

# Selective electroless metallization of non-conductive substrates enabled by a Fe<sub>3</sub>O<sub>4</sub>/Ag catalyst and a gradient magnetic field

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1 **Selective electroless metallization of non-conductive substrates enabled by a Fe<sub>3</sub>O<sub>4</sub>/Ag catalyst and**  
2 **a gradient magnetic field.**

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6 **Abstract:**

7 The formation of printed circuit patterns on non-conductive substrates has many applications in high  
8 value sectors such as the electronics sector. Current semi-additive and subtractive circuit  
9 manufacturing processes use photolithography to pattern substrates coated with a thin or relatively  
10 thick metal film. This process is often wasteful and expensive. Using an innovative approach;  
11 composite Fe<sub>3</sub>O<sub>4</sub>-Ag nanoparticles were synthesized and attracted to a magnetic field. The  
12 nanoparticles catalysed electroless copper deposition. Such a catalyst is new to electroless plating and  
13 was deposited selectively on a dielectric substrate using a gradient magnetic field. In this way,  
14 subsequent electroless copper plating occurred exclusively where the magnetic field was applied,  
15 whilst the remaining surface was free of deposited metal. The advantage of this additive method of  
16 manufacture is that less material is needed and less waste is produced.

17 **Keywords: Deposition, Electroless, Magnetic, Nanoparticles, Selective.**

18 **1. Introduction**

19 The utilization of a gradient magnetic field to enable selective metallisation via electrodeposition has  
20 been widely researched [1-3]. The gradient magnetic field was created by permanent magnets which  
21 were applied behind the substrate during electrodeposition. The electrodeposited layer had a higher  
22 thickness in the area of maximum magnetic field and formed a pattern which replicated that of the  
23 magnet array.

24 Selective metallization of **non-conductive** materials such as polymers is used extensively in a wide  
25 range of high value manufacturing processes such as the formation of radio frequency identification  
26 tags and the use of circuits for connecting wearable technology. Electroless deposition is often used  
27 to metallise non-conductive materials. Typically, a Pd/Sn colloidal catalyst is employed although  
28 alternatives have been investigated such as Ag and Cu [4-6]. Although several groups have attempted  
29 to study the effect of a magnetic field on electroless plating, none had the specific aim of selective  
30 deposition [7-9].

31 The synthesis of Fe<sub>3</sub>O<sub>4</sub>-Ag nanoparticles has been an area of research interest because of their unique  
32 properties [10]. The objective of the present research was to synthesize composite Fe<sub>3</sub>O<sub>4</sub>-Ag  
33 nanoparticles for electroless copper deposition. The paramagnetic Fe<sub>3</sub>O<sub>4</sub> particles would be attracted  
34 by the magnetic field and form the required pattern, whilst the silver would catalyse the oxidation and  
35 reduction reactions to initiate electroless plating. The aim of this study was to demonstrate that this  
36 innovative approach to selective metallization of non-conductive materials has the potential to be  
37 used for forming conductive circuitry on non-conductive substrates.

38 **2. Methodology**

39 The Fe<sub>3</sub>O<sub>4</sub>-Ag composite nanoparticles were synthesized according to a previously published  
40 procedure [11]. The synthesized particles were dried in an oven overnight at 50 °C. In order to prepare  
41 the catalyst solution, 0.01 g of Fe<sub>3</sub>O<sub>4</sub>-Ag composite nanoparticles were dispersed in 100 ml of reverse

42 osmosis (RO) water by magnetic stirring for 6 hours at 300 rpm. The pH of the solution was controlled  
43 at pH=2 and adjusted by addition of concentrated (37%) HCl.

44 A non-conductive epoxy polymeric substrate of dimensions 30x30x3 mm was used for the electroless  
45 plating. A Ni-Cu-Ni plated NdFeB magnet with dimensions of 10x5x2 mm was attached to one side of  
46 the plastic substrate (Figure 1 (b)). The substrate was then placed in 500 ml of a commercial  
47 'conditioner' solution which cleaned and functionalised the surface of the substrate. This was  
48 composed of 450 ml RO water and 50 ml Circuposit Conditioner 3320A (supplied by AGAS Electronic  
49 Materials Ltd) and was operated at 46 °C with an immersion time of 5 min. The substrate was then  
50 rinsed in water for 5 min and placed in the Fe<sub>3</sub>O<sub>4</sub>-Ag composite catalyst solution for 30 sec. The  
51 substrate was placed face-down horizontally in this solution in order to diminish the influence of  
52 catalyst particle sedimentation on pattern formation. The substrate was then rinsed in RO water and  
53 placed in a commercial electroless copper plating solution composed of 420 ml RO water, 75 ml  
54 Circuposit 3350 M-1, 5 ml Circuposit 3350 A-1, 5.25 ml Cuposit Z-1 and 5.7 ml Cuposit Y-1 (supplied by  
55 AGAS Electronic Materials Ltd) operated at 46 °C with an immersion time of 25 min. After electroless  
56 plating, the substrate with the obtained selective deposit was rinsed in tap water and dried in air.

57 An overall schematic representation of the process is presented in Figure 1 (a).

58 A Sigma 500 VP scanning electron microscope was utilized in order to characterise the size of the  
59 synthesised particles and the deposited film surface. An X-MaxN 80, Oxford Instruments silicon drift  
60 detector fitted in the SEM and was used to analyse the composition of the Fe<sub>3</sub>O<sub>4</sub>-Ag composite  
61 nanoparticles. ImageJ software was employed for analysis of particle size and distribution. Images of  
62 the deposited copper and catalyst film were obtained using an optical microscope.

### 63 **3. Results and discussion**

64 An SEM image of the synthesized Fe<sub>3</sub>O<sub>4</sub>-Ag nanoparticles is presented in Figure 2 (a). The EDX mapping  
65 of obtained image for Fe (Figure 2(b)) shows an even distribution of this element across the measured  
66 area. For Ag (Figure 2(c)) the highest density occurs at points corresponding to bright particles with  
67 diameter of approximately 100 nm. This suggests that a composite material is formed which consists  
68 of 36±9 nm Fe<sub>3</sub>O<sub>4</sub> nanoparticles and 83±19 nm nanoparticles of Ag. In addition, the analysis of the  
69 Fe<sub>3</sub>O<sub>4</sub>-Ag nanoparticles size distribution shows that there is an increase in the formation of larger  
70 particles from 60 to 90 nm compared to the Fe<sub>3</sub>O<sub>4</sub>, where no particles larger than 70 nm are apparent  
71 (Figure 2 (d)).

72 The composite Fe<sub>3</sub>O<sub>4</sub> – Ag nanoparticles were dispersed in an aqueous acidic solution (pH = 2). The  
73 addition of HCl was expected to enhance the electrostatic attraction of Ag and Fe<sub>3</sub>O<sub>4</sub> nanoparticles  
74 since the zeta potential of Ag nanoparticles is negative at all pH values[12] while Fe<sub>3</sub>O<sub>4</sub> nanoparticles  
75 are positive in an acidic environment [13], the maximum electrostatic attraction between Ag and Fe<sub>3</sub>O<sub>4</sub>  
76 nanoparticles should be achieved at an acidic pH. At neutral pH, Fe<sub>3</sub>O<sub>4</sub> nanoparticles reach the  
77 isovalent point and the nanoparticle surface will have no charge [13]. Under these conditions,  
78 electroless plating experiments gave inconsistent results.

79 Electroless copper plating experiments were conducted to determine the suitability of the  
80 nanoparticles to be patterned by a magnetic field and to act as a catalyst to initiate electroless copper  
81 plating. As described in the methodology (Figure 1(a)) a magnet was attached to the back of the  
82 substrate and it was observed that pure Fe<sub>3</sub>O<sub>4</sub> nanoparticles were patterned by the magnetic field but  
83 did not initiate electroless copper plating. The composite Fe<sub>3</sub>O<sub>4</sub> – Ag nanoparticles were also deposited  
84 selectively in the area of maximum magnetic field influence as shown in the optical microscope image  
85 Figure 3(a). These nanoparticles initiated subsequent electroless copper plating which occurred

86 exclusively in the area where the magnetic field was applied as illustrated in Figure 3(b).

87 The SEM image of the substrate surface was obtained after electroless copper deposition (Figure 3(c)).

88 The image reveals that the deposited layer has a similar morphology to that obtained using a Pd  
89 catalyst, although the coverage is not entirely continuous.

## 90 **Conclusion**

91 In this study, an innovative methodology for the selective metallisation of non-conductive materials  
92 has been demonstrated. From this study, it has been proven that:

- 93 • composite Fe<sub>3</sub>O<sub>4</sub>-Ag nanoparticles will act as a catalyst and initiate electroless copper plating,
- 94 • the magnetic properties of this catalyst enable it to be patterned on a substrate by a magnetic  
95 field, and
- 96 • the combined catalytic and magnetic properties of the composite Fe<sub>3</sub>O<sub>4</sub>-Ag nanoparticles  
97 enable selective metallisation of a non-conductive material.

## 98 **Acknowledgements**

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133

134 **Figure 1.** The schematic presentation of (a) standard and selective electroless plating under applied  
135 gradient magnetic field and (b) magnet attachment set-up.

136 **Figure 2.** (a) SEM image of synthesised  $\text{Fe}_3\text{O}_4 - \text{Ag}$  composite particles, (b) EDX mapping of Fe, (c) EDX  
137 mapping of Ag, (d) size distribution histogram of synthesised particles.

138 **Figure 3.** (a) The optical image of the selectively deposited composite  $\text{Fe}_3\text{O}_4 - \text{Ag}$  catalyst, (b) the  
139 optical image of the selectively deposited copper layer, (c) SEM image of the deposited copper layer  
140 obtained by gradient magnetic field application.

141