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Impact of Electroplating to Surface-Enhancement Raman Spectroscopy (SERS)

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Abstract: ***Electrochemical deposition methods are increasingly being applied to advanced technology applications. The growing need for device miniaturization and enhanced performance, vastly improved control of the growth process is required, which in turn necessitates a better understanding of the fundamental phenomena involved. The formation of metallic porous film has received much interest in the past due to their high surface area and specific structural orientation which make them attractive for application such as catalysis and sensors. The film is fabricated through a variety of method including electroless deposition, electrodeposition and chemical vapour deposition. Electrochemical growth phenomena particular attention is devoted to alloy and compound formation, as well as surface-limited processes and understanding of electrochemical interfaces and electrodepositing on surface of the substrates to improve surface enhancement.***

Keywords: Electrodeposition, Plasmonic, Spectroscopy, SEM, SERS, SHINERS

1. Introduction

1.1 Electroplating

Electroless plating of metals and process technology have important role along with other methods of plating. Today sophisticated electroless plating system are use in various electronic applications. Metallic deposits forms on a catalysed surface it has been referred to by these investigators as preferential deposition.. The term electroless platting is define as an autocatalytic deposition of a metal/alloy form an aqueous solution of its ion by interaction with a chemical reducing agent. The reducing agent provides electrons for the metals ions to be neutralised. The reduction is initiated by catalysed surface of the substrate and continues by the self-catalytic activity of the deposited metal/alloy as long as the substrate is immersed in the electroless bath and the operating condition is maintained.

Electrodepositing of Au, Ag, Cu and their alloys is a topic of applied metal electrochemistry with a remarkable commercial background in: electronic, electric, aircraft, medical instrumentation. Plating is usually performed in order to protect or decorate items as well as to increase their corrosion or wear resistance, thermal and electric properties or to enhance solderability. Extensive efforts have been made towards the understanding of the electrochemical and chemical behaviour involved in the deposition process, as well as on the impact of plating conditions on the functional properties of the electrodeposits. In situ Surface Enhanced Raman Spectroscopy (SERS) is an adequate method for such an approach, in terms of surface sensitivity to adsorption and interfacial reaction phenomena, as well as some degree of quantitative capability. In the present work, based on in situ SERS, we can obtained novel insight into the adsorption and reactivity ions at the surface of a growing Au, Ag and Cu cathodes.

1.2 What is SERS?

Surface enhanced Raman scattering (SERS) is a technique which offers orders of magnitude increases in Raman intensity, overcoming the traditional drawback of Raman scattering – its inherent weakness. Enhancement factors can be as high as 10^{14-15}, which are sufficient to allow even single molecule detection using Raman. SERS is of interest for trace material analysis, flow cytometry and other applications where the current sensitivity/speed of a Raman measurement is insufficient.

Advantages of SERS can be explored on any Raman system, and the actual measurement is made in the standard way. Typically it is necessary to use a laser wavelength which is compatible with the chosen SERS metal, but beyond this there are no major difficulties. SERS spectra do sometimes differ from a 'normal' Raman spectrum of the same material, so interpretation of data must be considered.

1.3 SERS Material

The main difference from one SERS method to the next is attributed to the different type of plasmonic substrates employed. These plasmonic Substrates range from simple metallic nano-particles to complex nano-scale structures created via Electrodepositing processes. Metallic nano-particles can now be engineered with specific sizes and shapes, in addition to being coated with special materials to tune their plasmonic properties. This has given rise to the Shell-isolated nano-particle enhanced Raman spectroscopy (SHINERS) method. Another type of substrate is created by depositing thin films of metal on top of Substrates.

The plasmonic properties of these substrates are controlled by the distribution and size of the nano-spheres as well as the thickness of the coated metal, and are called film over nano-sphere (FONs) substrates. The photo-resist derived structures are then coated with a thin metal film. The plasmonic properties of these substrates are highly tunable due to the ability directly control the geometry and dimensions of the surface structures.

2. Material and Method

Silver nitrate (AgNO3) and copper sulphate (CuSO4) are used for copper and silver co-deposition on surface of the substrate . Hydrazine sulphate is used as reducing agent and to stabilize the pH of the electrolytic bath. All chemical were of analytical grade without any purification The electrolytes were prepared with Millipore water. The electrolyte solutions were treated with hydrazine sulphate to obtain the inert atmosphere and to maintain the pH during electrolysis. The synthesis of nano-metal particles was performed in a conventional tow electrode electrochemical cell at room temperature .The working electrode is connected to cathode and counter to anode terminals. The electrodes were washed carefully with acetone or with methanol with water prior in the electrolysis. Single acid bath approach is used to simplify the process of electrodepositing nano- particles. During the electrodepositing applied current density was maintained at 0.01 ampere/second.

2.1 Material Characterisation and Result

2.1.1 SEM Result

The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample.

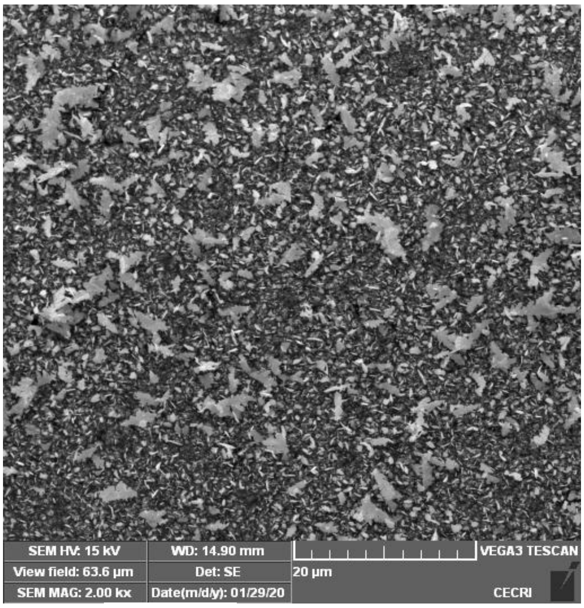

Figure 1: Morphology distribution of metal particles on surface of substrate at 5μm scale

SEM analysis is considered to be "non-destructive"; that is, x-rays generated by electron interactions do not lead to volume loss of the sample, so it is possible to analyze the same materials repeatedly. Energy dispersive x-ray spectroscopy, also referred to as EDX, EDS or EDAX, provides additional understanding of the surface material during the SEM analysis process. EDX analysis is used to acquire the elemental composition of a sample and allows for a more quantitative result than that provided by only SEM analysis. The combination of SEM and EDX analysis offers chemical composition and elemental investigation – providing a comprehensive metallurgical evaluation.

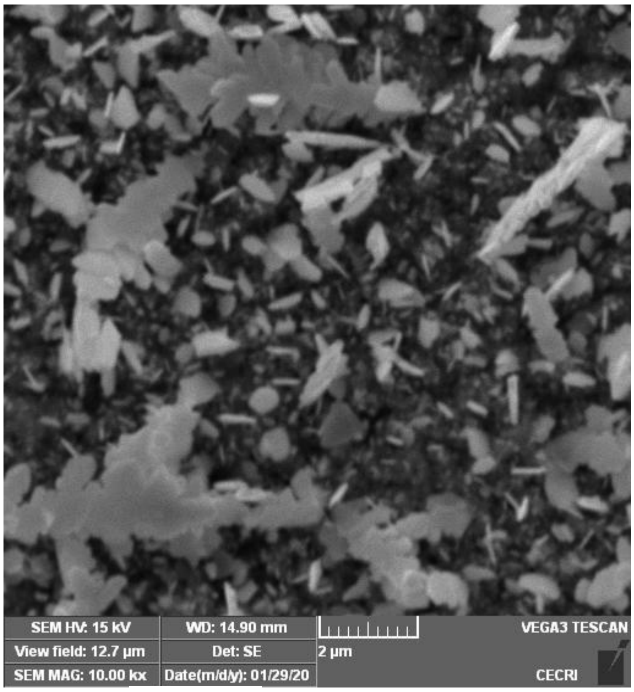

Figure 2: Morphology distribution of metal particles on surface substrate at 2μm scale

2.2.2 Laser Raman Result

Raman Spectroscopy is a non-destructive chemical analysis technique which provides detailed information about chemical structure, phase and polymorphy, crystallinity and molecular interactions. It is based upon the interaction of light with the chemical bonds within a material.

A Raman spectrum features a number of peaks, showing the intensity and wavelength position of the Raman scattered light. Each peak corresponds to a specific molecular bond vibration, including individual bonds such as C-C, C=C, N-O, C-H etc., and groups of bonds such as benzene ring breathing mode, polymer chain vibrations, lattice modes, etc.

Raman spectroscopy probes the chemical structure of a material and provides information about:

- Chemical structure and identity
- Phase and polymorphism
- Intrinsic stress/strain
- Contamination and impurity

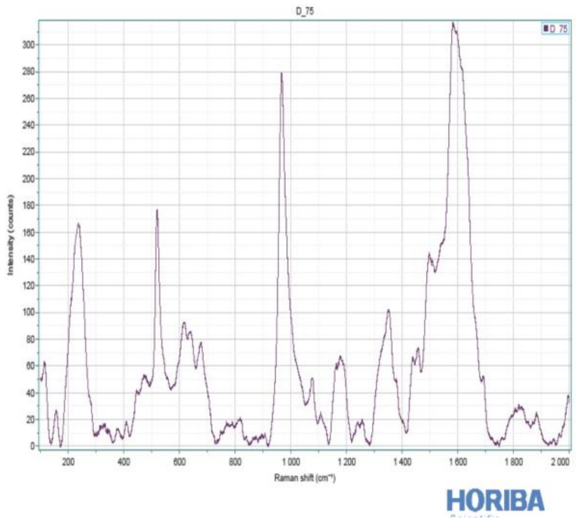

Figure 3: The Raman spectrum of metal particle form Simple Raman Surface

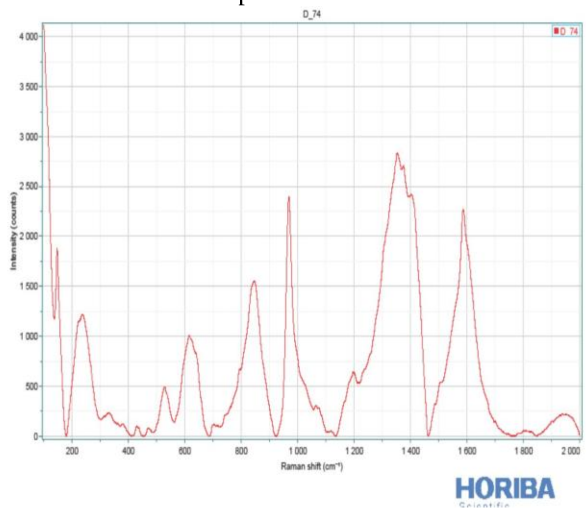

Figure 4: The Raman spectrum of metal particle **from the SERS**

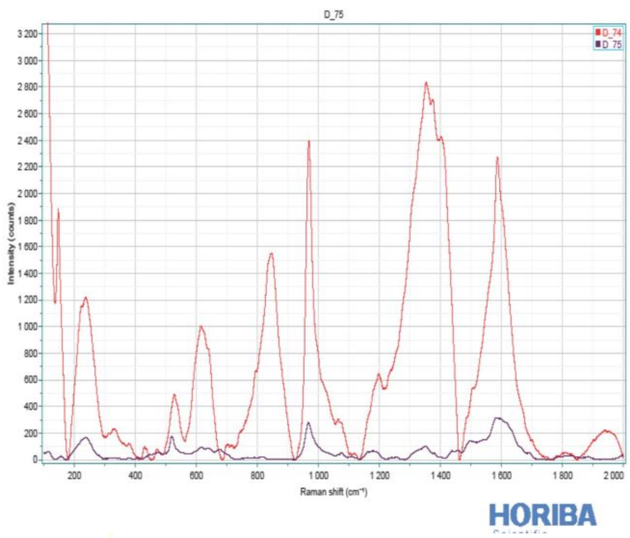

Figure 5: The Raman spectrum comparison of metal particle form the **Combine Simple Raman Surface and SERS**

3. Conclusions

In this paper we carried out an in-situ SERS investigation of Ag and Cu electrodepositing processes. SEM results indicate the Morphology of uniform distribution of metals over the surface of the substrate. Raman spectrum indicates the difference of Peak value of metals over simple surface and SERS (Surface –enhancement Raman Scattering) .Surface –enhancement Raman Spectroscopy or Surface –enhancement Raman Scattering is a surface sensitive technique that enhances Raman scattering by molecule adsorbed on rough metal surface. **The enhancement factor can be as much as 10^{10} to 10^{11}, which means the technique may detect single molecules.** This can be achieved proper selection electrodepositing processes to deposition the metal nanoparticles over the surface of the substrates.

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