Executive Summary Report: Development of a New Electroless Plating Technique

Approved in SAP by Workflow/Freigabe mit SAP-WF	**CM Release/Freigabe**
Prepared by/Ersteller Ralf Bölter (TESAT); Isabel Montero (CSIC)	
Engineering *Bereich* Ulrich Wochner	
Quality Stefan Jauerneck	
Configuration Management Iris Rock	
	TESAT This document has been configured electronically and is valid without handsignature. The TESAT configuration management department certifies, that this document has been approved by the responsible people/functions in accordance with the TESAT configuration management process. Iris Rock 2023.09.05 08:57:02 +02'00'

CHANGE RECORD/ÄNDERUNGSBESCHREIBUNG

Issue	Details of Change/Änderungsdetails	Date
A	Initial issue	2023-09-04

INDEX

1 Objective

The main objective of this project was to obtain metallic coatings using electroless and ionic liquids (ILs) for corrosion and radiation protection, as well as to enhance electrical properties of satellite components.

2 Introduction

The Literature Survey and the Process Development were developed by CSIC, ICMM-Materials Science Institute of Madrid of CSIC, Spain, and the Sample Testing and Design and Electrical Test of Demonstrators, Life Cycle Assessment by the main contractor TESAT Spacecom, Germany of this ESA ITT AO/1-9362/18/NL/AR/gp. This Executive Summary of the final report is focused on the results on the application of ionic liquids to metal deposition and surface modifications by electroless process.

A simple electroless procedure for depositing metal is a major challenge in materials research. It has a significant impact in various fields such as plating, electronics, energy storage and conversion, catalysis, sensors, photonics, and optoelectronics and space industry as a whole. Electroless plating is an auto-catalytic plating process that occurs without the use of external electrical power and it involves several simultaneous reactions in a solution. It can also be used to coat insulating or non-conductive substrates. The application of metallic coatings must be as simple as possible in order to be embraced by industry. Compared to electroless deposition using typical aqueous solutions, the electroless deposition method of noble metals from ionic liquids can result in thicker deposits, ranging from 100 nm to 10 µm. This is different from the typical few monolayers grown in aqueous solutions. This technique can be divided into three categories: 1) Galvanic displacement reaction, 2) Disproportionation reaction, and 3) Deposition in the presence of reducing agents. In the case of water solutions, water has a limited potential window, which hinders the deposition of metals with large negative reduction potentials like Cr and Zn due to poor current efficiencies, and hydrogen embrittlement of the substrate. Currently, few examples of electroless deposition in ILs have been shown in the published literature.

The physical and chemical characteristics of the ionic liquids explain their potential application to general chemistry as a "green chemistry" product. The simplest definition of an ionic liquid (IL) is: « A liquid composed entirely of ions..». In this sense, it can be said that molten common salt is an ionic liquid. But not only individual compounds in their liquid state can be ionic liquids, but also mixtures of salts. When speaking of ionic liquids, it should be understood that it not only applies to simple and common ions such as the [Cl] - ion or other ions such as the [SO4] 2- ion, but also includes complex ions formed by inorganic compounds. ILs have recently received a great deal of attention in the literature for a number of electrochemical processes. A large number of ILs and its mixtures as possible electrolytes to tune the redox reactions (M/Mn+) and to trigger the galvanic displacement process. However, compared to aqueous electrolytes, there is no universal electrochemical series in the case of ILs due to the lack of a standard reference electrode potential. ILs can be divided into three subcategories of protic, aprotic, and deep eutectic solvents (DES). As ionic liquids do not contain water it was felt that they would provide superior, corrosion free deposition environments. Difficulties in keeping water out of the hygroscopic mixtures led to select the most appropriate ILs.

We have reviewed the metal deposition and the improvement that we can expect from the substitution of water solutions by ionic liquids. The development of metallic coatings (layers and multilayers) on metals, dielectrics or magnetic substrates from electroless deposition, without the need for an external source is a fascinating concept that constitutes the challenge of this project. Thus, in this project we have highlight the progress in the electroless deposition of selected metals from ionic liquids and their applications toward new coating for RF devices. The report also concludes with a general discussion of future potential industrial developments, from a scientific, technological and economic point-of-view. Numerous studies of electroless deposition in aqueous systems can be found in literature, yet little has been reported from ionic liquids nither of them is on the metal/substrates investigated in this project.

3 Process Development

The coatings and substrates that were selected are listed in Table 1. An ionic liquid known as Deep Eutectic Solvent, which consists of choline chloride and ethylene glycol in a 1:2 molar concentration, was utilized as the solvent.

A significant accomplishment in materials research in this project is the development of a straightforward procedure for depositing metal coatings. In this report, we present a summary of the relevant innovative results of using ionic liquids for metal deposition on the metals, polimers, ceramics and ferrite substrates. We also showcase the surface modifications achieved and the sample characterization.

The metallic coatings are deposited from their respective chlorides, nitrates, or sulfates. The deposition process has been extensively studied in this project, considering the main parameters such as solution concentration, temperature, and deposition time.

Coatings	Substrate	Selection	Size
Ag, Cu, Ni	AA2024 aluminium alloy	Tesat Spacecom	*20x20 mm*
Ag, Cu, Ni	AA6061 aluminium alloy	Tesat Spacecom	*20x20 mm*
Ag, Cu, Ni	AA6082 aluminium alloy	Tesat Spacecom	*20x20 mm*
Ag, Cu, Ni	3D printed aluminium alloy	Tesat Spacecom	RF Filters
Ni, Au	NdFeB Ferrite	Vacodim, Tesat Spacecom)	*20x20 mm*
Ag	Copper	Cu foil (Goodfellow 99.99), CSIC	*20x20 mm*
Au	Copper	Cu foil (Goodfellow 99.99), CSIC	*20x20 mm*
Ag	PEEK	PEEK GF30, Tesat Spacecom	*20x20 mm*
Ag	Kapton	Tesat Spacecom	20X70 mm
Ag	Alumina	Electronic substrate, CSIC	20X70 mm

Table 1: Coatings and Substrates

Experimental set-up:

A diagram and photos of the electroless process assembly are shown in Fig. 1. The laboratory setup for electroless includes six hot plates with programmable temperature control, a data acquisition system, and a magnetic stirrer. Additionally, ethylene glycol baths are utilized for temperature control and testing purposes. The temperature range of 30°C - 90°C is required for different deposition processes. Glass cells are strategically placed symmetrically within the container, partially immersed in the ethylene glycol to avoid interference with the magnetic stirring. Each hot plate has eight cells for holding the substrates to be coated, securely clamped with metal forceps.

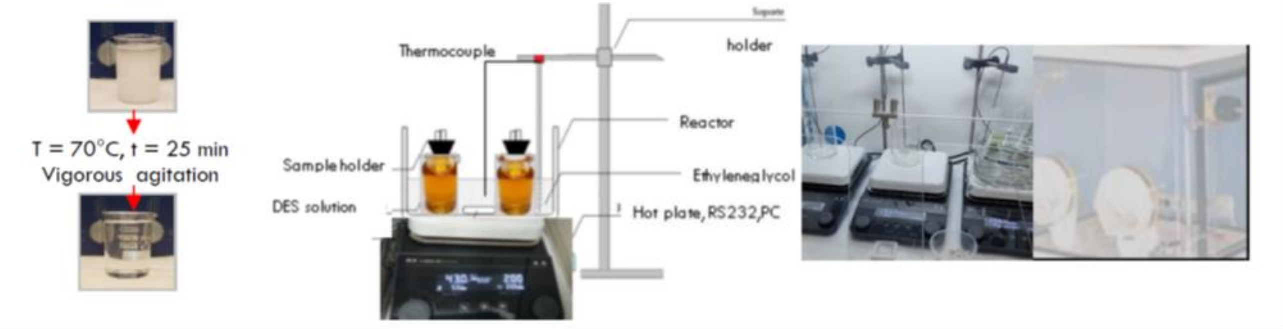


Fig. 1: Deep eutectic solvent preparation and conditions (left) . Schematic representation of the experimental setup for electroless deposition (center) and detail of some experimental plates IKA (RS232 ports) inside the cabinets (right).

The electroless plating process using ILs relies on controlling various parameters to achieve a high-quality coating with desired properties, depending on the substrate. The electrolyte composition, concentration, temperature, deposition time, and mechanical/ultrasonic stirring are key parameters influencing the deposition rate. The initial treatment or preparation of the substrate surface also affects the coating quality, involving operations to clean the surface and enhance roughness for better adhesion of the metallic coating.

The fundamental principle of electrolessusing ILs remains the same: reducing metal ions in the electrolyte without electrodes connected to an electrical source, resulting in a metallic coating on the substrate.

Results and discussion:

Fitsly, an attempt was made to deposit Ag, Ni and Cu using the following ILs:

1) Choline Chloride / Ethylene Glycol 1:2 molar, 2) Choline Chloride / Urea 1:2 molar, 3) Choline Chloride / Oxalic Acid 1:1 molar, 4) Choline Chloride / Imidazole 3:7 molar.

In all these four ILs Ag was successfully deposited on the pure Cu foil. However, there is no an adequate silver deposition on the AA6082 substrate, except when using ChCl: EG. For this reason, the ionic liquid (1) ChCl: EG in a 1: 2 molar ratio was selected.

Conversion coating, sensitization and surface activation was also required and these treatments were also optimized. Ni and Cu were deposited on aluminium alloys (intermediate layers) to improve the adhesion of the silver coating to the aluminium alloy and also on ferrites (top layer). In addition, the influence of Cu as an intermediate layer for the nickel deposition on ferrites was checked. For this reason, this additional activity was included expanding the objectives of this project. Silver deposited on dielectrics do not require intermediate layers but a specific activation process is found for each type of sustrate. A detailed flow chart of the electroless process of AA6061, copper, NdFeB ferrite, alumina, Kapton and PEEK is shown in Fig. 2.

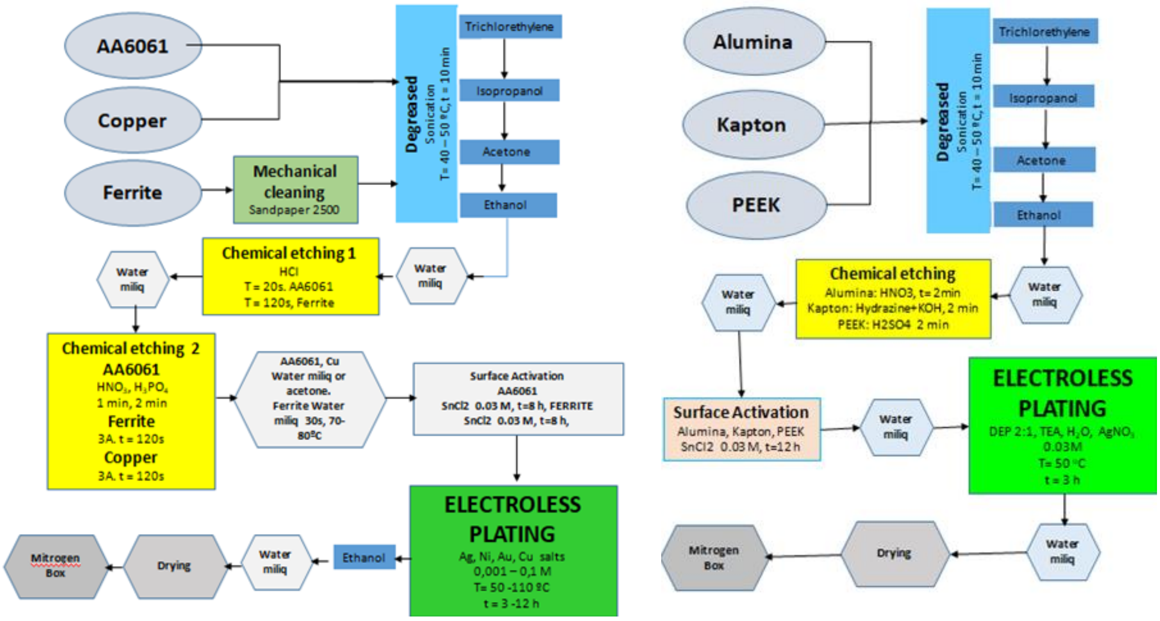


Fig. 2: Detailed flow chart of the electroless process of AA6061, copper, NdFeB ferrite, alumina, Kapton and PEEK.

The deposition of Ag, Ni, Cu and Au was evalutared using different metallic salts, bath temperatures, concentrations and deposition times. It was concluded that the best coatings are obtained from: Silver salt: AgCl, Temperature = 60 - 65°C, Concentration: 0,02 – 0,04M (2,8668 – 4,3002 g/L) Time: 2 – 4 h. Silver coatings were also deposited onto 3D printed filters (this task was not included n the initial program) using a specific electroless process with ILs developed in this project. Two similar 3D printed filters made of AlSi10Mg, were coated with silver. These RF filters are single-piece structures. Chemical procedures were developed to treat the internal part of these 3D RF filters for silver coating. Small 3D samples were used for optimization and characterized by SEM and EDX before and after silver deposition. Copper films (99.9% wt) were used as substrates for gold deposition. Gold chloride was selected as the ion source for gold deposition. The gold coatings were directly deposited on copper foil without surface activation. Depositions were performed at different temperatures while maintaining a constant solution concentration: Concentration = 15 mM, T = 50°C, 55°C, and 60°C. Also Ag wasdeposited on dielectrics aand i and Au was depositd on ferrites. The detailed information about the parameters of the depostion of all metallic coatings can be found in the Final Report. Some examples of the results are shown in Fig. 3.

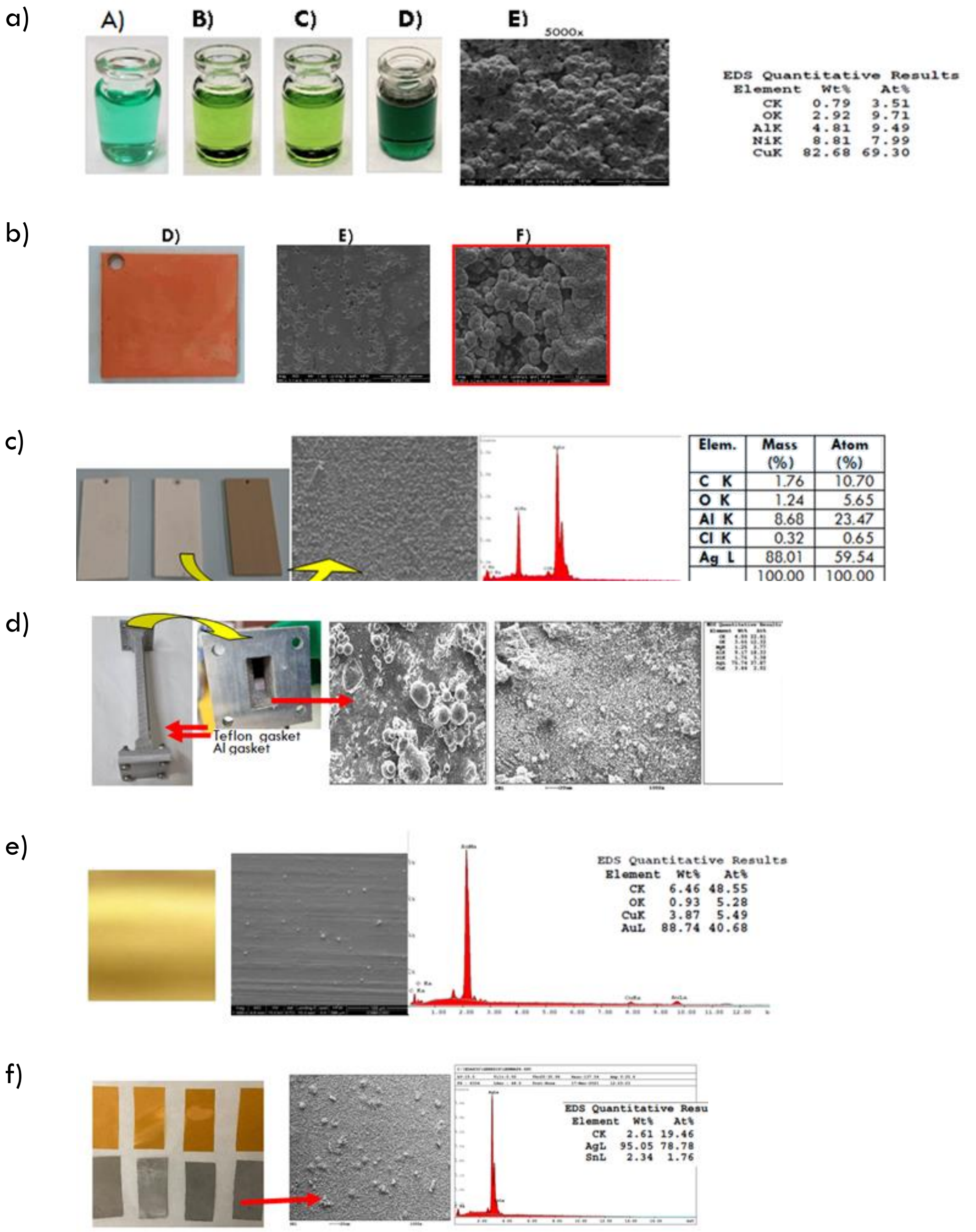


Fig. 3: a) Ni IL solutions. thermocromic behaviour. NiCl2. A) aqueous medium. B) Ni IL, C) T = 80°C, D) T = 100°C. E) Cu/ Ni/AA6061, F) EDX composition. b) Color of CuCl2 • 2H2O solutions. A) Aqueous medium. B) ionic liquid, DES. before and C) after the copper deposition process. D) Cu/AA6082, E) and F)SEM mages of the Cu coating IL, AA6061. T=60°, 25 min., c) Photograph of the silver coated AA6082 test samples and copper coated sample before silver deposition, right (left), SEM images, EDX spectrum and chemical composition of silver coated AA6061 (right). d) 3D Printed Filters used as a reactor. Teflon and aluminium gaskets made at CSIC (left). Detail of the inner part of the 3D Printed Filter. SEM image of the as-received 3D printed sample (center). SEM image and EDX results of the silver coated 3D printed samples. e) Photograph, SEM images of gold coated copper, T= 50°C, C= 15 mM EDX spectra and sample composition of the gold coated copper, T= 50°C (left), 55°C. f) Fig. 1. Left) photograph of the silver coated kapton test samples, before (top) and after silver deposition □4□m (bottom). Right) SEM images, EDX spectrum and composition of Ag coated kapton, 60°C. (center) and 60°C (right).

Characterization during Process Development at CSIC:

SEM was employed to analyze the surface morphology of the coating, including factors such as uniformity, presence of pores, and other relevant data for the study of the metallic deposit. EDX was used to obtain the chemical composition of the samples. Inductively coupled plasma atomic emission spectroscopy (ICP-AES). For the characterization of the adhesion of the coatings to the different substrates, we used procedures of the ASTM B571-97 standard. There is only one interface in the case of the adhesion of coatings deposited on a substrate. For this reason, to test the adhesion of the coatings one of the best procedures is the Cross Hatch Adhesion Test using a commercial Cross Hatch Adhesion tester. Excellent metallic adhesion, rating of 5 (0-5) is observed on the different substrates. Electrical conductivity measurements wer performed using the four probes method. It was necessary for the coating to be deposited on an insulating substrate. The conductivity of the silver-coated Kapton substrates has been verified, and promising results have been obtained. The conductivity is comparable to that of pure silver (99.99% Goodfellow foils). Additionally, the RF insertion losses also confirm these positive results.

4 Sample Testing

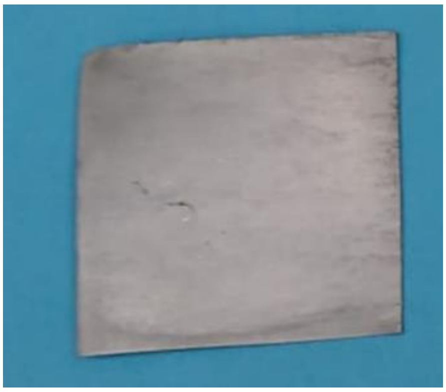
The plating of silver and gold on three different substrate materials has been tested: Aluminium, Copper, Alumina, Peek, Polyimid and NdFeB magnets. Key topics of the investigations were uniformity and thickness of the deposition, adhesion of the plating on the substrate even after thermal storage and thermal cycling and corrosion protection (in case of metal substrates). The tests were performed with flat samples.

The silver plated aluminium samples were completely covered with silver with a thickness of several micrometers. A good adhesion of the silver even after thermal loads was found. A good corrosion protection of the aluminium was found.

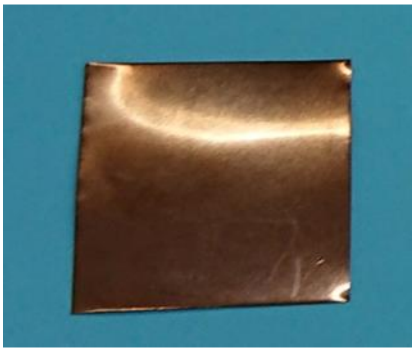
A scan of the surface of the gold plated copper samples by a scanning electron microscope demonstrated that the gold layer and the intermediate nickel layer were not completely dense. Although the surface was gold shining. Therefor the complete surface showed corrosion after corrosion testing. The adhesion of the gold and the intermediate nickel layer was good even after temperature tests.

For the silver plated Peek, Polyimid and Alumina samples a complete coverage of the substrate by the plating and a good adhesion was found. The silver had a thickness of several micrometers.

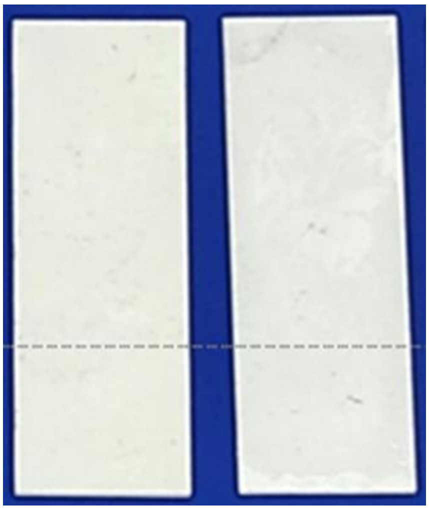
The Nickel plating was not sufficient for a good corrosion protection of the NdFeB magnets. But with an additional gold layer corrosion protection could be demonstrated.



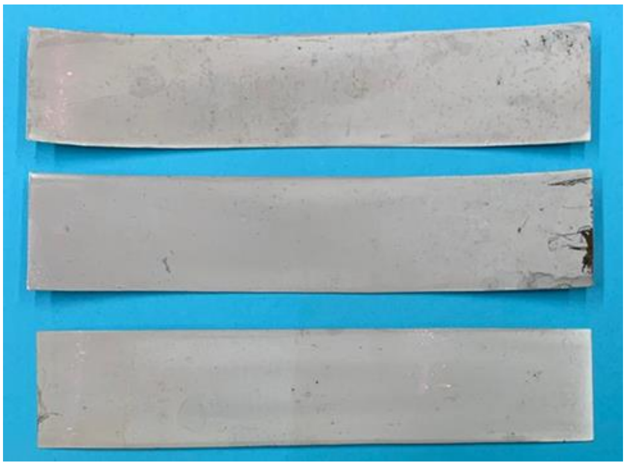
Silver Plated Aluminium



Gold Plated Copper



Silver Plated Alumina



Silver plated Polyimid

Fig. 4: Different Substrates with Electroless Plating

5 Demonstrator Testing

To demonstrate that the electroless plating process with ionic liquids is able to pate complex geometries a bandpass filter was chosen. Especially the inner electrical channel with the resonator structures had to be silver plated. The filters was manufactured by additive manufacturing in one piece. The results were compared to the performance of a conventional filter with same design manufactured with tradional machining processes in two halves (EN AW 6082) and silver plating of the two halves each by electroplating. The bandpass filter has a center frequency of 11 GHz and a bandwidth of 100 MHz. The high frequency electrical performance of the filters was analysed by measuring of the S-parameter, the input and the return loss. Both filters were measured without and with silver.

The filter is made by additive manufacturing of AlSi10Mg that has a relative high content of silicon. Therefor the pre-treatment of the plating process for this filter had to adjusted. In addition a plating process without an intermediate layer of Nickel was found that is much more environmental friendly.

For both filters the silver plating process leads to an improvement of the insertion loss. As the filter made by additive manufacturing needs a more intensive pre-treatment due to the higher silicon content this filter shows a higher shift of the center frequency than the conventionally manufactured and plated filter. The S-parameter measurements showed no anomalies.

It was demonstrated that the complex geometry of the filter made by additive manufacturing could be successfully silver plated by an electroless process with ionic liquids without an intermediate layer of Nickel.

6 Summary

Electoless Plating processes based on Ionic liquids have been developed for silver and gold plating. Good adhesion on different substrates was demonstrated (even after environmental tests). The complex electrical channel of a bandpass filter made in one piece by additive manufaturing was successfully sliver plated by electroless plating with ionic liquids. The electrical performance of this filter is comparable to conventiona filters.

Electroless Plating with ionic liquids offers metallic plating of metallic and non metallic substrates with complex geometries.