

Nanocharacterization studies on Surface modified Nanoporous Gold Films for Sensor applications

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ABSTRACT

Nanoporous Gold Film (NPGF) was fabricated using electroless plating of e-beam deposited Cu substrate with Potassium Gold Cyanide (PGC) as electroless plating solution. Nanocharacterization of both NPGF and surface modification of NPGF was performed. SEM studies revealed the pore size to be 100 ± 20 nm for the fabricated NPGF. The surface modification of NPGF was done using L-Cysteine, an amino acid, for different time intervals (30 min and 24 h). The AFM and STM results of both NPGF and surface modified NPGF revealed that by increasing adsorption time the surface roughness can be reduced upto 90%. The STM results proved that there is an increase in surface coverage of the L-cysteine SAM on NPGF that would help in building a highly selective nanosensor with lesser limit of detection (LOD) by chelating more heavy metal ions onto the surface of sensor.

Keywords: electroless plating, nanoporous gold film, nanocharacterization, sensor.

1 INTRODUCTION

Presently metallic nanofilms are being widely studied because of their unique physical and chemical properties and functionalities compared to their bulk counterparts. These constitute the basic components for the development of devices related to electronics, sensing, catalytic activities etc.[1] and have also been able to add an extra edge in the functionality of these devices due to their high surface to volume ratio. Also, the modification of nanofilms with various chemical functional groups allow them to conjugate with antibodies, ligands etc. This open a wide range of potential applications in biotechnology, sensing and targeted drug delivery. Modification of nanofilms lead to the formation of ordered molecular assemblies due to the adsorption of an active surfactant on a solid surface known as self-assembled monolayers (SAMs) [2]. The ease of preparation and the possibility of introduction of different chemical functionalities makes it highly desirable. For the surface modification of sensors, SAMs are typically prepared on a noble metal. In this study

it was gold, that has the potential to act as a transducer in a nanosensor. There have been several studies on the stability and selectivity of organic thiols chemisorbed on gold [1, 2].

The present study includes the interaction of L-cysteine, the only naturally occurring amino acid [3], with Au (111) nanofilm to understand its roughness characteristics through a time interval with the help of STM and AFM. There has been studies on the characteristics of L-Cysteine SAM on Au film since decades [4-8]. Dakkouri et al. studied the adsorption of L-Cysteine on Au (111) with the help of STM and concluded that there is a formation of roughened surface with large number of monoatomic high gold islands and monoatomic deep holes [4]. Qing-Min Xu and coworkers used cyclic voltammetry and in situ electrochemical scanning tunneling microscopy to propose a structural model of L-Cysteine SAM on Au (111) [5]. Similarly, Wenrong Yang et al investigated the adsorption of L-cysteine on gold electrodes by electrochemical reductive desorption [6]. Jingdong Zhang et al reported the formation of two-dimensional Cysteine and Cystine cluster networks on Au (111) by employing electrochemistry and in situ STM and also studied assembly dynamics and detailed structure of 1-Propanethiol monolayers on Au (111) surfaces observed real time by in situ STM [7, 8]. In this study, L-Cysteine was used to modify the surface of Au (111) that can be further utilized for heavy metal ion sensing because X-ray photoelectron (XPS) [9] and Fourier transform infrared spectroscopy (FTIR) [10] spectroscopic studies had shown that sulphur-gold interaction is strong when cysteine binds onto gold surface and thus functionalizing the gold surface with amino acids [18]. Due to the formation of strong bondage between sulphur and gold, the monolayer takes short time to assemble and are reasonably stable upon cyclic voltammetric scanning in buffer solutions as well as for other optical characterizations [5]. After surface modification of the gold electrode, the samples were studied using Tapping mode AFM and constant current mode STM. The nanocharacterization studies on surface modified NPGF was carried out to analyze the surface roughness parameters at different adsorption times allowing an increased protein interaction towards detection of heavy metal ions.

2 EXPERIMENTAL

2.1 Equipments and reagents

The e-beam deposited copper substrates were used for electroless plating and to obtain nanoporous gold film. SEM photographs were taken using Carl Zeiss EVO 18 Special Edition. Characterization of samples were done using STM and AFM (Nanosurf EasyScan 2). AFM was used in tapping mode operated in constant force mode and STM was operated in constant current mode. Potassium Gold Cyanide solution was used for electroless plating of e-beam deposited copper substrate. Chemicals such as L-Cysteine, phosphate buffer, cysteamine, glutaraldehyde, ethanol and acetone were used for the surface modification of the NPGF. All chemicals were used as received.

2.2 Fabrication of NPGF

NPGF was fabricated using electroless plating in which redox reaction takes place to deposit metal on an object without the passage of an electric current. Since the metal is dipped in the solution, it forms a uniform layer of desired metal on the substrate. It can also be used to deposit a conductive surface on a nonconductive object to be electroless plated. In this study, Potassium gold cyanide (PCG) was used as the plating solution. Double layered heating technique was implemented using the boiling water to prevent the solution from solidifying after sometime. The e-beam deposited copper substrate was dipped in the plating solution, that was maintained at 70°C, for different time durations (2 min, 6h, 9h, 18h). Due to low reduction potential of copper than gold, the gold ion from plating solution replaced copper ion leaving behind a NPGF on the substrate. The deposited gold on Si substrate exhibit pore size 100 ± 20 nm [11].

2.3 Preparation of L-Cys/Au SAMs

The gold substrate was cleaned by rinsing it with deionized water to remove all the physically adsorbed species and dried. The gold substrate was immersed in 8mM of L-Cysteine solution containing phosphate solution, for 30 min. The substrate was removed after 30 min and copiously washed with distilled water (Figure 1).

2.4 Atomic Force Microscope Characterization

The NPGF modified with L-Cysteine SAM was characterized using tapping mode AFM to determine its surface roughness and surface topography. In tapping mode, the AFM scans the sample surface with a very tiny and sharp tip mounted at the end of a flexible cantilever. The tip is oscillated and moved towards the sample. Only intermittent touching or "tapping" occurs on the sample. Hence the dragging forces during scanning are greatly

reduced. The sample size was cut down to 5 mm X 5 mm. It was mounted in the sample stage of the equipment.

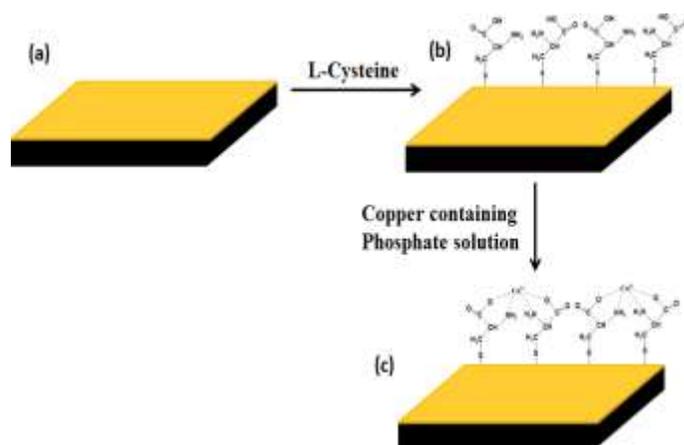


Figure 1. Proposed Scheme for L-Cysteine SAM

2.5 Scanning Tunneling Microscope Characterization

The sample was attached to the magnetic sample disc with silver paste for STM experiments (Figure 2). Atomic and molecular level interactions are also pivotal for many research areas including biology and nanoscience. It would be advantageous to use conventional STM set-up which would help to measure the tip-atom interaction. Before the STM experiments, the conductance between the sample holder and the sample was determined. Tip voltage of 200 mV was given for 200 nm sacn, tip current of 644 pA was measured.



Figure 2. Sample preparation (a) The sample mounted on the spare disc shaped sample support (b) The sample holder and its magnetic end (c) The sample holder ready for mounting on the STM stage.

3 RESULTS AND DISCUSSION

3.1 SEM images of electroless plated Cu sample

SEM images of a pure Au e-beam sample and the 9h e-beam deposited Cu sample were captured. The electroless plated e-beam Cu deposited sample showed a

NPGF whose porosity ranges from 116 nm to 140 nm (Figure 3).

Nano porous gold films(NPGF) is a porous structure having nanopores of 116-140 nm. The self assembled monolayer of L-Cysteine was formed on NPGF by immersing it into solution for 30 min and 24 h respectively. Formation of Self-assembled monolayer of cysteine molecules on NPGF are confirmed by AFM topography. The gold e-beam sample is atomically flat because its roughness is less than 1 nm whereas the nanoporous gold film has high surface roughness. However the surface coverage decreases on modification. When NPGF was immersed in L-Cysteine solution for 24h, the surface roughness reduced by 90% resulting into more molecular deposition of cysteine molecules on NPGF (Figure 4).

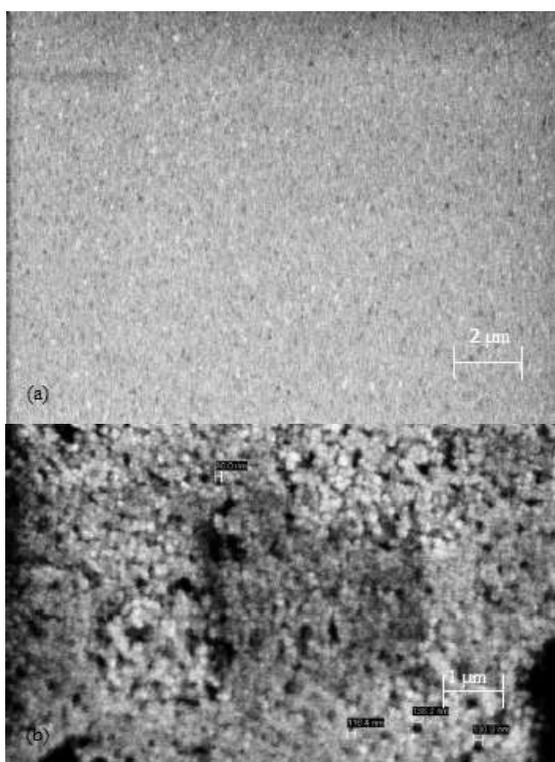


Figure 3. SEM images of (a) E-beam deposited Au (b) SEM image of electroless plated Cu sample.

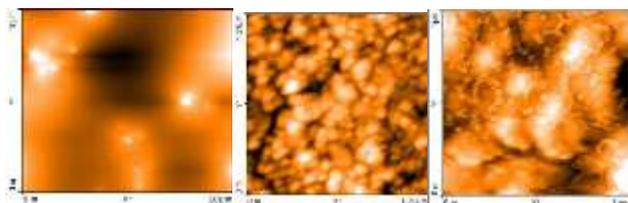


Figure 4. AFM images taken in tapping mode for 1 μm scan of (a) Bare NPGF (b) NPGF L-Cysteine 30 min immersion (c) NPGF L-Cysteine 24 h immersion.

Samples	Average Roughness (nm)	Valley depth (nm)	Peak height (nm)	Peak-valley height (nm)
Gold e-beam	0.73	-4.99	15	20.09
Bare NPGF	19.3	-56.5	135.9	192.41
NPGF with cysteine (30 min)	17.4	-64.2	139.36	203.6
NPGF with cysteine (24 h)	2.3	-17.8	33.6	51.5

Table 1. Average roughness values investigated from AFM characteristics.

3.2 Characterization of Nanoporous Gold film by STM

Based on the roughness values, it was inferred that average surface roughness is a function of adsorption time. The number of cysteine molecules per nanometer square would provide the estimation of chelation sites for copper binding. Therefore, STM characterization technique was used to quantify the molecular coverage of molecules per nanometer square. The STM characterization is carried out in ambient conditions. Figure 5 reveals that when the tip voltage was 200 mV, a tip current of 644 pA was generated. This technique would help in determining the interaction strengths of molecules and biomolecular systems on surfaces[12]. Therefore this experiment can be further extended to find the sulphur-gold interaction strength that may be used to find the reusability of surface modified electrodes opening a new dimension in surface chemistry.



Figure 5. STM image of Gold on mica with L-Cysteine molecules.

4 CONCLUSIONS

Nano porous gold films attracted attention in nanotechnology research. It is defined as the building blocks for potential applications in nanosensors and nano electro mechanical systems. Fabrication of such nanostructures were done by using electroless plating by immersing the copper sample in potassium gold cyanide bath at 70°C for 9 h.

The microscopic characteristics of the L-cysteine modified NPGF were determined by atomic force microscopy (AFM) working in tapping mode. AFM topography images were used as image analysis at low magnification levels. AFM images of both surfaces has been presented and the corresponding roughness values were measured as shown in Table 1. The average roughness of NPGF decreases from 17.4 nm for 30 min to 2.3 nm for 24 h implying that increase in surface modification time decreases the average surface roughness. From the figures, the self-assembled monolayer of L-cysteine on NPGF were observed. The L-cysteine coverage on the NPGF appeared to depend on the adsorption time when subjected to similar immobilization conditions, specifically at 30 min and 24 h. As NPGF was immersed in L-cysteine solution for 24 h, the surface roughness reduced by 90% resulting in high surface coverage of L-cysteine molecules on NPGF. Thus modification of such nanoporous gold film was performed using L-cysteine by changing the immersion time to monitor the surface roughness and also the monolayer coverage. The surface roughness analysis and molecular coverage was investigated by using sophisticated nanocharacterization techniques such as Tapping mode AFM and STM respectively. Apart from surface roughness, this study may be used to determine interaction strengths of molecules and biomolecular systems of surfaces in the near future.

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