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Selective electroless metallization of non-conductive substrates enabled by a Fe₃O₄/Ag catalyst and a gradient magnetic field.

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Abstract:

The formation of printed circuit patterns on non-conductive substrates has many applications in high value sectors such as the electronics sector. Current semi-additive and subtractive circuit manufacturing processes use photolithography to pattern substrates coated with a thin or relatively thick metal film. This process is often wasteful and expensive. Using an innovative approach; composite Fe₃O₄-Ag nanoparticles were synthesized and attracted to a magnetic field. The nanoparticles catalysed electroless copper deposition. Such a catalyst is new to electroless plating and was deposited selectively on a dielectric substrate using a gradient magnetic field. In this way, subsequent electroless copper plating occurred exclusively where the magnetic field was applied, whilst the remaining surface was free of deposited metal. The advantage of this additive method of manufacture is that less material is needed and less waste is produced.

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

1. Introduction

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

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

The synthesis of Fe₃O₄-Ag nanoparticles has been an area of research interest because of their unique properties [10]. The objective of the present research was to synthesize composite Fe₃O₄-Ag nanoparticles for electroless copper deposition. The paramagnetic Fe₃O₄ particles would be attracted by the magnetic field and form the required pattern, whilst the silver would catalyse the oxidation and reduction reactions to initiate electroless plating. The aim of this study was to demonstrate that this innovative approach to selective metallization of non-conductive materials has the potential to be used for forming conductive circuitry on non-conductive substrates.

2. Methodology

The Fe₃O₄-Ag composite nanoparticles were synthesized according to a previously published procedure [11]. The synthesized particles were dried in an oven overnight at 50 °C. In order to prepare the catalyst solution, 0.01 g of Fe₃O₄-Ag composite nanoparticles were dispersed in 100 ml of reverse
osmosis (RO) water by magnetic stirring for 6 hours at 300 rpm. The pH of the solution was controlled at pH=2 and adjusted by addition of concentrated (37%) HCl.

A non-conductive epoxy polymeric substrate of dimensions 30x30x3 mm was used for the electroless plating. A Ni-Cu-Ni plated NdFeB magnet with dimensions of 10x5x2 mm was attached to one side of the plastic substrate (Figure 1 (b)). The substrate was then placed in 500 ml of a commercial ‘conditioner’ solution which cleaned and functionalised the surface of the substrate. This was composed of 450 ml RO water and 50 ml Circuposit Conditioner 3320A (supplied by AGAS Electronic Materials Ltd) and was operated at 46 °C with an immersion time of 5 min. The substrate was then rinsed in water for 5 min and placed in the Fe₃O₄-Ag composite catalyst solution for 30 sec. The substrate was placed face-down horizontally in this solution in order to diminish the influence of catalyst particle sedimentation on pattern formation. The substrate was then rinsed in RO water and placed in a commercial electroless copper plating solution composed of 420 ml RO water, 75 ml 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 AGAS Electronic Materials Ltd) operated at 46 °C with an immersion time of 25 min. After electroless plating, the substrate with the obtained selective deposit was rinsed in tap water and dried in air.

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

A Sigma 500 VP scanning electron microscope was utilized in order to characterise the size of the synthesised particles and the deposited film surface. An X-MaxN 80, Oxford Instruments silicon drift detector fitted in the SEM and was used to analyse the composition of the Fe₃O₄-Ag composite nanoparticles. ImageJ software was employed for analysis of particle size and distribution. Images of the deposited copper and catalyst film were obtained using an optical microscope.

3. Results and discussion

An SEM image of the synthesised Fe₃O₄-Ag nanoparticles is presented in Figure 2 (a). The EDX mapping of obtained image for Fe (Figure 2(b)) shows an even distribution of this element across the measured area. For Ag (Figure 2(c)) the highest density occurs at points corresponding to bright particles with diameter of approximately 100 nm. This suggests that a composite material is formed which consists of 36±9 nm Fe₃O₄ nanoparticles and 83±19 nm nanoparticles of Ag. In addition, the analysis of the Fe₃O₄-Ag nanoparticles size distribution shows that there is an increase in the formation of larger particles from 60 to 90 nm compared to the Fe₃O₄ where no particles larger than 70 nm are apparent (Figure 2 (d)).

The composite Fe₃O₄ – Ag nanoparticles were dispersed in an aqueous acidic solution (pH = 2). The addition of HCl was expected to enhance the electrostatic attraction of Ag and Fe₃O₄ nanoparticles since the zeta potential of Ag nanoparticles is negative at all pH values[12] while Fe₃O₄ nanoparticles are positive in an acidic environment [13], the maximum electrostatic attraction between Ag and Fe₃O₄ nanoparticles should be achieved at an acidic pH. At neutral pH, Fe₃O₄ nanoparticles reach the isovalent point and the nanoparticle surface will have no charge [13]. Under these conditions, electroless plating experiments gave inconsistent results.

Electroless copper plating experiments were conducted to determine the suitability of the nanoparticles to be patterned by a magnetic field and to act as a catalyst to initiate electroless copper plating. As described in the methodology (Figure 1(a)) a magnet was attached to the back of the substrate and it was observed that pure Fe₃O₄ nanoparticles were patterned by the magnetic field but did not initiate electroless copper plating. The composite Fe₃O₄ – Ag nanoparticles were also deposited selectively in the area of maximum magnetic field influence as shown in the optical microscope image Figure 3(a). These nanoparticles initiated subsequent electroless copper plating which occurred
exclusively in the area where the magnetic field was applied as illustrated in Figure 3(b).

The SEM image of the substrate surface was obtained after electroless copper deposition (Figure 3(c)). The image reveals that the deposited layer has a similar morphology to that obtained using a Pd catalyst, although the coverage is not entirely continuous.

Conclusion

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

- composite Fe$_3$O$_4$-Ag nanoparticles will act as a catalyst and initiate electroless copper plating,
- the magnetic properties of this catalyst enable it to be patterned on a substrate by a magnetic field, and
- the combined catalytic and magnetic properties of the composite Fe$_3$O$_4$-Ag nanoparticles enable selective metallisation of a non-conductive material.

Acknowledgements

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References


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

Figure 2. (a) SEM image of synthesised Fe₃O₄ – Ag composite particles, (b) EDX mapping of Fe, (c) EDX mapping of Ag, (d) size distribution histogram of synthesised particles.

Figure 3. (a) The optical image of the selectively deposited composite Fe₃O₄ – Ag catalyst, (b) the optical image of the selectively deposited copper layer, (c) SEM image of the deposited copper layer obtained by gradient magnetic field application.