



Electroactive copper(II) bimetallic self-assembled multilayers on Si(100)

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ABSTRACT

Silicon (100) surfaces were modified by reacting 4-aminopyridine and Si–Cl bond. These surfaces were further used for tethering copper bimetallic complexes and growing monolayers and multilayers by changing the axial position via Lewis acid–base reactions. In this way, coordination chemistry approach can be used as building blocks for controlling the design of functional surfaces. Furthermore, the outcomes of the several characterization techniques indicate that the complex is spatially oriented suggesting that this simple strategy allows the preparation of three dimensional molecular structures exhibiting spatial order. The structures on surface show interesting electroactive behaviors leading two cathodic signals, that can be related to Cu(II)/Cu(I) and Cu(I)/Cu(0) electro-reduction species (signals at -0.15 V and -0.50 V) and one peak in the anodic region (-0.15 V) ascribed to the Cu(0)/Cu(II) electro-oxidation reaction, using an Ag/AgCl saturated electrode and platinum wire as reference and counter electrodes, respectively.

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1. Introduction

The employment of metallic complexes functioning as building blocks via metallic atoms or ions is currently an area of great interest, because such structural arrays promote the assembly and dictate the structural features of the supramolecular products. Considerable success has already been achieved by using bimetallic bonding and polymetallic chain-like entities. These units are assembled together through axial or equatorial linker molecules, for example, amines or dicarboxylic acids, and show some properties of the multinuclear coordination compounds including their redox activity and switched electronic communication from one metal center to the other by metal–metal bond formation. Hence, the results obtained of compounds containing such metallic entities in the solid state could open a path for the construction of new molecular devices including molecular wires and interesting novel materials incorporating multi-metal units. [1–10]

The enquiry of how to translate this chemistry to the silicon surface is the motivation of this research and shows the employment of copper(II) acetate as versatile and stable model of bimetallic coordination motifs. We surmise that these compounds are useful structural units for covalently-attached monolayers and self-assembled multilayers (SAMs) on Si(100) surfaces supported by the utilization

of bipyridine as linker molecules between copper centers that could generate multilayers of different thicknesses, as shown in Scheme 1.

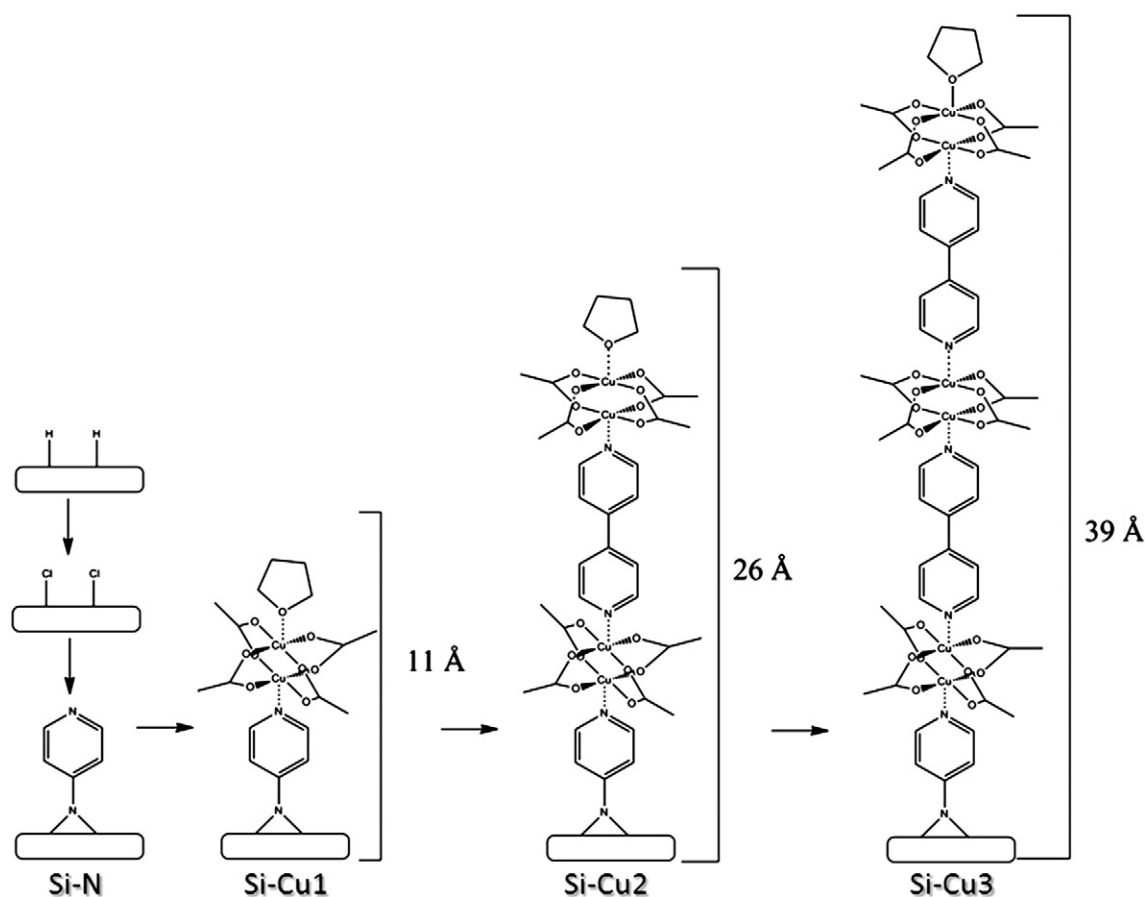
The nature of the anchoring atom and the bond formed between the molecule and the surface is important in the attachment of copper bimetallic complexes to silicon and is also one of the main challenges in the implementation of molecular/silicon architectures. In the case of Si–C, Si–O and Si–N linkages that exhibit strong bonding situation require grafting reaction conditions being relatively more aggressive compared to the functionalization when considering the self-assembly of thiol molecules on gold. In our case, the pathway studied was the reaction of 4-aminopyridine with Si–Cl-terminated surfaces leading to the formation of Si–N bond. It is generally accepted that the ability of silicon atom to act as an electron acceptor in the interaction of molecules based on Group V elements (for instance, ammonia) and is further important in controlling the overall reaction chemistry and the electron transfer. [11–15]

The integration of such cluster units onto silicon surfaces is a necessary step toward the development of novel electrically addressable and switchable functional devices. This kind of hybrid semiconductor-molecule structures have already been used to prove the conservation of the physicochemical activity of some molecular species once covalently immobilized on semiconducting surfaces. Therefore, this hybrid approach is promising for combining the advantages of semiconductor technology (doping, processing) and the large flexibility in molecular structure designing. [16–35]

In addition, since metallic copper exhibits versatile conducting material properties, the quest for aluminum replacement by copper is of

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Scheme 1. Representation depicting Si(100) modification surface with copper(II) acetate growing by layer-by-layer construction. The calculated height as obtained from MM2 force field calculations using ChemDraw3D version 12.

outstanding importance for the manufacturing of microelectronic devices due to the better conductivity and superior resistance to electromigration and stress migration [36–38]. Also, the recent stringent decreasing dimensions in electronic devices, demands alternative copper sources as feedstock for fabrication at this scale. In this frame, we report on the copper(II) bimetallic self-assembled multilayers on Si(100), their characterization by X-ray photoelectron spectroscopy (XPS), contact angle measurements (CA), atomic force microscopy (AFM), X-ray reflectivity (XRR) and the electroactive behavior studies through cyclic voltammetry (CV).

2. Materials and methods

2.1. General information

All the solvents (Sigma–Aldrich) were purified and dried according to conventional procedures and freshly distilled prior to use. The compounds 4-aminopyridine (Aldrich), 4,4'-bipyridine (Sigma–Aldrich) and copper(II) acetate (Merk Co.) were used as received. The substrates were *n*-type flat silicon (100) from Ultrasil Corporation (0.001–0.002 Ω/cm).

2.2. H-terminated Si(100) surface preparation. (Si–H)

A piece of silicon (100) wafer (1 cm²) was oxidized at high frequency for 5 min in a Harrick plasma cleaner PDC-32G, and etched with an HF solution (1%) for 3 min.

2.3. Cl-terminated Si(100) surface preparation (Si–Cl)

Si–H wafer was chlorinated in a home-made chlorine gas chamber at 80 °C for 30 min [39]. The microreactor system includes a test tube for each sample. The excess of chlorine gas was eliminated with a N₂ gas flux for 30 min.

2.4. Monolayer preparation of 4-aminopyridine (Si–N)

In the same microreactor system a piece **Si–Cl** wafer was immersed in a 4-aminopyridine solution (1 mM in THF) under nitrogen atmosphere. The reaction mixture was heated for 2 h at 60 °C, and then the functionalized wafer was washed several times with THF in an ultrasonic bath for 10 min.

2.5. Self-assembly monolayer of Si(100)-4-aminopyridine-copper(II) acetate

The wafer with **Si–N** was immersed in a copper(II) acetate solution (1 mM in THF) for 50 h. Then, the sample was washed twice in an ultrasonic bath for 10 min (**Si–Cu1**).

For multilayer formation, the **Si–Cu1** grafted sample was dipped in a solution of 4,4'-bipyridine (1 mM, THF) for 50 h at room temperature, and again 50 h in the copper(II) acetate solution (1 mM in THF) to obtain sample **Si–Cu2**. This process was repeated in order to prepare sample **Si–Cu3**. Between every new layer formation, samples were washed two times with dry THF in ultrasonic bath for 10 min.

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