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SHORT COMMUNICATION

Fabrication of Submicron-Sized Copper Structures on Pre-Patterned Self-Assembled Monolayer and Langmuir-Blodgett Films

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Abstract−The fabrication of a metal microstructure on pre-patterned organic templates, prepared using SAM and LB techniques is described. The OTS derivatized substrate was oxidized by AFM anodic oxidation at the threshold voltage. Site-selective copper structure was then fabricated on the locally modified monolayer based on pre-designed patterns. The sequential adsorption-reduction of copper ion was carried out, leading to improved metal coverage and a reduction in defects.

Key words: AFM Anodic Oxidation, Copper, Self-assembled Monolayer, Langmuir-Blodgett Film

INTRODUCTION

In recent years, numerous studies have been reported on the construction of site-defined metal structures on pre-patterned surfaces, which may have applications in future generations of microelectronics, miniaturized sensors, and micro-electromechanical systems [Zhang et al., 2004].

Site-defined patterns can be formed by printing organics using microcontact printing [Lee et al., 2003] or by the decomposition of organic films using e-beam, photolithography and scanning probe lithography (SPL) [Maoz et al., 1999]. A critical requirement for the use of patterned SAMs in advanced applications is the ability to produce them in the most economical and practical manner [Lee and Sung, 2004]. Microcontact printing has limitations with respect to patterning in a nanometer size, and decreasing the wavelength of the light source for reducing pattern size for photolithography entails a high cost, whereas, in the case of SPL, submicron- or nano-sized patterns can be easily prepared at a low cost. Therefore, among the available patterning methods, the SPL technique (*i.e.*, AFM anodic oxidation) is the most practical method for producing submicron-sized metal structures, because a site-defined nanostructure with spatial resolution can be formed repeatedly.

The desired patterns are generated on a silicon wafer, based on the site-selective self-assembly of metal particles. Patterns are formed by constructive nanolithography using a conductive Ti-Pt coated tip. Chemical information is inscribed in a nondestructive manner on the top surface of the highly ordered organosilane monolayer [Maoz et al., 2000]. Alteration in the morphology and height of the organosilane monolayer is negligible, but functional groups of the organic monolayer are changed into another form.

The site-selective chemical growth of a noble metal, such as silver and gold, has been studied by Maoz and co-workers [1999, 2002]. Their study provided conclusive evidence that the site-defined self-assembly of metal ions, both chemically and nanoelectrochemically, was possible on patterned monolayer templates with sulfur-containing outer groups. To date, acceptable results for a copper nanostructure, however, have been rarely reported, due to its diffusive property. Herein, we report on the preparation of a continuous copper structure at a site-selective area, which can be used as a nano-metal line for electronic devices or sensing devices.

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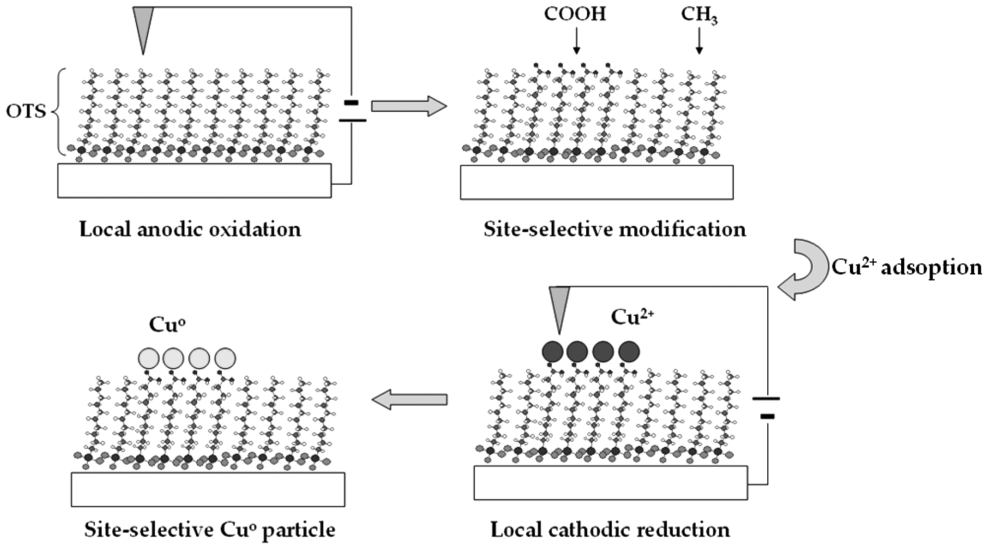
EXPERIMENTAL

OTS ($C_{18}H_{37}SiCl_3$, Aldrich), as a resist material, was dissolved in anhydrous toluene. Copper solution was prepared with 0.6 M $CuSO_4 \cdot 5H_2O$, 0.5 M H_2SO_4 and 0.025 M thiourea. OTS was deposited on a B-doped *p*-type Si(100) wafer. Before using the Si wafer, it was treated with piranha solution ($H_2SO_4 : H_2O_2 = 7 : 3$ v/v) at 130 °C for 60 min, followed by sequentially rinsing with DI water, acetone and ethanol, and then dried in a stream of N_2. For the preparation of OTS SAM, the cleaned Si substrates were then immersed in a solution of 5 mM OTS for 48 hr at room temperature. This process was accomplished in a sealed vial in order to minimize water contact chances in the air. The OTS deposited substrate was treated by sonication in pure toluene, acetone, and ethanol, to remove excess OTS molecules. For the OTS LB film, a 2 mM OTS solution was layered on the water surface on LB-through under conditions of 293 K and pH 5.8. The OTS monolayer was transferred to the substrate by an upward drawing method at a surface pressure of 30 nN/m, and then, strongly immobilized on the solid substrate by the Si-OH groups [Kojio et al., 2000]. OTS monolayers deposited on Si wafers were stored in a glove box filled with N_2 gas.

A schematic diagram for the site-defined modification is shown in Scheme 1. Pattern inscription was carried out by pre-controlled, automated AFM oxidation. The substrate was placed in a non-conductive sample-holder. A silicon cantilever coated with Ti-Pt (CSC12 series, MikroMasch, Estonia) was used. The force constant (k_c) and resonance frequency (fo) were 0.03 N/m and 10 kHz, respectively. AFM patterning was performed under ambient conditions (23-25 °C and 60-70% relative humidity). The threshold voltage (V_o) was measured by the extent of oxidation of the surface with the applied voltage. The copper solution added dropwise onto the modified region for 5 min [Azzaroni et al., 2003]. An inverse bias was applied to



Scheme 1. Procedure used in the site-defined self-assembly of metal particles on a pre-patterned organosilane template.

achieve the reduction of Cu^{2+}.

This process was performed in a humidity controlled box equipped with an atomic force microscope (METRIS-2000, Burleigh Instrument, USA) and an additional power supply (WPG-100 potentiostat, Wonatech, Korea). The thickness and contact angle of the OTS monolayer were measured by the ellipsometry (L116B, Gaertner, USA) and a contact angle measuring system (DSA10, KRUSS), respectively.

RESULTS AND DISCUSSION

The uniformity of the OTS monolayer was confirmed by AFM (Dimension-3100 SPM), ellipsometry and contact angle analysis. As shown in Fig. 1, the AFM images of OTS SAM and LB film obtained by the tapping mode showed a nearly close-packed structure, and the RMS roughness was 0.842 and 0.638, respectively. The water contact angle was increased from 11.8° to 107.0° (for SAM) and 107.4° (for LB films) due to the increase in hydrophobicity. A very small contact angle (11.8°) was observed for the piranha-treated bare Si substrates because the surface was dominated by OH groups. The high hydrophobicity due to the methyl groups in the OTS, prevents the aqueous drops from spreading over the substrate. The monolayer thickness prepared by using both the SAM and LB techniques was 2.2-2.5 nm, in good agreement with those reported by other investigators [Styrkas et al., 1999]. The LB film showed a more close-packed monolayer than that produced by the SAM technique in our results. And, thus, the LB technique might be more effective for preparing a monolayer template.

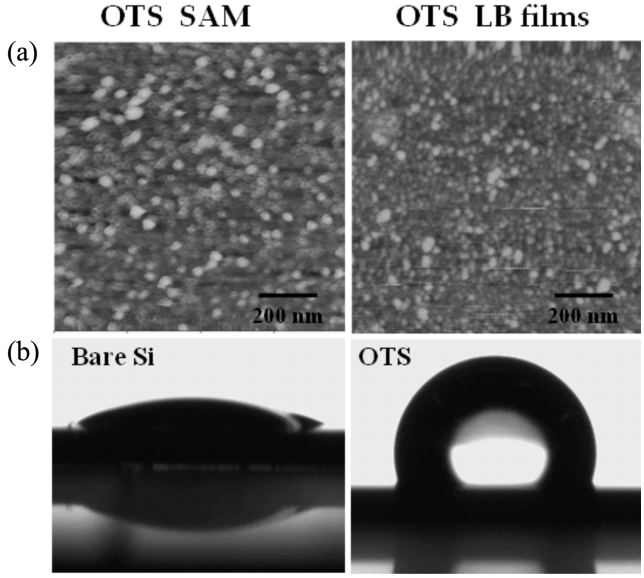


Fig. 1. (a) AFM images of OTS SAM and LB films obtained by the tapping mode, and (b) contact angle after the deposition of an OTS monolayer.

The piranha-treatment transformed the surface silicon oxide into silanol groups (ca. 5 per nm^2) [Ulman, 1991]. This concentration of OH groups is approximately equivalent to the number of alkyl chains that can be fully packed per nm^2. It should be noted that a densely packed and defect-free monolayer is essential for high coverage by the tip-induced electrochemical reduction of surface-bound metal ions.

The terminal groups ($-CH_3$) of the organic resist were converted to carboxyl groups (-COOH) by AFM local anodic oxidation, as shown in Scheme 1. At the point of the threshold voltage, no topographic image appeared, while a lateral image appeared as shown in Fig. 2. The height of the pattern obtained was almost the same as that obtained before anodic oxidation. However, the corresponding lateral image showed bright areas corresponding to the presence of polar head groups. This implied that surface composition had changed [Choi et al., 2004]. LFM measures lateral deflections of cantilevers that arise from a change in surface friction which can arise from inhomogeneity in the surface material, as well as from a change in the slope, even in the same material [Jung et al., 2002].

These locally modified monolayers could then be used to induce the site-selective self-assembly of different materials (organic, metal, and semiconductor), based on a pre-designed pattern. The metal ions adsorbed on the pre-patterned templates are reduced to metal

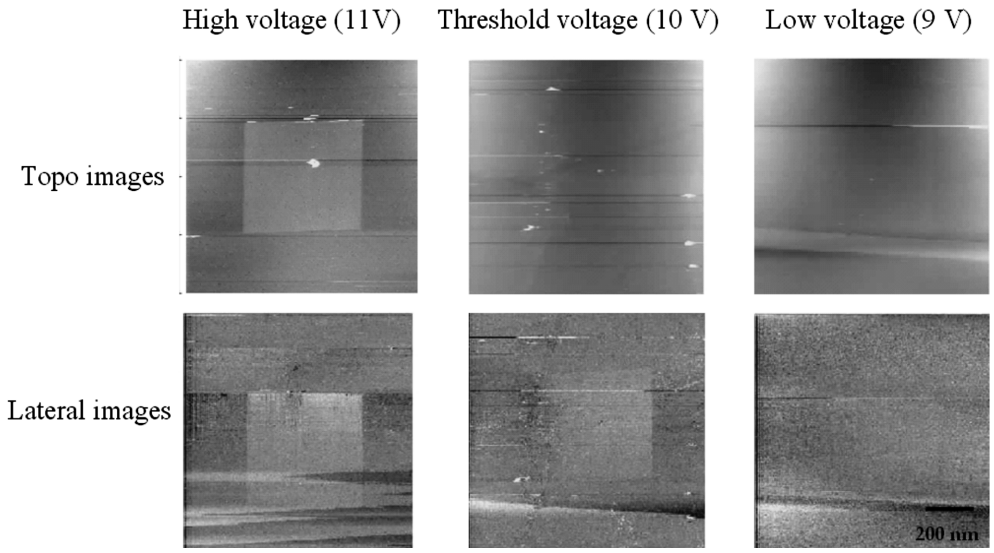


Fig. 2. Topography and lateral images at 9 to 11 V.

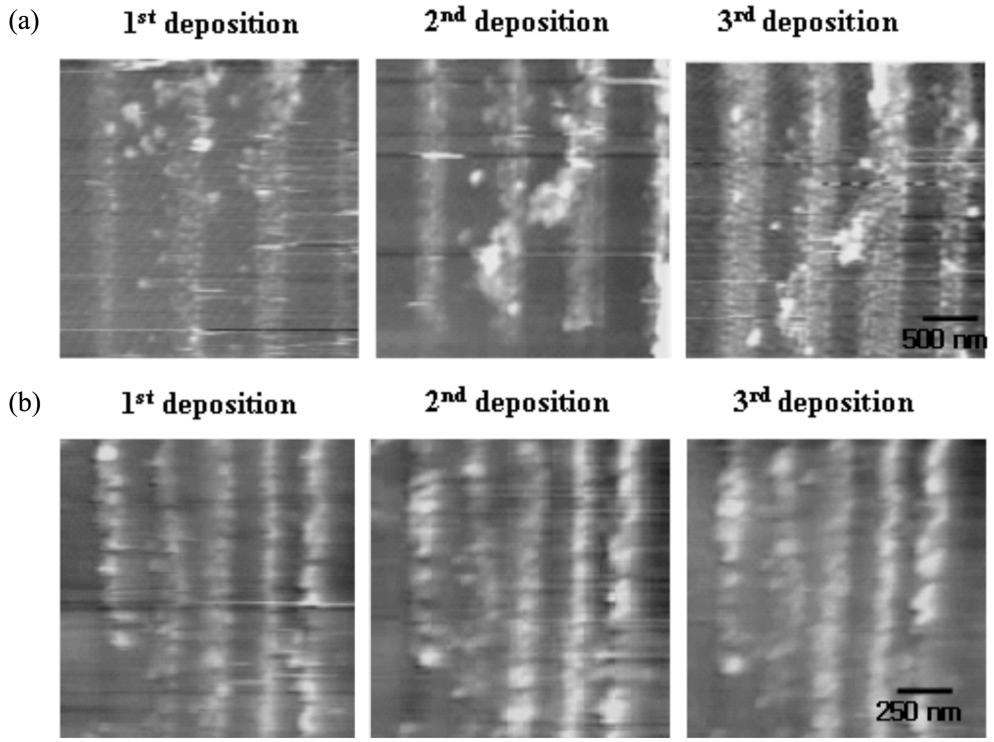


Fig. 3. AFM images of copper deposition with periodic lines: (a) copper lines formed on a pre-patterned OTS SAM, (b) copper lines formed on a pre-patterned OTS LB film.

nanoparticles by the inverse process (tip positive and surface negative) of AFM anodic oxidation. The formation of copper particles was achieved by the electrochemical reduction of Cu ions adsorbed to the OTS SAM or LB film surface (cathode) and oxidation of the water at the tip (anode).

AFM images of metal particles, generated by the tip-induced and electrochemical reduction of COOH-bound copper ions, are shown in Fig. 3. As shown in Fig. 3a, four lines with copper could be fabricated on a pre-patterned OTS SAM, and the sequential adsorption-reduction of copper ion was repeated at the same position. The line width of the copper line was approximately 360 nm, and the height was approximately 4 nm, 7 nm and 10 nm respectively from left to right. The thickness of the deposited copper continues to increase as the repetitive procedure is increased by further deposition. The height or thickness of the copper lines can be controlled by number of sequential adsorption-reduction repetitions, which can improve the coverage of copper lines. The nucleation and kinetics of growth of copper crystallites was accomplished by the reduction

of copper ions bound within the domains modified by the AFM tip. The size of the Cu-pattern was adjusted by controlling the pattern magnification and pre-patterning size.

The same process used for OTS SAM was applied to OTS LB films. Fig. 4b shows a 5-line copper structure, which was formed on a pre-patterned OTS LB film. The line width decreased down to 180 nm due to the densely packed monolayer prepared by the LB technique. The metallic grains were formed by the reduction of surface bound copper ions under the tip.

In summary, an OTS monolayer prepared by two methods (LB and SAM) was successfully used as a resist for selective modification. We were also able to fabricate site-defined copper structures in a submicron size on a pre-patterned monolayer. The high spatial precision offered by AFM lithography is a clear advantage for the fabrication of nanoparticle-based devices. The microfabrication of a monolayer has attracted tremendous attention because patterned monolayers can be used as resists for pattern transfer and as templates to pattern organic materials and bio materials as well as metals [Liu et al., 2000].

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