \mu}}, \quad (6)$$

with f representing the frequency, σ the electrical conductivity, and μ the magnetic permeability. Substituting (6) into (5) and solving for f yields

$$f = \frac{n^2}{\mu \pi} \cdot \frac{1}{\sigma t_{Ag}^2}, \quad (7)$$

which forms the analytical basis of the plot. The gray shaded region indicates the achievable parameter space for the investigated silver layers. It is bounded by

$$[\sigma t_{Ag}^2]_{\min} \quad \text{with} \quad \sigma = 15 \text{ MS/m}, \quad t_{Ag} = 100 \text{ nm}, \quad (8)$$

and

$$[\sigma t_{Ag}^2]_{\max} \quad \text{with} \quad \sigma = 30 \text{ MS/m}, \quad t_{Ag} = 300 \text{ nm}. \quad (9)$$

The dashed lines in the grey shaded area represent the results of the repeated silver depositions listed in Table 3. Considering the mmWave frequency range from 30 GHz to 300 GHz, it becomes evident that the silver layer thickness is usually smaller than the corresponding skin depth. Even for components subjected to three metallization cycles, which therefore approach the upper boundary of the achievable range, the skin depth exceeds the silver layer thickness over most of the mmWave band and becomes comparable only at frequencies above approximately 100 GHz.

Compared with conventional PCB copper layers or bulk metal structures, the ratio $n < 1$ in Fig. 15 over most of the mmWave band suggests that the current density cannot be assumed to be confined to a thin surface region of the conductor. Instead, it may extend over a substantial fraction of the metal-layer volume, with the exact distribution and field penetration being affected by grain boundaries, local discontinuities, and the agglomerate layer. This limits the direct use of conventional surface-impedance-based descriptions for estimating the propagation constant and conductor losses, since these approaches generally assume an electromagnetically thick conductor for which the influence of the opposite material interface is negligible [52].

For thicker films obtained by repeated metallization, the ratio n may become larger than unity. In this case, the silver layer approaches the behavior of an electromagnetically thick conductor. However, the modeling problem is then shifted toward the accurate representation of roughness and morphology-related length scales. In particular, the heterogeneous agglomerate layer and local film discontinuities, and grain-boundary-limited conduction may affect the effective current path. Therefore, commonly used conductor-roughness models for predicting loss and propagation behavior, such as Huray-type [53], Groiss-type [54], or gradient-based models [55], should not be applied without adaptation and validation for the morphology and current-density distribution of Tollens-derived silver films. Developing such a morphology-aware RF model is beyond the scope of the present work.

VII. TRANSFER OF THE METALLIZATION PROCESS TO A DEMONSTRATOR

This section provides a component-specific proof of concept and a consistency check showing that the selected process can be applied to a typical waveguide component and yields measurable RF transmission behavior consistent with the sample-based process characterization.

A helically wound WR-15 waveguide with a length of 1 m was used as demonstrator, as shown in Fig. 16(a). The helical geometry reduces the overall footprint and was verified by simulation to not significantly affect the loss characteristics. The waveguide was fabricated from *Grey Resin* with a layer height of $25 \mu\text{m}$. After thorough cleaning using the extended cleaning protocol and subsequent post-curing, the waveguide was metallized with one single silver layer. For this purpose, the ultrasonic-assisted process described in Section III-C was

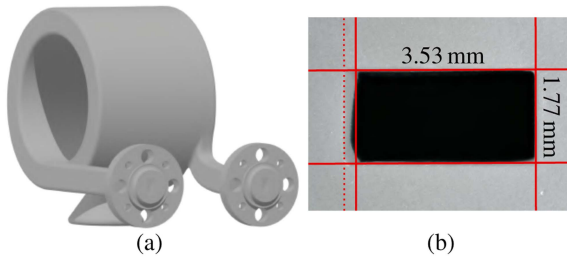


FIGURE 16. (a) Rendering of the 1 m helically wound WR-15 waveguide and (b) photograph of the printed flange geometry.

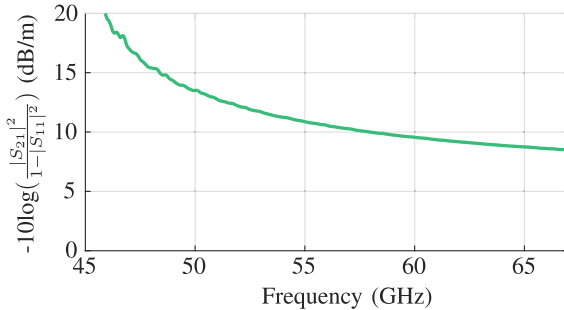


FIGURE 17. Attenuation per meter of the 3D-printed helically wound WR-15 waveguide.

applied. To metallize the internal waveguide surfaces, the reaction solution was circulated through the waveguide using a peristaltic pump.

The measured flange geometry in Fig. 16(b) shows that the printing process reduced the WR-15 channel dimensions by 229 μm along the broad wall and by 110 μm along the narrow wall. The reduction in the waveguide width is mainly associated with the inward deformation of the left side wall, as indicated by the dashed line, and is likely related to the print orientation.

The scattering parameters were measured using an Agilent PNA E8361A vector network analyzer. A thru-reflect-line calibration was used to shift the reference planes to the input flanges of the waveguide. The attenuation per meter, extracted from the measured scattering parameters, is shown in Fig. 17.

The reduced waveguide cross section increases the cutoff frequency by approximately 2.6 GHz, which partially explains the pronounced attenuation increase below 55 GHz. Above this frequency range, the measured attenuation of 8.75 dB/m at 65 GHz shows that the selected metallization process yields sufficient RF transmission for a functional waveguide demonstrator, while a general performance qualification remains component- and requirement-specific.

VIII. CONCLUSION

This work provides the first systematic quantification of the fundamental material properties of Tollens-deposited silver on SLA-printed polymers and establishes process-property relationships relevant to microwave devices. By evaluating how key process variables affect layer thickness, electrical conductivity, sheet resistance, and surface roughness, the study

identifies both critical failure mechanisms and optimization strategies. For the investigated resin system, the incorporation of custom fillers provides a possible route for adjusting surface energy and supporting material-specific process tuning, but its applicability must be verified for each resin formulation. Process purity, including thorough cleaning of the 3D-printed part, is confirmed as a central prerequisite, as impurities lead to severe conductivity degradation, whereas ultrasonic agitation simultaneously enhances conductivity and layer thickness. The main microstructural and size-dependent limitations that keep the conductivity of the polycrystalline silver layers significantly below that of bulk silver are discussed. Sequential metallization is shown to be an effective method for increasing the compact-film thickness.

A particular focus was placed on analyzing the morphology of the deposited silver. The structure and growth behavior of porous agglomerates were documented, and the atypical ratio between effective film thickness and surface roughness was quantified. This multilayer morphology comprising a thin, dense conductive film overlain by a heterogeneous agglomerate layer raises fundamental questions regarding the applicability of surface-impedance-based simulation approaches to Tollens-derived silver films. At the same time, the WR-15 waveguide demonstrator shows that the metallization process can be applied to a typical microwave component and can provide sufficient RF functionality for component-level proof-of-concept validation. Overall, this study establishes a quantitative basis for assessing RF-relevant properties of Tollens-based metallization on SLA-fabricated components. Morphology-aware modeling of loss mechanisms is identified as the next step toward predictive component-level RF analysis.

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