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Design complexity of DPN patterning with Cr^{3+} and Co^{2+} metallic ions on Au (111) thin film

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ABSTRACT

We present in this work a fabrication chain of an electrochemical sensor platform based on detection of Cr^{3+} and Co^{2+} metallic ions species. Through molecular beam epitaxy (MBE) technique, a high quality Au (111) thin film was firstly fabricated in ultra-high vacuum (UHV) conditions, and used as support for chemical SAMs functionalization with 1,4-dithiothreitol (DTT) spacers. On the formed hybrid surface/linker structures, we employed Dip Pen Nanolithography (DPN) for patterning various templates of Cr^{3+} and Co^{2+} metallic ion species. Coated AFM tips with metallic molecular inks were used to fabricate different paths on the Au substrate, offering a unique functional design complexity. By varying the tip speed and/or dwell time, micro-nano-scale templates of both species were patterned in the form of square, double-square, triangle and lines. A full control of molecular ink transport mechanisms during the drawing process was assured, succeeding the writing of Cr^{3+} and Co^{2+} metallic ions on Au film substrate. Surface topology analyzed by Lateral Force Microscopy demonstrated the chemical contrast of patterned species, being a clear indicative of DPN tracing paths. Molecular recognition of both Cr^{3+} and Co^{2+} metallic ions has been made by potentio-electrochemical impedance spectroscopy (PEIS) measurements. The Nyquist plots were compared and the equivalent circuits obtained in both conformations (Cr^{3+}/DTT/Au, Co^{2+}/DTT/Au) were discussed in the light of experimental parameters.

1. Introduction

As a continuous tailoring of current electronic architectures [1–3], nanoparticle devices incorporating transition elements of d-block were intensively investigated in the last years due to their tremendous potential in various technological applications. Their scientific importance, in particular in the fields of photovoltaics [4], bio-nanotechnology [5] or integrated molecular electronics [6], was already demonstrated and certified as an emerging route to further miniaturization. Beside the possible response to nano-electronics of the future, molecular electronics allows to assemble a large number of nanoscale structures on the same substrate, which finnaly lead to the fabrication of new devices and/or circuit architectures. As such, the main goal is focused nowadays to the development of new technologies that incorporate molecular – scale elements.

Towards molecular electronics, biological and biomedical applications implying SAM functionalization [7] of molecular systems are of great interest, in particular for the development of sensor platforms based on molecular recognition engineering [8–10]. The final aim is to provide both switching and sensing characteristics at single particle scale [11]. Moreover, the possibility to assembly a large palette of nanoscale subjects will open new paths to circuit architectures and electronic devices [12–15]. The drawback in all cases, whatever the application, arrives from the method used for the fabrication at reduced scale [16,17]. The technological limits are drastically affected depending on the chosen substrate, linker, or the anchored molecular species. If we strictly refer to the design of a powerful miniaturized sensing platform, which is the case of this work, then the substrate quality and the fabrication conditions are very important in order to obtain, a defect-free Au thin film. A clean environment, such as ultra-high vacuum (UHV) is vital to minimize the incorporation of unintentional impurities, avoiding to affect the surface morphology and the lithographic process.

In this perspective, we present here a fabrication chain of a miniaturized electrochemical sensor platform for detection of Cr^{3+}

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and Co^{2+} metallic ions, from the Au(111) thin film manufacturing, chemical SAMs functionalization, to Dip Pen Nanolithography (DPN) ink patterning of metallic ion species.

Molecular beam epitaxy (MBE) deposition technique was firstly employed to fabricate a high quality Au(111) thin film. By using UHV conditions we have minimized the incorporation of unintentional impurities, leading to large atomically flat terraces. The deposited Au film was used as working electrode in the electrochemical impedance analysis.

In a second step, a chemical protocol for SAMs functionalization of 1,4-dithiothreitol (DTT) has been developed. The formed hybrid surface/linker structures were then employed to attach by DPN approach [18] the Cr^{3+} and Co^{2+} molecular species. DTT linker, adsorbed on Au substrate, has been previously used by the group of Mandler et al. [19] to investigate the heterogeneous binding of Mg^{2+}, Ca^{2+} and Sr^{2+} metal ions. In the same register, DTT- modified Au thin films were reported by Magura et al. [20], while the group of Vela [21] used SAMs of DTT on Au surface for phospholipid bilayer formation.

However, our particular feature in comparison with the above mentioned investigations is the use of high resolution DPN technique, which allowed us to deposit the Cr^{3+} and Co^{2+} metallic ions on the same fabricated Au thin film, offering a unique functional design complexity. Through the coated AFM tip, we were able to directly place at a defined location the Cr^{3+} and Co^{2+} species on the previous functionalized Au thin film. The capillary forces enabled a sustained and perpetual flow of both molecular inks, while the attraction and repulsion forces which appeared at interface solute/substrate has afforded the self – assembly processes [22]. During the patterning process, the working parameters of AFM tip were carefully controlled in order to establish the high resolution of the Au film and even of the lithographic protocol itself. Tip immersion time, writing speed or scanning speed, corroborated with the diffusion characteristics of novel formatted molecular inks were critical parameters that assured the DPN patterning process.

The topological characterization of fabricated Au thin film was firstly made by Scanning Tunnelling Microscopy (STM) in UHV environment, without contaminating the surface. After DPN depositions, high-performance AFM imaging was employed after each DPN pattern deposition.

Finnaly, a molecular recognition analysis was performed through impedance spectroscopy measurements [23]. Potentiostatic Electrochemical Impedance Spectroscopy (PEIS) method was used in particular, emphasising the benefits of using the electrochemical approaches in determination of biological and environmental analysis [24–30]. The Nyquist plots were compared and the equivalent circuits were obtained in both conformations (Cr^{3+}/DTT/Au, Co^{2+}/DTT/Au).

2. Materials and methods

2.1. Au (111) thin film formation

The metallic substrate used in this experiment was a Au/Si(111) thin film deposited in UHV environment (~10^{-10} mbar) by MBE technique using a Lab - 10 MBE, Omicron GmbH system. A 7×7 reconstructed Si(111) (p-type, resistivity 0.01 Ω cm) substrate was obtained through a well-established thermal treatment [31]. The quality of the reconstructed Si(111) surface was demonstrated in the early works of our group [32,33]. Gold pellets (99.9995% purity, Premion, Alfa, Germany) were evaporated from an effusion cell on a substrate heated at 580 °C, with an evaporation rate of 1.6 nm/min and a deposition time of 1 h. The film deposition was followed by a 1 h annealing treatment at the deposition temperature of 580 °C and a controlled decrease of the substrate temperature with 13 °C/min, until it reached room temperature. The thickness of the film was 95 nm and determined by using a beam flux monitor attached to the deposition manipulator. Scanning tunnelling microscopy (STM) images of the Au film were obtained using an UHV, variable temperature STM (VT-STM by Omicron GmbH, Germany) and analyzed through SPIP (Scanning Probe Image Processor – SPIP, version 6.0.10, Image Metrology ApS, Lyngby, Denmark) software package.

2.2. Self-assembled monolayers (SAMs) of 1,4-dithiothreitol(DTT)

(i) The DTT compound has been achieved as powder from Sigma Aldrich and used without any complementary purification procedures. It was prepared as ethanol solution following the concentration of 0.5 mg/mL. The resulting mixture was stirred magnetically for 10 min. Immediately after formation, the solution was light screened and deposited at a temperature of 4 °C.

ii) (A carefully cleaning procedure of Au substrate was performed, being repeatedly washed with ethanol and deionized water (Millipore Gradient) and dried under nitrogen flow. Then, it was immersed in the above obtained ethanol solution of DTT for 24 h at room temperature. After extraction from solution, the substrate was washed again following the same protocol.

2.3. Molecular inks

Two solutions containing Cr^{3+} and Co^{2+} metallic ions were prepared as molecular inks for DPN patterning. $Cr(NO_3)_3 \bullet 9H_2O$ (0.48 g) and $CoCl_2 \cdot 4H_2O$ (0.35 g) compounds were firstly weighed, then 2 ml of deionized water were added, obtaining a concentration of 0.6 M for the both solutions. The formed solutions were stirred magnetically 10 min and immediately used for DPN molecular attachment to DTT - SAMs linkers previously attached.

2.4. Dip Pen Nanolithography

DPN 5000 equipment of NanoInk USA, has been used for micro-nano-lithography templates. The system was protected by a E-chamber glove box connected to a humidity NanoScriptor controller that was set to relative humidity (RH) of 53%. The experiments were performed at room temperature of 23 °C. High resolution contact golden silicon cantilevers, namely CSG30 series, were purchased from NT-MDT and used as AFM – dip pen writer. Their compatible specifications (cantilever - length 190 μm, width 30 μm, thickness 1.5 μm, resonant frequency in the range 24–76 kHz, force constant in the range 0.13–2 N/m) with DPN technology assured both functionality and control during the patterning process. Contact mode operation was employed, while for the surface topological imaging we used Lateral Force Microscopy (LFM) technique.

As a preparation procedure for writing process, the AFM tips were initially cleaned in piranha solution, rinsed several times with deionized water and dried under nitrogen stream. After removal, they were fully immersed in molecular solutions for 60 s, and then gently dried under nitrogen. Immediately, the probes were mounted in the clip holders and installed on the DPN instrument.

2.5. Potentio electrochemical impedance spectroscopy (PEIS)

We used Potentiostatic Electrochemical Impedance Spectroscopy method, which basically apply a constant potential E and perform impedance through potentiostatic mode to a frequency