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Activation of non-metallic substrates for metal deposition using organic solutions

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ABSTRACT

Non-metallic substrates, such as plastics or oxides, need to be activated before electroless metal deposition. In this paper, a novel process of using metal Pd and Pd–Cu ion loaded organic solutions for surface activation of non-metallic substrates is described. The organic media used are strong polarizing and low ionic conducting solutions of the type commonly used in the solvent extraction industry. Different types of non-metallic substrates, including polyester, alumina and carbon nanotubes, have been evaluated, and it was shown that a uniform and complete Cu coating can be electrolessly deposited after activation in metal ion loaded organic solutions.

1. Introduction

Metal coatings have been made on non-metallic materials, such as ceramics, carbon and plastics are increasing for a wide range of commercial applications. For example, polished alumina has been used as an interconnect substrate onto which a conductive metal layer, such as gold or copper, can be applied. Metal coated carbon nanotubes offer various applications due to their excellent mechanical properties and unique electrical properties [1–6], while metal coated plastics have been used extensively in PCB, automotive, home appliance and microelectronics industry over the past few decades [7].

Currently, non-metallic materials can be metallized (or metal coated) by several techniques or processes, such as chemical vapor deposition (CVD), physical vapor deposition (PVD) technique and thermal spray. Electrochemical processes from aqueous solutions are also used but they require special conditions in order to be successful. For example a mature electrochemical process for depositing metals such as Pd onto non-conductors usually involves multiple steps and is limited to metal species that are water soluble. Generally, the first step in the existing process is "sensitization" using a tin chloride reducing agent. Then a palladium chloride solution is added and the metallic Pd seed forms by a redox reaction. Finally, the tin must be removed by a leaching/washing process [8].

The most popular commercial method used in the activation steps is a two-step $SnCl_2$–$PdCl_2$ (sensitization-activation) pre-treatment [8]. According to the two-step $SnCl_2$–$PdCl_2$ pre-treatment procedure, a non-metallic substrate is dipped into a $SnCl_2$–HCl solution, whereby the stannous ions are adsorbed onto the substrate surface. After rinsing, the substrate is then immersed into a $PdCl_2$–HCl solution, which allows the palladium ions to be adsorbed onto the substrate. On the substrate surface, the adsorbed stannous ions reduce the palladium ions to metallic palladium seed. The reduced palladium metallic seed can then act as catalytic nuclei for subsequent metal (such as Cu) electroless deposition [9]. The process of making a catalytic metal seed layer is commonly called "activating."

The $SnCl_2$–$PdCl_2$ (sensitization-activation) pre-treatment process has been utilized for decades; however, concerns about the low efficiency and risks of contamination remain unresolved. Many attempts have been made to find a single-step catalyzing procedure to replace the two-step method with a more efficient method, such as the Pd–Sn colloidal deposition, noble metal prints, and vacuum deposition methods. However, these techniques are either costly or require additional processing steps which reduce the efficiency.

A novel, single-step metal catalyzing process using organic solutions for electroless metallization applications has been under development. The origin of the method is a deviation of an earlier process called galvanic stripping [8] and a metal deposition process called Metal Immersion Deposition from Organic Solutions (MIDOS) [10]. Galvanic stripping is a spontaneous electrochemical process, potentially useful for metal ion separation in the metal extraction industry [11]. The mechanism of galvanic stripping is based on displacement reactions, where a more noble metal ion is reduced by a less noble solid metal.

Modification of the galvanic stripping process led to the development of metal plating onto metal substrates from organic solutions. Since organic media have unique characteristics, such as strong polarization tendencies and low electrical and ionic conductivity, the MIDOS Process could be used in a wide range of selective metal/metal ion systems with good morphology control. For example, Ag and Au were successfully deposited on Ni or Cu surfaces for use during

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printed circuit boards and MEMS fabrication [12]. The metal organic deposition method has also demonstrated the feasibility for metal nano-particle deposition of Cu and Pd on barrier layers, like TiSiN, TaSiN and TaN, as activating seeds for subsequent electroless Cu deposition [13–15].

Further evaluation of the organic metal displacement deposition method has led to the current process, and the feasibility of activating non-metallic substrates, including carbon nanotubes, alumina and polyester. Subsequent electroless Cu deposition gives a smooth, complete coating on the substrate. The method has some advantages that might be preferred over a conventional aqueous method in selective applications. The reaction mechanism for non-metallic substrate activation could be a combination of metal ion adsorption and electroless deposition with organic solution components as the reducing agent [16–18].

2. Materials and methods

2.1. Substrates

Three categories of non-metallic materials, ceramics, plastics and carbon, were used in this investigation. The specific material for each category selected for the experiments were:

- Carbon: 140 nm × 7 μm multi-walled carbon nanotubes from Strem Chemicals
- Ceramic: 99.5% polished alumina plate 1 cm × 1 cm × 0.2 cm
- Plastic: PC21 Green polyester tape 2.54 cm × 2.54 cm × 0.09 mm.

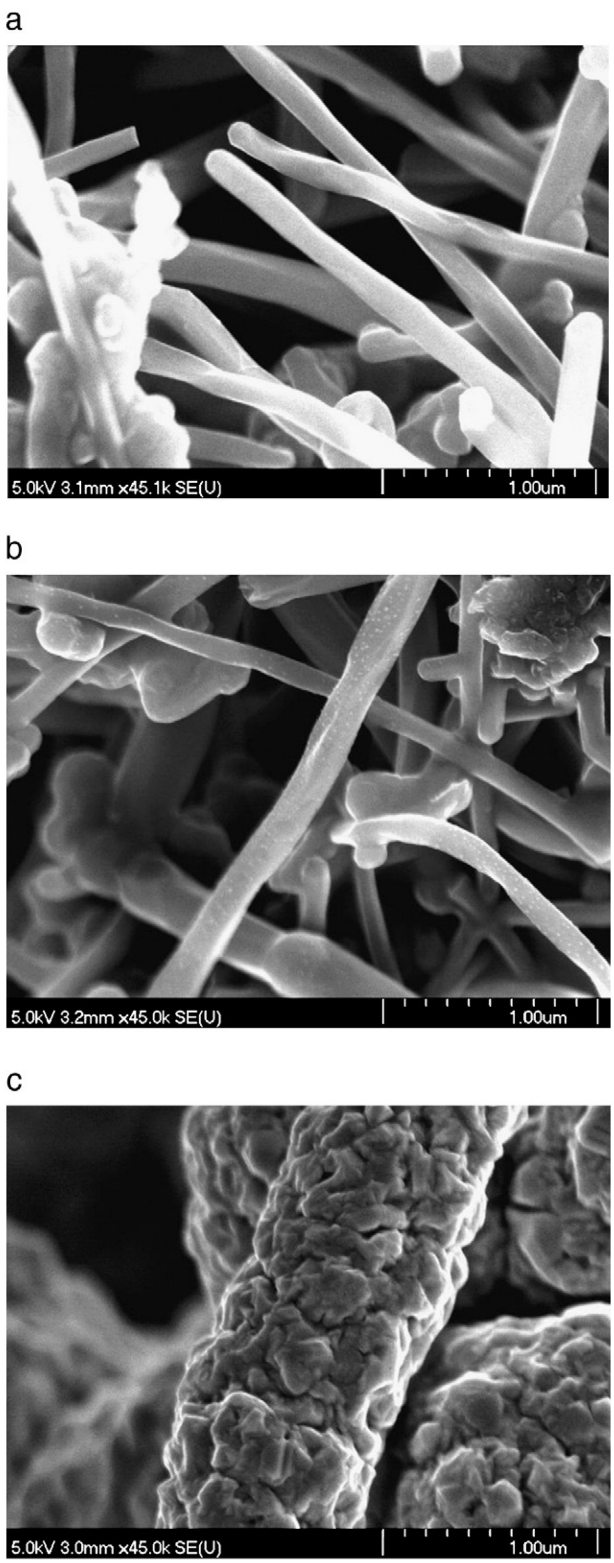

Fig. 1. SEM of the multi-walled carbon MWCNTs: a) bare MWCNTs, b) after Pd organic activation, and c) after electroless Cu coating.

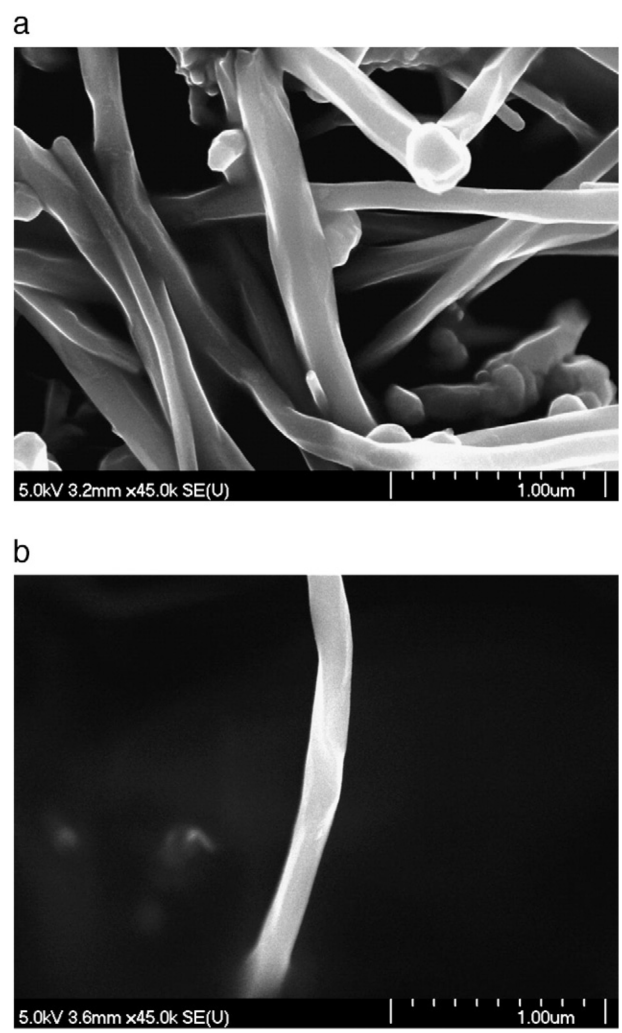

Fig. 2. SEM of MWCNTs after Cu electroless deposition: a) without metal organic activation, and b) activated by blank organic solution.