

Conducting Copper Patterns on Paper Using Inkjet Printing

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By

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I certify that this report is written adhering to the department guidelines.

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(Sushant Kumar)

Dedicated
to
My Family

Acknowledgement

I would like to thank many people for their technical and mental support without whom this work was not possible.

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Abstract

A simple method is proposed for patterning of conductive copper directly on paper as substrate. The method comprises of reactive inkjet printing of an aqueous solution of palladium salt followed by reduction to metallic palladium by tannic acid. This patterned palladium is used to catalyze further electroless deposition of copper to form conducting pattern of copper on paper. The copper solution for electroless deposition of copper is prepared by mixing a reducing agent (formaldehyde) and a complexant ethylenediaminetetracetic acid (EDTA). The complexant maintains the stability of copper ion in the solution and prevents reduction in solution. Hence, a catalytic surface required for the initiation of the reaction for deposition, palladium used as catalyst here. This report begins with a brief introduction to various application of printed copper. The objective of the present work presented next. A review of the literature on fabricating printed copper lines on paper follows. A description of the experimental methodology and some preliminary result presented next. Different patterns were printed on different scales and observed. The design of UWB antenna given by Electrical and Electronics department is fabricated on paper using Inkjet printing and study of antenna is shown. The report concludes with a section of future work proposed.

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Chapter 1

Introduction

Conductive metal patterns on flexible substrates have the potential to replace expensive and inflexible electronic (silicon) substrates by flexible substrates for various applications like fabrication of cheap sensor arrays¹, thin film transistors¹, electro-optic devices², flexible batteries³ and radio frequency identification tags⁴. Conducting patterns on the flexible substrate will also reduce cost of the electronic devices and make them light weight. Inkjet printing is economical and less time-consuming as compared to traditional photo lithography, when used for printing of conductive patterns on flexible substrates. Another disadvantage of traditional photolithographic techniques is that it can cause discontinuity of conducting lines during etching and lead to wastage of material used for patterning. The goal of this work is to use reactive inkjet printing of catalytic precursors in conjunction with electroless of copper to form conductive patterns on paper.

Typically, chemical reduction method is used for synthesizing conductive nano ink for printing different patterns. It includes precursor, reducing agent and stabilizer for synthesis of metallic colloidal dispersions. The size of nanoparticles depends on the rate of reaction and hence, on the reducing agent. As particles form, surface to volume ratio increases and particles begin to agglomerate because of their high surface energy. Stabilizer prevents agglomeration, by surrounding the particle. The particle size depends on concentration of particle, pH of solution, and temperature.

Electroless deposition is a complex chemical method for metallic plating on substrates without using electricity. It requires a catalytic surface for the initiation of reduction as shown below:

Cathodic reaction



Anodic reaction

Reducing agent + $\text{H}_2\text{O} \longrightarrow \text{C} + n\text{H}^+ + ne^-$ ('C' denotes the compound formed after reaction depending on choice of reducing agent e.g. (formaldehyde)).

Oxidation of reducing agent employed in electroless deposition forms H^+ ions. Consequently, pH of solution changes and it can lead to precipitation of metal in bulk solution. Complexant in solution prevents precipitation. In addition to preventing precipitation within the solution, complexant (EDTA) allows the solution to be stable at higher pH values. Concentration of the complexant must be considered, because in highly complexed solution availability of metal ions will become insufficient for deposition. Also, the pH changes during plating and can affect the rate of deposition⁵.

Printing of conductive patterns by ink jet printing requires pH optimization of solutions, for instantaneous occurrence of reaction. Printing of conducting lines becomes difficult for slow reaction as the reactants can permeate/diffuse into the substrate prior to reaction. Since, printing requires various chemical solutions, precaution is required to prevent damage to the printer and cartridge.

Copper is chosen instead of gold or silver for plating, as copper is cheaper than the two with conductivity almost equal to that of silver. Paper is chosen as flexible substrate as it is cheap and widely available. The porous structure and hydrophilic character of paper allows it to absorb suspension of nanoparticle precursors by capillary forces, yielding high loading of nanoparticles on reaction and drying⁶. Fabrication of conducting pattern of copper on paper using reactive inkjet printing and electroless plating can be accomplished only if the following issues are addressed:

A: Oxidation of copper:

Copper oxidizes at room temperature on exposure to air and forms copper oxide. These oxides are non-conductive. Hence, a minimum thickness is to be used, such that the skin of oxide on patterned structure acts as barrier layer for underlying copper and thereby ensures the durable conductivity of printed pattern.

B: Formation of percolating film:

Patterns should be continuous for being conductive, so fusing of printed or deposited copper nanoparticles is required, but sintering of copper cannot be done at higher temperature as the substrate is paper. Plasma treatment is another option for fusing deposited copper particles but optimization of power, flow rate of gas and time span is required such that the substrate may not get damaged.

C: Adhesion between copper particles and substrate:

Contact between copper and paper should be strong enough that the patterned structures are robust enough to withstand folding or bending of substrate.

D: Clogging of cartridge:

A frequent problem is clogging of cartridges due to deposition of salt on the metal head which closes the holes on them. Tannic acid polymerizes upon storing at room temperature this also causes clogging.

E: Wear and tear of paper sample:

When the catalytic activated sample is dipped in electroless copper solution, deposition initiates and evolution of hydrogen gas takes place from the catalytic surface causing blisters on the sample. This happens when the sample is dipped for longer period or if there is not enough catalytic surfaces.

F: Non-uniform deposition:

The deposition of copper film on paper is not uniform. For obtaining a conducting film there has to be continuous film with enough thickness so that it can retain its continuity on bending or folding the paper substrate. Hence, for getting thick layer in less time span the amount of formaldehyde in electroless solution is increased by 3-4 times initially and during deposition 1ml is added continuously at regular intervals.

Chapter 2

Literature Survey

2.1 Fabrication of conducting copper patterns using inkjet printing

Chemical reduction method is being used for synthesizing copper nano ink, which includes copper precursor, reducing agent and capping agent. Synthesis of copper nano ink is feasible using various reducing and capping agents⁷⁻¹⁴.

Synthesis of conductive copper colloid takes place along with impurities like “copper oxides” which warrants further processing to obtain high purity conducting metallic copper colloids. Apart from this, at nano scale the oxidation of copper is rapid compared to micro scale because of high surface area. Use of toxic and corrosive chemical like sodium- borohydride and hydrazine has to be avoided. Conducting lines on paper substrate have also been accomplished, using reactive inkjet printing after printing 370 cycles, which is not scalable⁹. Typically, printing of conductive patterns is done by coating substrate with polymer (polyimide) for smoothening of the surface¹⁵.

2.2 Electroless copper deposition

Work has been done on deposition of conducting copper tracks over the patterned palladium. Palladium acts as a catalyst on flexible polyimide substrate while sodium borohydride is the reducing agent¹⁵. Direct printing of sodium borohydride solution as ink should be avoided as it can damage the printer and as it is toxic. Preparation of Cu/Pd bimetallic nanoparticle which acts as an activator for electroless copper deposition is also reported¹⁶. 3 and 4 nm sized particles were obtained on using sodium citrate as complexing agent. This approach can be used for patterning the catalyst on the surface prior to electroless deposition.

2.1.1 Objective

The objective of this project is to pattern conducting copper patterns on paper and optimize thickness of the lines without using toxic and corrosive chemicals, such that patterned lines retain their conductivity for extended periods. Fabricating conducting lines on paper has potential to reduce the cost of printed electronics. In particular, this work focuses on the fabrication and characterization of RFID antenna structures. There are several potential applications of conducting patterns on paper discussed below:

2.1.2 Ultra wideband antenna (UWB)

As the name suggests these antennas have larger frequency range. Federal Communications Commission (FCC) defines UWB as emissions in frequency range from 3.1 to 10.6 GHz¹⁷. It deals with short pulses which spread the signal over large spectrum which are not affected by existing narrowband interferers. UWB technologies are increasingly used as a means of short range, high bandwidth communication utilizing very low power levels for spreading the transmitted signals over significantly large portion of radio spectrum¹⁸. UWB micro strip antennas consist of metallic patch and grounded patch. It is low profile, conformable to planar and non-planar surfaces and inexpensive to fabricate using modern printed circuit technology¹⁹. Since the bandwidth of UWB is very large it can be used in several applications such as those mentioned below:

1. They are applied in bio medical imaging to detect cancerous tissues. An array of UWB antennas are exposed to human tissues and the reception and transmission of signals in the set up helps in early detection of malignant tissue depending on the dielectric properties of the tissues. The defected tissue has high dielectric properties which reradiates the transmitted pulse, while rest of them absorb.
2. As ground penetrating radars, these antennas are designed to operate over the widest possible bandwidths and frequently designed to radiate pulsed waveforms²⁰. It can also be used for imaging through walls. It can also be used finding buried land mines.

Transmission and reception of pulses becomes critical in UWB communication. So, antenna is a critical component in UWB systems. Antennas radiation pattern and band width should be satisfactory for the intended communication application. The radiation intensity for UWB depends on inherent properties of antenna and strongly on the frequency, which means different spectral component in UWB will be radiated in various directions with varying strength thus, UWB pulse has different power in different direction as well as exhibit temporal dispersions²¹.

2.1.3 Radio Frequency Identification (RFID)

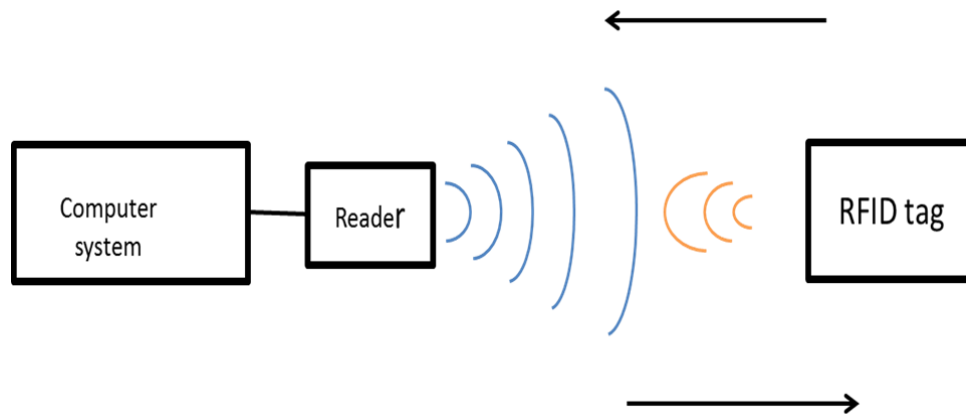


Figure 1 Schematic showing the working of RFID tag.

RFID system uses radio frequency to identify the object. The system composed of reader, active/passive tag and computer. The components of active tag are antenna and chip. When radio frequency passes across the antenna, it generates ac voltage which can be used to power the tag²². Once the tag receives sufficient energy to operate correctly, it divides down carrier and begins to clock its data to an output transistor, connected across the coil input. This output shunts the coil and causes fluctuation in amplitude. The reader detects the amplitude and process the data received. The antenna in the tag can be made on paper, by patterning conducting lines using, inkjet printing which will reduce its cost²³ and enable its application, in traffic/inventory management of various objects.

2.1.4 Sensors and Detectors

Sensors play a vital role in industrial, transport security and safety-based applications. There are numerous classes of sensors including photo detectors, gas sensors, and mechanical stress sensors¹. Sensors can be based on materials, whose conductivity changes in the presence of a vapor or liquid phase. Instrumentation of the device will become simple by using inkjet printing. Electronic components of the sensor may be easily miniaturized using micro fabrication and making these sensors highly portable. These sensors can also be applied in biological and pharmaceutical applications.

Chapter 3

Experimental Methods

Following procedures were involved in the experiment:

3.1 Volume printed per cycle using commercial inkjet cartridge

Printer has two cartridges (color and black), each one having different capacity of printing (volume printed per cycle). It is necessary to quantify their capacity to estimate the amount of reagent printed.

The proposed methodology involves measuring the weight of the cartridges before and after printing. The cartridges (both black and color) filled with water, without spilling over, in the cavities provided for ink reservoir. The weight of the cartridges was measured, before and after printing.

3.2 Reactive inkjet printing of Palladium

Stock solution prepared by dissolving palladium salt in 0.2 N hydrochloric acid²⁴ and kept in the refrigerator for 16-20 hours. Tannic acid, a benign chemical extracted from plants was used as the reducing agent.

A preliminary experiment was carried out in solution to verify the feasibility of reaction. A drop of salt solution was placed on paper and the same quantity of reducing agent was then added to it. This process repeated by varying pH of the tannic acid. At pH value of 10, it was found that color of salt solution changes from yellow to black instantaneously after addition indicating the occurrence of reaction. Based on the need to print arbitrary thick layer of palladium, the number of printing cycles was estimated for both salt and reducing agent. In the latter half of the work, Silver formed by reactive inkjet printing of Silver nitrate and tannic acid was used as catalyst to avoid issues of clogging.

Different patterns printed on paper by varying the concentration of palladium salt and reducing agent, typically using the black cartridge.

Following settings were used for printing the patterns:

- a) Grey scale mode was selected.
- b) In printer property tab, paper size was changed to A4.
- c) Printing option is selected as high quality grey scale, under advance settings.
- d) Resolution (drops per inch) is varied for different configuration of patterns.

3.3 Electroless Copper deposition

The printed sample treated with ozone for 20 minutes to remove the byproducts of reactive precipitation of Pd and to activate the catalyst. The sample then dipped in copper sulphate solution of varying concentration and dipping time. After that, the sample was dried in a desiccator.

The electroless copper solution was prepared by mixing the following chemicals¹⁵.

- a) NaOH solution
- b) Ethylene diamine tetracetic acid (EDTA) solution
- c) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ solution
- d) Formaldehyde solution




The above mentioned materials are basic components of copper electroless solution. Apart from them, other additives can also be added for better control over reaction. As the reaction goes on, formation of copper oxides takes place, to prevent this, stabilizer like potassium ferrocyanide were added. But on addition of stabilizers the rate of reaction decreases and hence the rate of deposition slows down.

Chapter 4


Printing Configuration

Printed configurations are listed below with variation in patterns, surface area, palladium concentration, copper sulphate concentration and dipping time for the sample in copper solution.

Palladium as catalyst:

	Configuration	Area/ variation in area (cm ²)	Palladium concentration (M)	Copper electroless concentration (M)	Dipping time (minutes)
1.		1.5	0.0564	0.025	60 - 300
2.		1.6 - 25	0.0564 – 0.225	0.025 – 0.1	30 - 60
3.		10 - 32	0.225	0.05- 0.15	5- 60

Silver as catalyst:

	Configuration	Area (cm ²)	Palladium concentration (M)	Copper electroless concentration (M)	Dipping time (minutes)
3.		32	0.09	0.025	5-8

Configuration 1 and 2 were test patterns for optimizing conditions for electroless deposition of copper. The configuration 3 is designed in electrical and electronics department is the desired shape of UWB planar antenna.

Chapter 5

Results and discussion

5.1 Electroless deposition with palladium as catalyst

As mentioned in section 3.1, the volume per print was measured for both black and color cartridge. It was observed that the volume per print for both cartridges exhibit run to run variation. [See appendix- A].

Appearance of faint grey color observed, when reduction of palladium salt takes place. Samples were obtained by printing, 9 x tannic acid and 8 x palladium salts and dried at room temperature for 10 minutes and 24 x tannic acid and 16 x palladium, color cartridge used for printing. When number of printing cycle's increases, appearance of black color is observed as shown in Figure 2 and Figure 3.

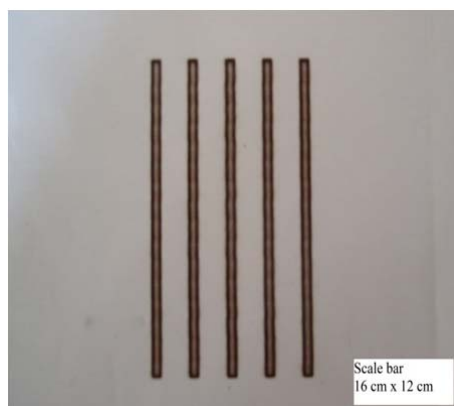


Figure 1 Digital photograph of palladium Nanoparticles formed by printing 6 prints of tannic acid and 4 prints of palladium salt, repeated 4 times

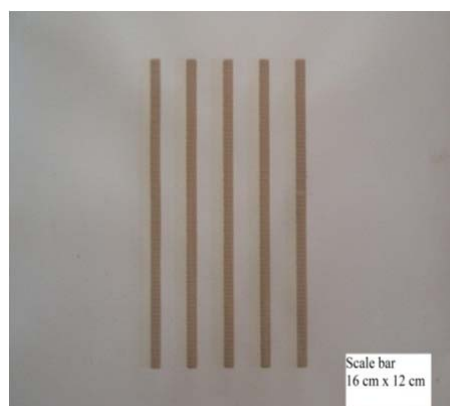


Figure 3 Digital photograph of palladium nanoparticles formed by printing 9 prints of tannic acid and 8 prints of palladium

5.1.1 Testing the formation of palladium

UV- Visible spectra of palladium salt solution and reduced palladium were measured. The salt solution peak, at ~421 nm wavelength in Figure 4, is absent after tannic acid addition. The spectra further confirms reduction of palladium chloride by tannic acid.

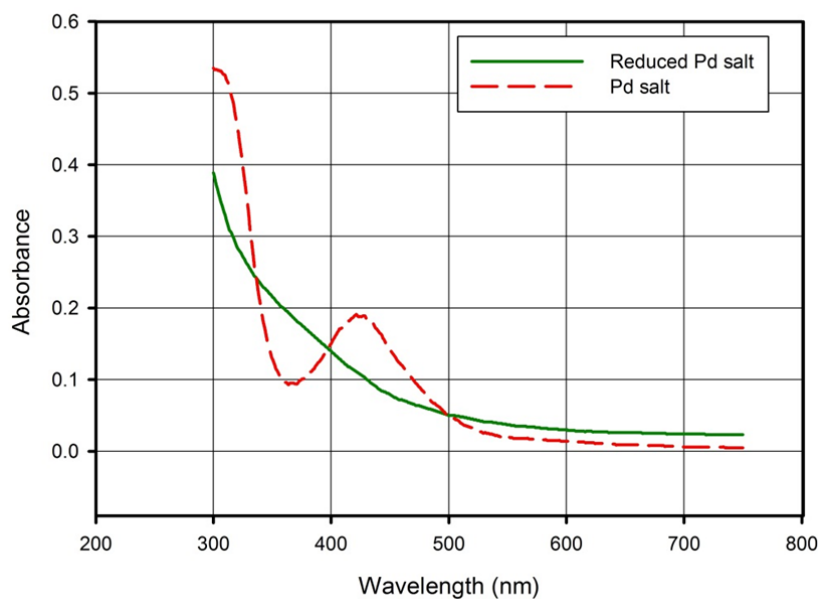


Figure 1 UV-Vis of palladium salt solution (red curve) and reduced palladium salt by tannic acid (green curve)

5.1.2 Test of electroless copper solution

To verify whether the prepared electroless copper solution was working or not, a test was performed by placing a layer of conductive silver paint on paper and then dipping it in the electroless plating solution for 24 hours. Appearance of brown color was observed on the silver paint as shown in Figure 5 and Figure 6. There is a clear indication of the deposition of copper film.



Figure 2 Digital image of silver paint on paper.



Figure 3 Digital image of silver paint dipped in electroless solution for 24 hours.

5.2 For configuration 1:

Disappearance of grey color was observed, when the sample was kept for few hours in the copper plating solution, for one sample. However, the sample with 24 prints of tannic and 16 prints of palladium salt gets darker in comparison to sample with 9 prints of tannic acid and 8 prints of palladium salt as shown in figure Figure 7. In sample 1, there was no deposition of copper and in sample 2, reaction occurs and copper deposition takes place on catalytic surface. Thus it is seen that a minimum amount of catalyst is needed for electroless deposition.

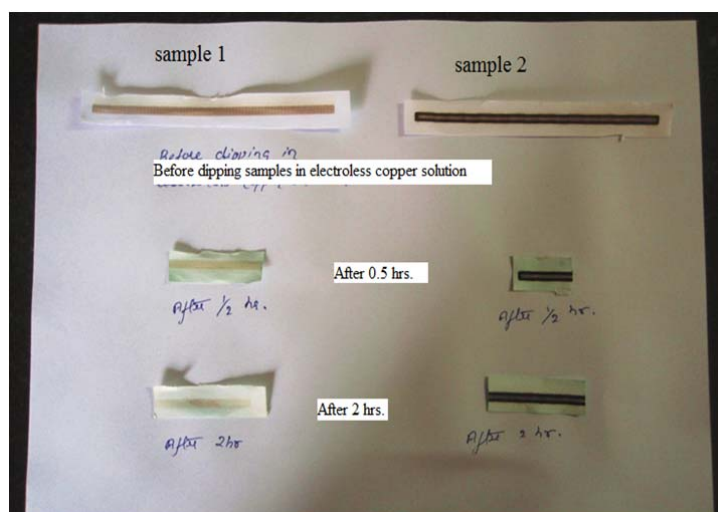


Figure 4 Color difference between two samples after dipping for 0.5 hour and 2 hours in the electroless copper solution without UV- Ozone treatment of sample.

As the amount of catalyst printed was large, it was hypothesized that the by-products of the were blocking most of the catalytic sites. So, UV-Ozone treatment was carried out with an aim of oxidising the organic by-products, i.e. tannic acid.

A sample that was UV-Ozone treated for 15 minutes and then dipped in electroless copper plating solution shows the appearance of a brown color observed which becomes darker when the sample was kept for extended time in the electroless solution as shown in Figure 8 and Figure 9. However, these patches were not conductive indicating that there is not enough catalytic surface for the reaction to occur so that printed area is fully covered by copper.

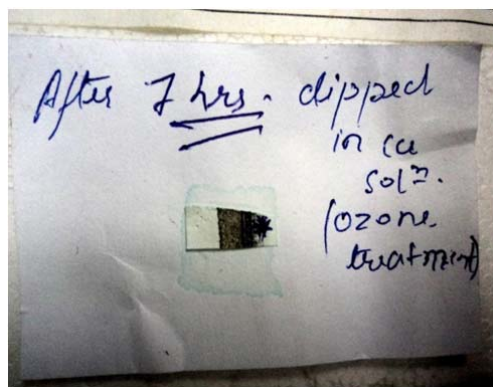


Figure 5 Sample dipped in copper electroless solution for 7 hours.

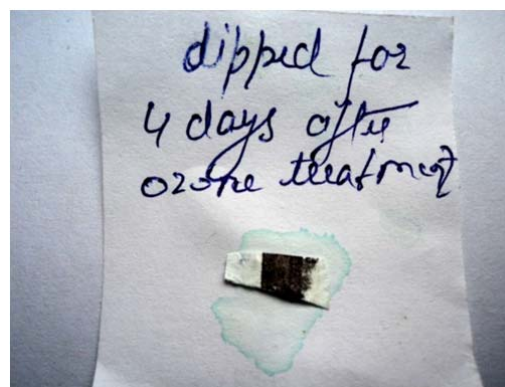


Figure 6 Sample dipped in copper electroless solution for 4 days.

SEM analysis of the reduced palladium salt shows particles, of size ~20 nm. After dipping in copper solution for 4 day particles of size~100 nm seen in the image shown below in Figure 10, showing not enough amount of deposited copper to get continuous conducting pattern. The white patches in the above image shows charging of paper due to accumulation of electrons as it is an insulator. So, we can infer that for getting the conducting patterns there have to be enough amount of catalytic, so that deposited layer is continuous.

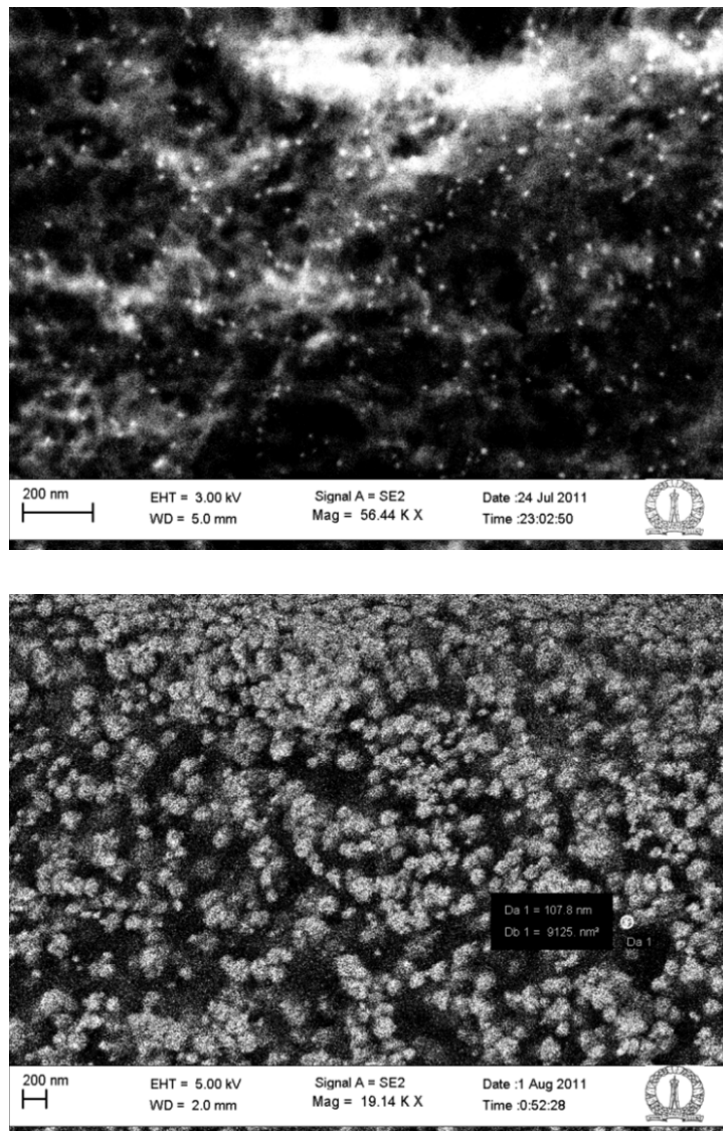


Figure 7 SEM image of sample before dipping and after dipping in copper electroless solution for 4 days.

5.3 For configuration 2

First, ten squares of dimension 1.27 cm x 1.27 cm were printed, with concentration of 0.0564 M of palladium salt. These were then dipped in electroless copper deposition solution for 30 and 60 minutes respectively, the copper concentration was 0.025 M. The samples were not conducting.

Then, same pattern printed by increasing the concentration of palladium to 0.1184 M. Concentration of tannic acid is 0.02039 M. The solution was salt printed 3 times and tannic acid 5 times respectively. Average value of volume printed per centimeter

square is 1.5×10^{-6} L. The concentration of copper solution was also increased to 0.05M. SEM image of reduced palladium is shown in Figure 11.

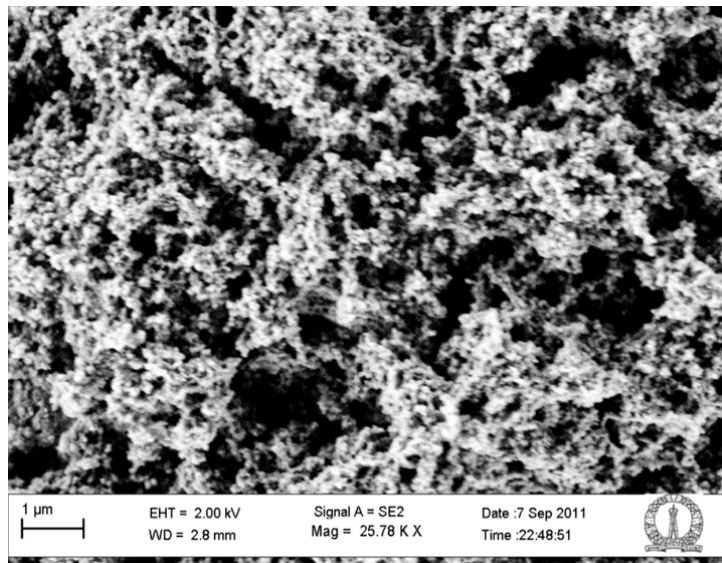


Figure 8 SEM image of reduced palladium after printing 5.3×10^{-6} moles of salt and 1.5×10^{-7} moles of tannic acid per cm^2 .

These samples were then treated with UV-Ozone for 20 minutes and dipped in electroless solution for 60 and 30 minutes. All these samples were found to be conducting. A sample was dipped for 30 minutes without ozone treatment is also found to be conducting.

SEM images of the samples after dipping in copper solution for 60, 30 with ozone treatment and 30 minutes without ozone treatment respectively are shown in Figure 12, Figure 13 and Figure 14. All these images show enough deposition of copper on catalytic surface over paper which makes the printed portion of paper conducting. The samples treated with ozone look grainy, but the sample without ozone treatment shows plain structures along with the granular particles which is different from the ozone treated sample. These plain structures are probably a film of organic residues.

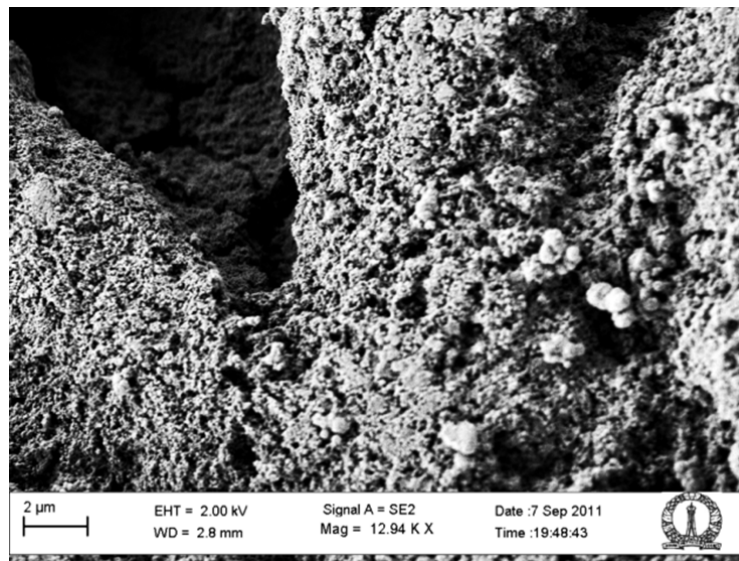


Figure 9 SEM image of sample dipped in electroless solution for 60 minutes after 20 minutes of ozone treatment.

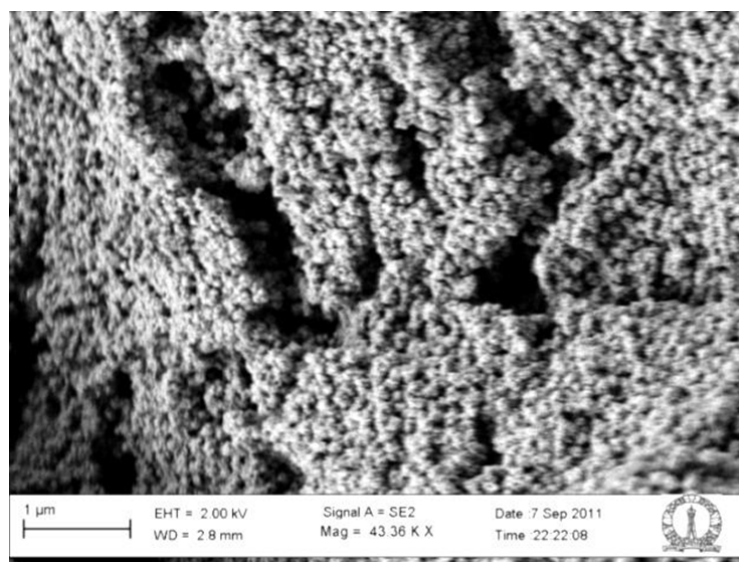


Figure 10 SEM image of sample dipped in electroless solution for 30 minutes after 20 minutes of ozone treatment.

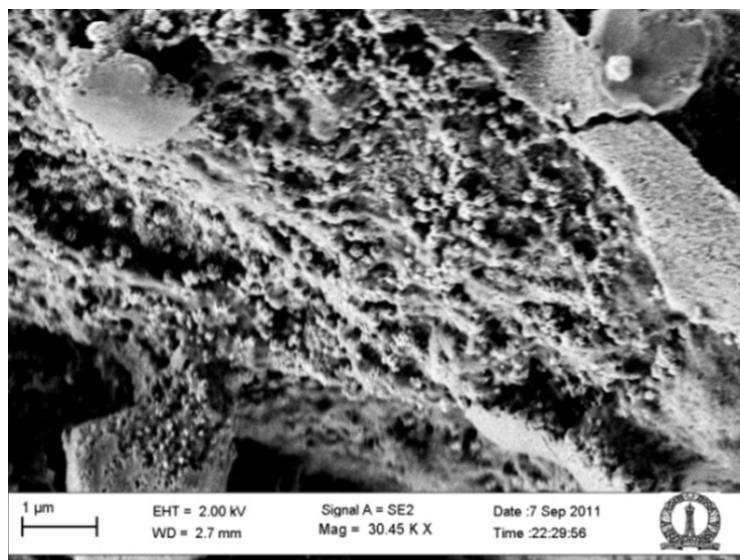


Figure 11 SEM image of sample dipped in electroless solution for 30 minutes without ozone treatment.

Same procedure was repeated with squares of dimension 2 cm x 2 cm, 3cm x 3 cm, 4 cm x 4 cm, 5cm x 5cm with palladium concentration of 0.225 M and tannic acid 0.0245 M. Volume printed per unit area of the cartridge is 2×10^{-6} L/cm². Concentration of copper solution increased to 0.1 M. The patterns were printed, with variations as given below:

Dimension	No. of prints of Palladium salt	No. of prints of tannic acid
2 cm x 2 cm	2	2
3 cm x 3 cm	4	6
4 cm x 4 cm	3	4
5 cm x 5 cm	4	6

Table 1 Data of printed squares of different area with varying number of print of palladium salt and tannic acid.

All the samples were dipped in electroless solution for the period of 45 minutes. The first two samples were conducting and last two were partially conducting. The test is done with multimeter by moving the probe over the whole printed area where deposition took place.

5.4 For configuration 3

UWB antenna of area 13 cm^2 was printed with palladium concentration 0.225 M and tannic acid 0.0245 M . Two black cartridges were used, one for salt and other for reducing agent. For tannic acid cartridge the average volume is $1.3 \times 10^{-6} \text{ l/cm}^2$ and for salt it was $1.5 \times 10^{-6} \text{ l/cm}^2$. Both solutions were printed 5 times and dipped in copper solution of concentration 0.1 M , for 15, 20 and 30 minutes. The three samples were conducting because of deposition of black particles.

Then the same configuration tried with area 10 cm^2 and same concentration of salt and concentration of tannic acid was 0.022 M . Volume/ cm^2 for tannic acid and salt cartridge were $1.5 \times 10^{-6} \text{ L/cm}^2$. Both solutions were printed thrice. Black particles deposit on the surface hence, the sample was hung vertically in copper solution and as the formation of black particles takes place fresh solution was used to replace old one. The sample was immersed for 60 minutes. Deposition of copper took place in between the gaps of patterns shown in Figure 15 and the whole area was conducting. The back side of the pattern shown in Figure 16 is also conducting with a gap between the structures. The samples that were horizontally dipped for the same duration were not conducting. Dipping of lesser time (5 minutes) also does not give conducting pattern.



Figure 12 Front side of scaled down antenna

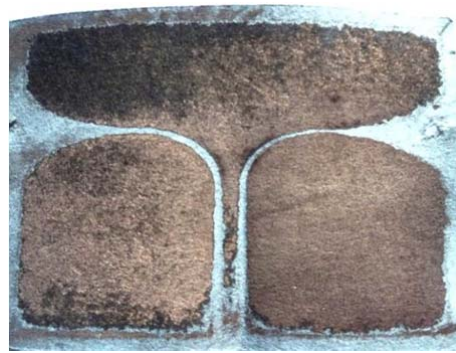


Figure 13 Back side of antenna.

with deposition in between gaps after dipping in
copper electroless solution for an hour

SEM image of the cross section of above mentioned sample is shown in Figure 17. This image enables an estimation of the thickness of deposited layer on printed side and on back side shown in Figure 18.

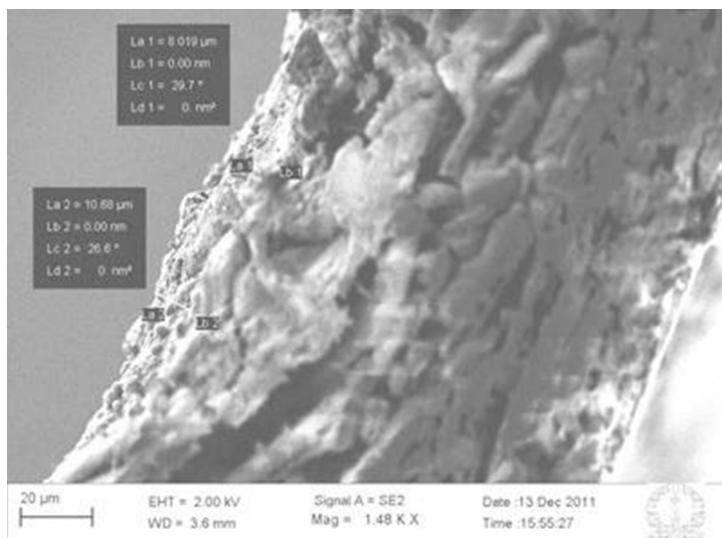


Figure 14 Cross-sectional image showing 8–10 micrometer thick layer of copper deposition on the printed side of paper by focusing the crosssection of paper.

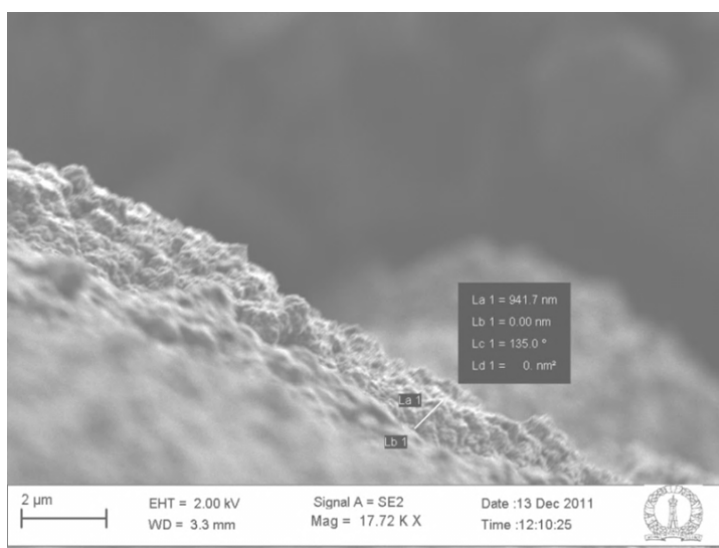


Figure 15 Image showing 1 micrometer thick layer of copper deposition on back side of the pattern

Copper deposition took place on the back side hence it is conducting, which shows that catalytic surface is not staying on the paper surface but also penetrating. Surface of the back side shown in Figure 19.

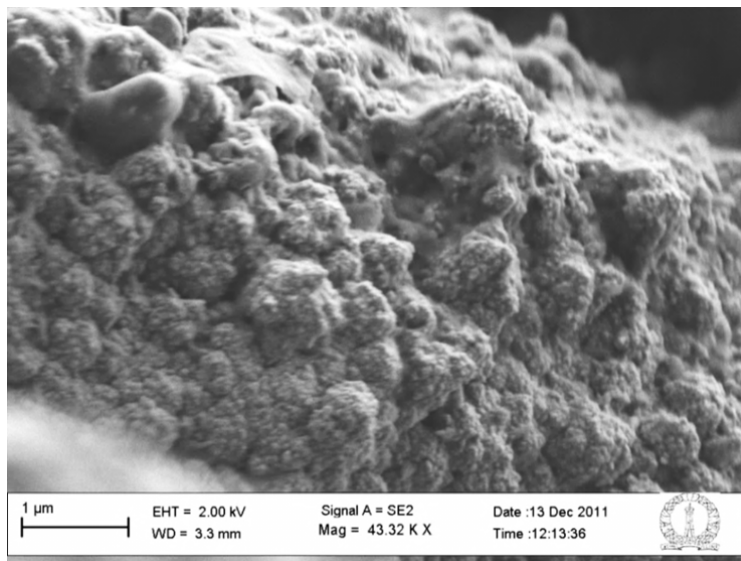


Figure 16 SEM image showing the back side surface of sample hanged in 0.1M of copper solution for 60 minutes.

Since the gaps between the antenna were filled with copper, hence the initial gap in the design was increased by 2 mm and the area increased to 32 cm². Salt and tannic acid solution are of similar concentration. Volume/cm² of cartridge for tannic acid is 2×10^{-6} L/cm² and for salt is 1×10^{-6} L/cm². Both solutions were printed thrice. Samples hanged in 0.1 M concentration of copper solution for 30 minutes. Again deposition took place in between the gap and the whole area was conducting, along with the back side. Images are shown in Figure 20.

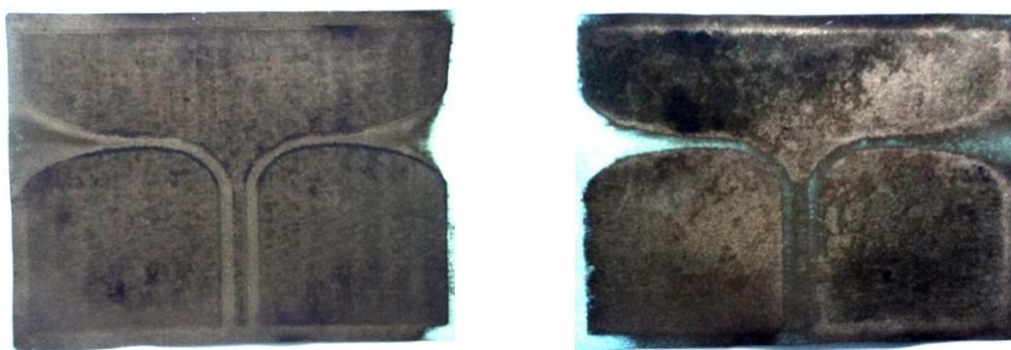


Figure 17 Digital image of front and back side of antenna after dipping in electroless solution for 30 minutes.

Tween-20, a surfactant was printed by inverting the image to prevent deposition in between the gaps. Salt and tannic acid solution are of similar concentration. Volume/cm² for tannic acid cartridge is 2.1×10^{-6} L/cm² and for salt 1.3×10^{-6} L/cm². Salt printed 4 times and tannic acid 3 times. In this run, the recovered copper solution was used as electroless solution. Color of printed palladium was lighter than in previous case and copper deposition does not occur upon dipping the sample in solution. As formaldehyde was added to the solution, deposition began.

The reaction starts to take place in the solution itself without the necessity of catalytic surface after adding formaldehyde in excess amount. The printed sample was removed after 4 minutes as there was reasonable change in color as shown in Figure 21.

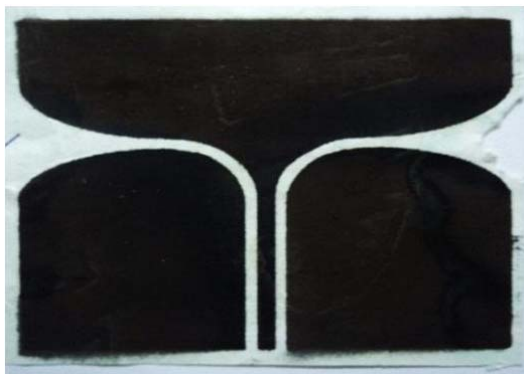


Figure 18 : Image showing no deposition in between gaps has taken place after printing tween-20 in gaps, and putting the sample in recovered copper solution for 4 minutes by adding 5 ml of formaldehyde.

The other sample prepared with similar configuration in recovered copper electroless solution for 4 minutes after addition of 12 mL formaldehyde. The sample was conducting but, powdery deposition has taken place on the surface and on brushing off the powdery deposition it was no more conducting, as shown in Figure 22. It is seen the surfactant tween-20 can be used to make paper hydrophobic to avoid deposition in gaps.

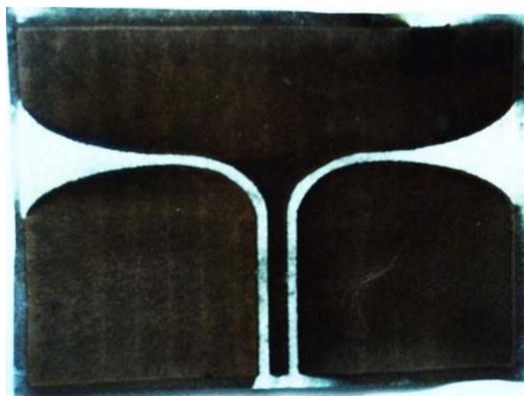


Figure 19 Image showing no deposition in between gaps has taken place after printing tween-20 in gaps.

5.5 Electroless deposition with silver as catalyst

Tween-20 prevented deposition of copper in the gaps having 1 and 2 mm, but as it could not be applied for the original configuration as given by electrical and electronics department, which had 0.5 mm gap between the structures of antenna. Hence, silver is used as catalyst for copper electroless deposition. The spread of silver salt across the printed area was less in comparison to palladium salt since it is not acidic. It was hypothesized that the acidic palladium salt corroded the orifices in the cartridges leading to poor resolution. The gaps of size 0.5 mm are maintained with silver as shown in Figure 23. The pH of palladium and silver salt is 2 and 6 respectively.

The sample in Figure 24, is conducting as tested by multimeter and its sheet resistance was measured using four probe station by applying 10mV. Resistivity of three parts of antenna varies due to the non-uniform deposition and is order of $10^{-5} \Omega\text{m}$ as shown in table 2, assuming a 10 μm thick film.



Figure 20 Digital image of antenna after printing 2.63×10^{-7} moles of silver salt and 4.24×10^{-8} moles of tannic acid.

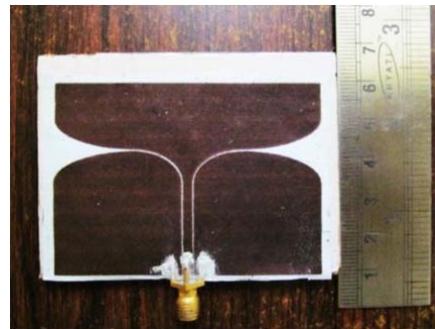


Figure 21 Digital image of antenna after dipping on electroless solution 8 minutes.

Position	Resist- ance (Ω)	a(mm)	d(mm)	s(mm)	a/d	d/s	Correction factor	Resistivity $\times 10^{-5}$ (Ωm)
Center	1.796	70	18	2	3.88	9	4.235	2.282
Right	3.434	32	31	2	1.03	15.5	0.9994	1.03
Left	2.574	32	31	2	1.03	15.5	0.9994	0.772

Table 2 Resistivity data of the deposited copper layer after dipping printed sample in electroless sample for 8 minutes [as per ref. ²⁵].

SEM image of surface of the sample before and after electroless plating is shown in Figure 25 and Figure 26.

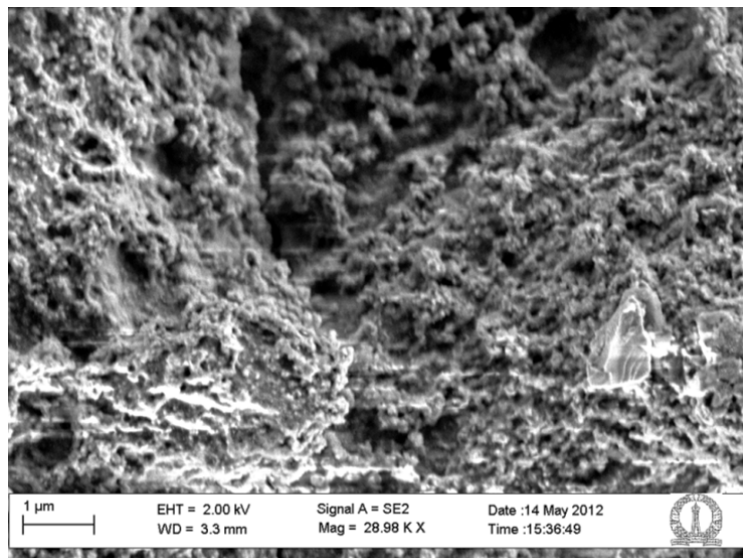


Figure 22 SEM image of surface of sample before electroless deposition.

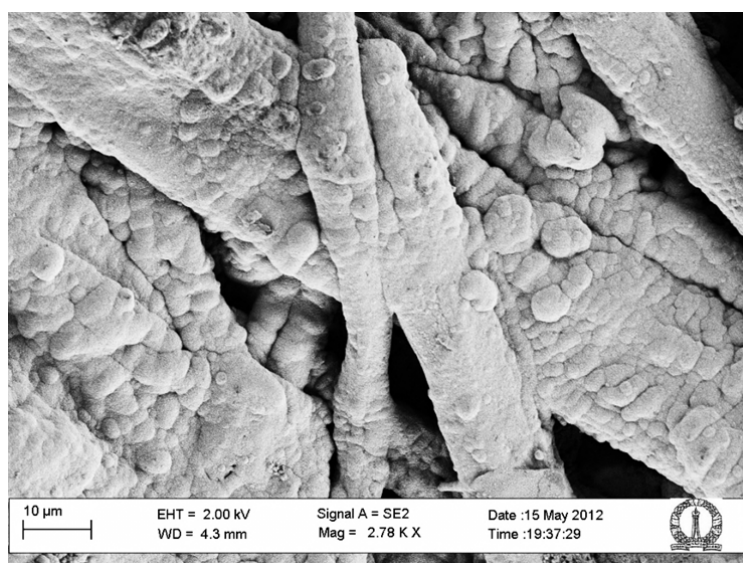


Figure 23 SEM image of surface of sample after electroless deposition

SEM image of cross-section of the sample shown in Figure 27 shows that thickness of the deposited copper varies from 3-5 μm which can explain the variation in resistivity across the sample. The rough and fibrous nature of the paper substrate is also a major contributing factor.

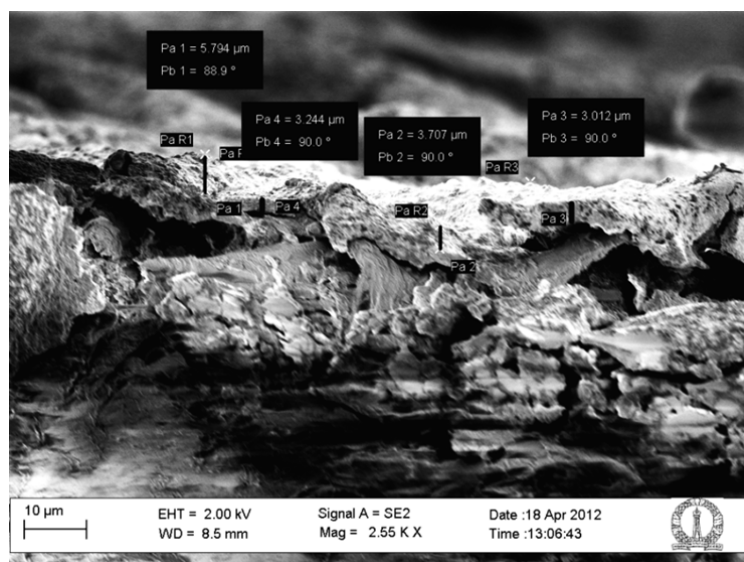


Figure 24 SEM image of cross-section the copper deposited sample.

X ray diffraction analysis of the sample is done before and after electroless deposition showing the presence of silver as seen in Figure 28, copper and its oxide in Figure 29.

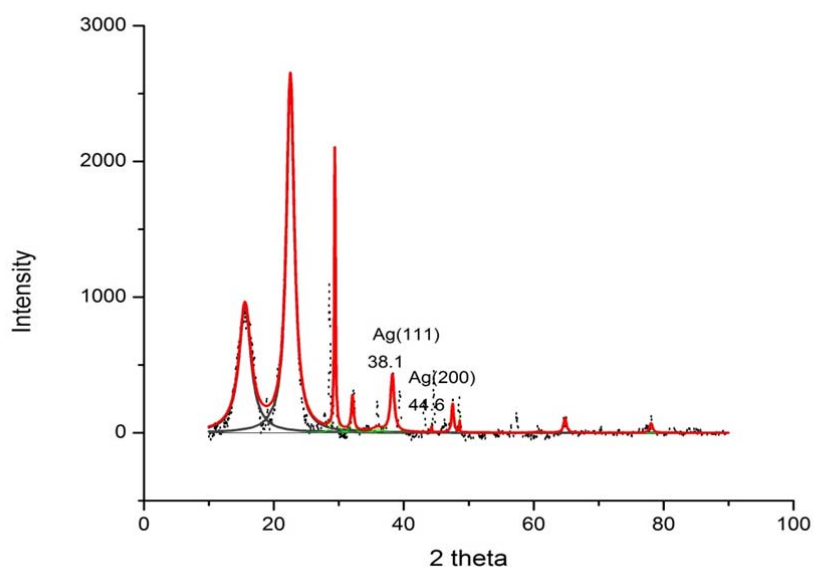


Figure 25 XRD of printed sample before electroless deposition.

Figure 28, shows the presence of silver in the sample printed with silver salt followed by tannic acid, implies that silver is present in metallic form having oxidation state

zero. This is confirmed by xps analysis shown in Figure 31.

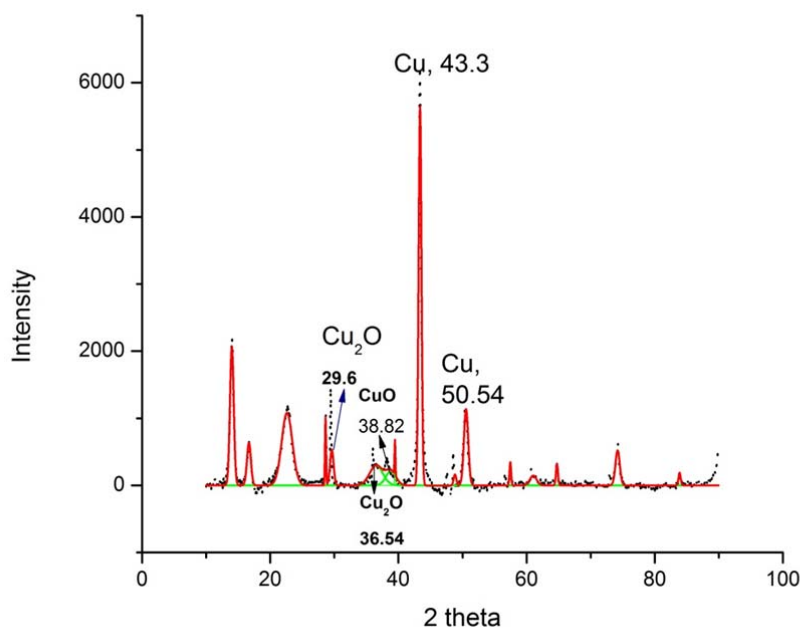


Figure 26 XRD of the printed sample after electroless deposition

Figure 29 shows the presence of metallic copper as well as its oxide in the sample after electroless deposition which shows that copper oxidises at room temperature. The presence of copper and its oxide are also confirmed by XPS analysis shown in Figure 30. The metallic copper peak at 43.3° is present in the plane(1,1,1) and at 50.54° is present in the plane(2,0,0).

X-ray photoelectron spectroscopic (XPS) analysis of the sample is shown below:

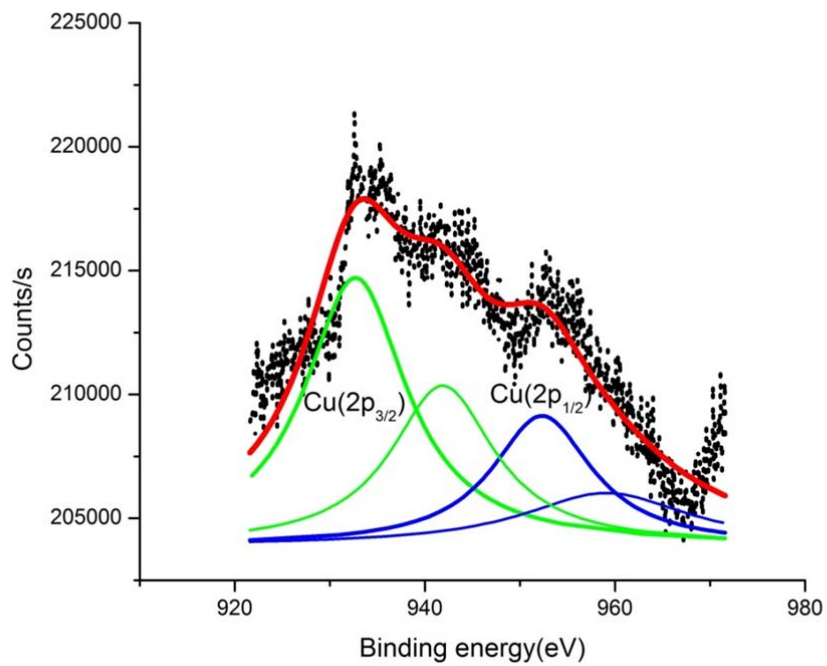


Figure 27 Image showing curve fitting with the original xps of copper

In Figure 30, the first peak appears at 932.7 eV and second at 952.3 eV. First one corresponds to Cu(2p_{3/2}) and other corresponds to Cu(2p_{1/2}) and other two peaks corresponds to their respective oxides²⁶.

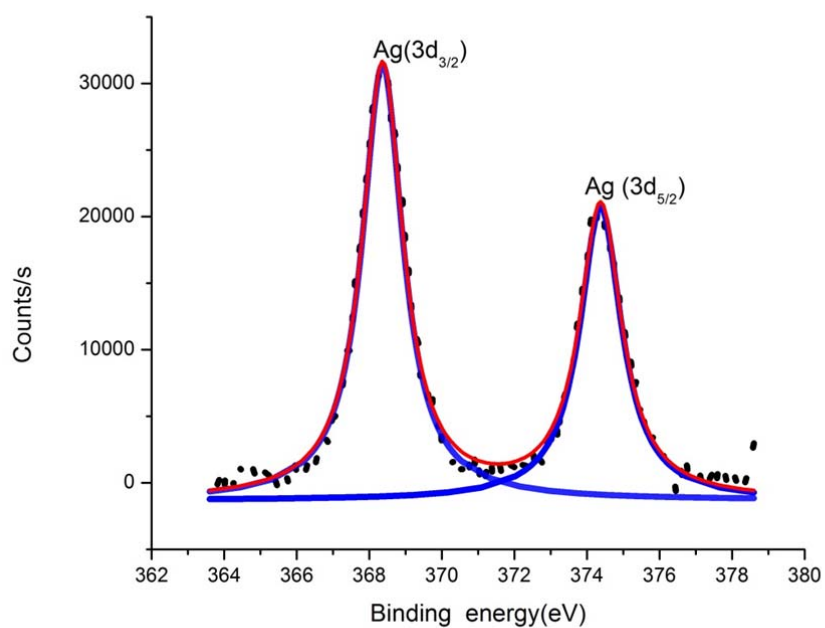


Figure 28 Image showing curve fitting with raw xps data for silver

In Figure 31, peaks are at 368.3 eV and 374.4 eV values of binding energy (ev) showing presence of metallic silver²⁷ in the sample after printing silver salt followed by tannic acid.

5.5 Characterization of UWB antenna

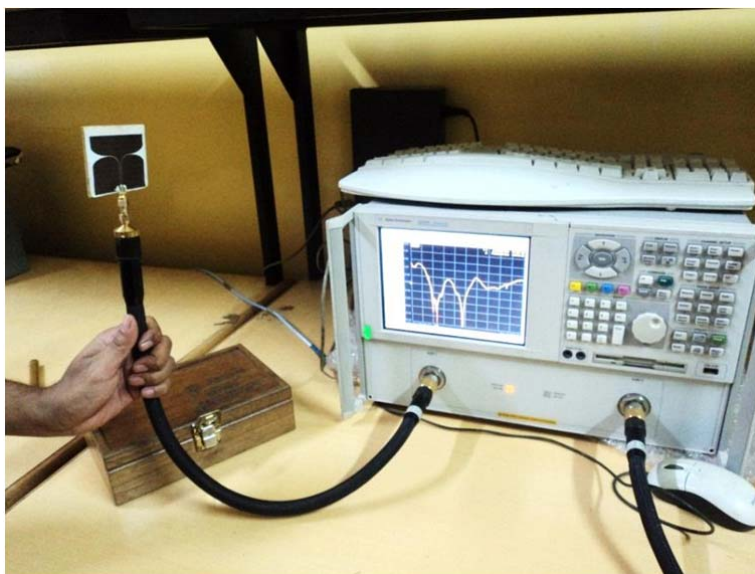


Figure 29 Digital image showing the set up for UWB antenna testing [Prof. K.J.Vinoy's lab, ECE dept., IISc]

The instrument shown in figure 32, is used for measuring scattering parameters often called 'S' parameters. The scattering parameter denotes reflection and return loss. The instrument used is 'Agilent 2-port PNA-Vector Network Analyzer' model N5230A. Its working frequency lies between 10MHz-50GHz.

The network analyzer is used for analyzing various kinds of microwave engineering circuits like wave guide cavity set ups, material characterization with or without magnetic fields, transmission, reflection and radar modeling. Here, we are using it for printed UWB antenna characterization. It is also used for measuring the radiation pattern of antenna, defining the radiation of the received energy in all directions, so that the angle at which the antenna will radiate maximum can be determined.

There are four scattering parameters S_{11} , S_{12} , S_{21} and S_{22} . The number suffix shows the port in function. In the image above the S-11 configuration for measuring return loss of antenna fabricated on paper using reactive inkjet printing is shown. The characterization results of antenna are shown next.

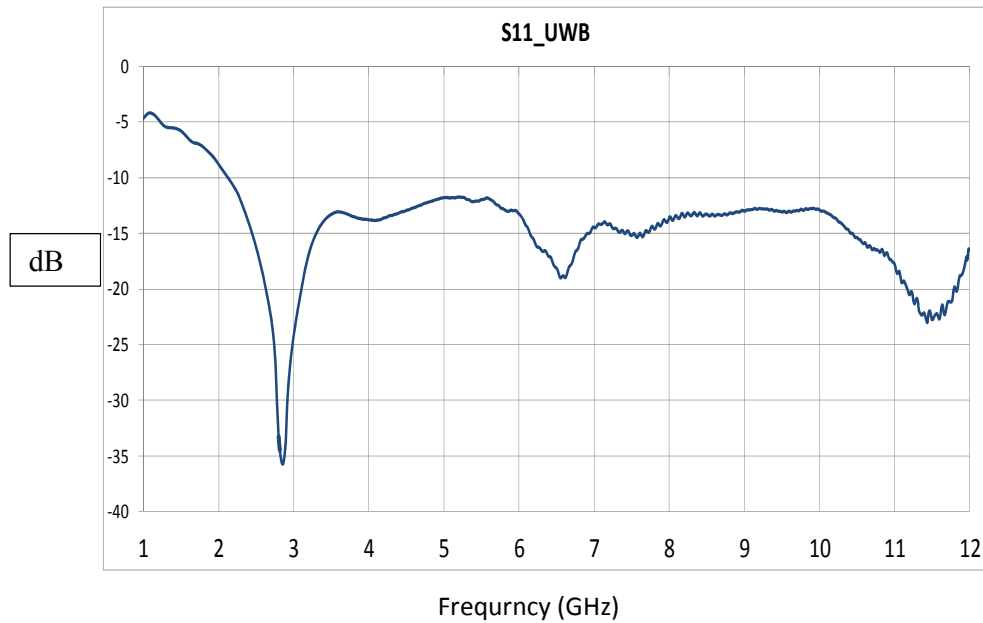


Figure 30 Image showing the S-11 measurement plot of UWB on paper substrate

Figure 33, shows the return loss of UWB antenna, it characterizes the frequency at which antenna's radiation is maximum. It tells that energy received by antenna is not reflected back but is accepted in form of loss within it or as radiation. Calibration sets the initial parameter to zero dBm. Hence, we conclude that paper based ultra wideband antenna is radiating energy received from transmitter. The frequency for radiation ranges from 1 GHz to more than 12 GHz. In between 1- 12 GHz the radiation peak at the frequencies 2.8 GHz, 6.5 GHz and 11.4 GHz. Out of the three, radiation is maximum at 2.8 GHz. Power supplied for above measurement is -15 dBm. For Example if $S_{11} = 0$, denotes that all power from the antenna is reflected and nothing is radiated.

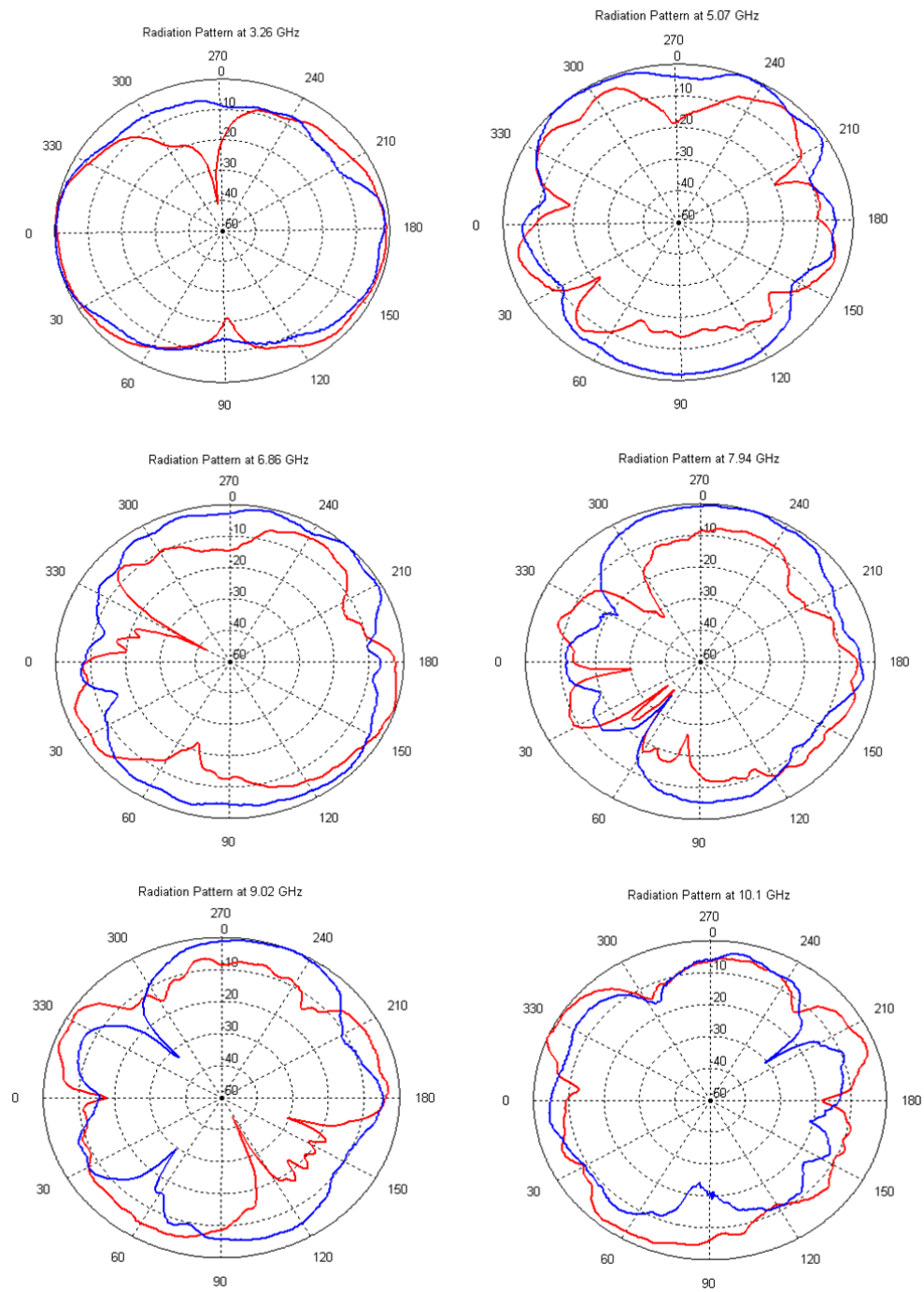


Figure 31 Radiation pattern of UWB antenna

Radiation pattern of antenna describes the strength of the radiated field in all directions at fixed distance.

For measurement radiation pattern the set up consist of following:

- 1) Position controller: To change the position of antenna with respect to the transmitter.
- 2) Transmitter: Horn antenna of frequency width from 2GHz- 18GHz acts as transmitter.
- 3) Receiver: The paper based UWB antennae is receiver.

Steps involved in measurement of radiation pattern:

- 1) First the PNA-vector network analyzer is set to S-21 mode.
- 2) Run the position controller to find power radiated in all directions (360^0).
- 3) Save, extract data and post process in Matlab to obtain the co-plan and cross-plane polarization.

Two co-planes for different frequencies plots are shown in Figure 34. Two co-planes denote that feeding point for configurations are kept same. The plots are similar to the simulated result [see Appendix-c].

Conclusion and Future Work:

A simple method is followed for the fabrication of UWB antenna on paper using reactive inkjet printing for the in-situ preparation of catalytic surface by printing palladium/ silver salt followed by tannic acid of pH value 10 at room temperature. These catalytic surfaces are subsequently used for the electroless plating. The conducting pattern is obtained by printing enough catalytic surfaces so that deposition takes place throughout the printed surface.

The fabricated antenna is operable in the frequency range 2.1GHz - 12GHz. The return loss data suggests that radiation peaks at frequency values 2.8, 6.5, 11.4 GHz, with maximum being at 2.8 GHz. The cost for paper based UWB antenna has been estimated as Rs. 6 per unit [Appendix-D].

In future work, optimization of concentration of copper in the electroless solution can be done to discard wastage. Patterns of different configuration can be printed which can be used in sensing application for detecting vapor as well as liquid.

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Appendix –A

Sample Calculation:

No. of lines = 5

Width = 0.2032×10^{-2} m, length = 7.62×10^{-2} m,

Thickness of palladium to be printed = 5×10^{-9} m

Total area = 7.742 cm^2 , Total volume = $3.871 \times 10^{-6} \text{ cm}^3$

Molarity of salt solution = 0.0564 M

Density of palladium = 11.99 g/cm^3

Mass of palladium to be printed = volume x density of palladium = $46.413 \times 10^{-6} \text{ g}$

Molecular wt. of palladium= 106.3 g/mole

Moles of palladium required = 4.365×10^{-7} mole

Volume required to be printed = moles of palladium required/ concentration of salt = $7.739 \times 10^{-6} \text{ L}$

One mole of tannic acid gives 20 electrons so moles required = 4.365×10^{-8} moles

Concentration of tannic acid = $4.489 \times 10^{-3} \text{ M}$

Volume required = mole / concentration = $8.912 \times 10^{-6} \text{ L}$

Table 1 : Black cartridge

Before printing(g)	After printing(g)	Change in weight(g)
26.553	26.521	0.032
26.597	26.564	0.033
25.964	25.93	0.034
25.983	25.953	0.03
25.989	25.96	0.029
26.482	26.453	0.029
25.362	25.333	0.029
25.595	25.565	0.03
25.473	25.553	0.03
Average		0.03
Standard deviation		0.002

Volume printed in one cycle = 3.06×10^{-5} L

Volume printed/ cm^2 = 3.952×10^{-6} L

No. of prints required for Tannic acid = 3

No. of prints required for salt = 2

Table 2 : Black cartridge (after printing)

Before printing(g)	After printing(g)	Change in weight(g)
26.66	26.649	0.011
26.058	26.048	0.01
26.497	26.484	0.013
26.25	26.238	0.012
26.27	26.259	0.011
26.409	26.398	0.011
26.04	26.028	0.012
26.099	26.088	0.011
26.727	26.716	0.011
Average		0.01
Standard deviation		0.0008

Volume printed per cycle = 1.14×10^{-5} L

Volume printed / $\text{cm}^2 = 1.47 \times 10^{-6}$ L

No. of prints required for Tannic acid = 6

Appendix-B

Experimental set up:

The experimental set up requires following:

1: HP Deskjet 1000 J110 Series (Figure B.1)



Figure B.1: The HP Deskjet printer used

2: Empty cartridges (1 color + 1 black) of model HP 802.

3: Electronic weighing machine

4: Desiccator

5: Pipettes, measuring cylinders, 100 ml round bottomed flasks

6. Reagents required:

6.1: Palladium chloride – Used to prepare H_2PdCl_4 solution with HCl for printing palladium salt followed by reduction using tannic acid or AgNO_3 in DI water.

6.2: Hydrochloric acid- Solvent for palladium chloride.

6.3: Tannic acid- Reducing agent for palladium salt.

6.4: Formaldehyde- Acts as reducing agent in the electroless copper solution.

6.5: Ethylene Diamine Tetracetic Acid- Used as complexant to maintain stability of metal ion in the solution.

6.6: Sulphuric acid- It is used for adjusting the pH of the electroless copper solution.

6.7: Potassium carbonate- Used for adjusting pH of tannic acid solution.

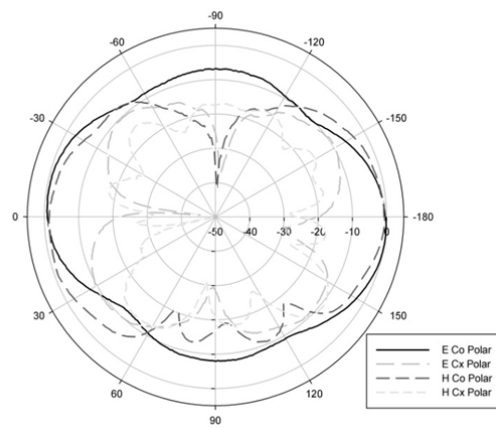
6.8: Copper sulphate pentahydrate- Main component of electroless solution.

6.9: Potassium FerroCyanide- Acts as stabilizer and prevents formation of copper oxide during deposition.

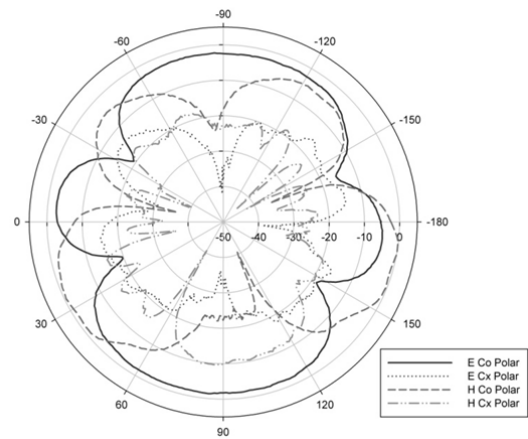
Appendix-C

Simulated radiation pattern of UWB antenna:

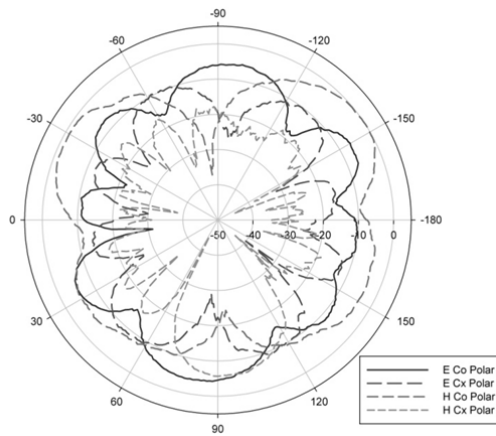
Measured Radiation Patterns



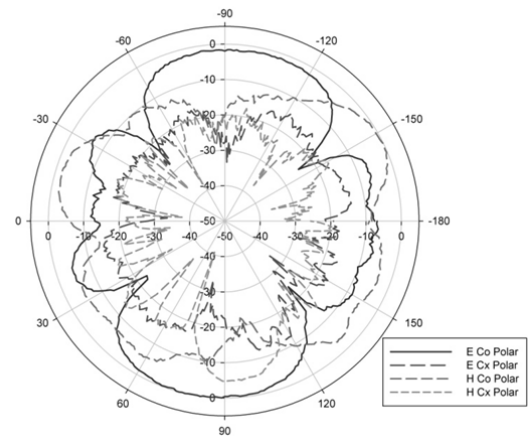
3.26 GHz



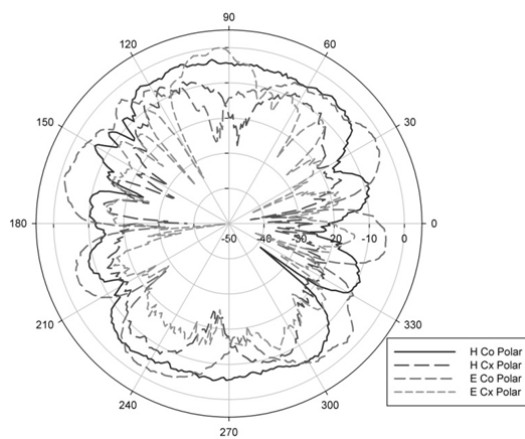
5.06 GHz



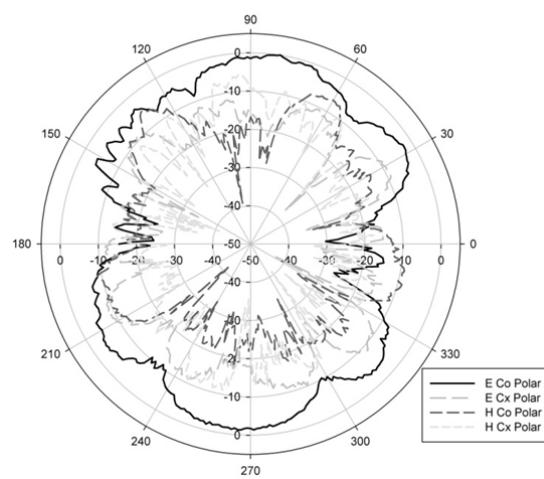
6.86 GHz



7.94 GHz



9.02 GHz



10.1 GHz

Appendix-D

Cost estimation:

Cost of chemicals required for preparation of 3 samples:

- Cost of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ – Rs. 3.98
- Cost of EDTA – Rs. 7.15
- Cost of formaldehyde – Rs. 3.94
- Cost of NaOH – Rs. 2.67
- Cost of Potassium FerroCyanide – Rs. 0.372
- Cost of paper – Rs. 0.50

Total cost= Rs. 18.6