

## Site-Defined Micropatterning Using Atomic Force Microscopic Lithography

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**Abstract.** Site-defined metal microstructure was fabricated on the pre-designed organic template *via* a surface modification of Si(100) wafer. Site-defined substrate with octadecyltrichlorosilane (OTS) was oxidized by AFM (Atomic Force Microscopy) at threshold voltage ( $V_0$ ). Terminal group ( $-\text{CH}_3$ ) of OTS was changed into carboxyl group ( $-\text{COOH}$ ). Then, locally modified monolayer surface was used to induce the site-selective self-assembly of different materials (organic, metal, and semiconductor), according to the predefined patterns. The target metal selected is copper ions for the feasibility examination of conductive metal line fabrication

### Introduction

Recent advances in supramolecular chemistry have made possible the fabrication of a variety of nanoscopic entities such as metal and semiconductor quantum particles, organized mono- and multi-layers of organic molecules, and various hybrid assemblies containing both organic and inorganic components [1]. The objective of this research is to develop a basic device of electronic circuit components *via* a nano-sized metal growth using AFM lithography [2]. Desired patterns are generated on a silicon wafer using a bottom-up approach, based on the site-selective self-assembly of metal particles on a pre-designed organic template. The patterns are laterally defined by constructive nanolithography and a novel surface patterning process using conductive AFM tip. Nanoscale chemical information is inscribed in a nondestructive manner (in the form of a localized chemical modification) on the top surface of highly ordered organosilane monolayer [3]. Copper ions show a good affinity to carboxyl ( $-\text{COOH}$ ) groups. Here we report the preparation of the site-defined deposition of copper particles, which can be used as a circuit material.

### Experimental

Octadecyltrichlorosilane ( $\text{C}_{18}\text{H}_{37}\text{SiCl}_3$ , Aldrich) was used as a resist material for anodic oxidation. Anhydrous toluene (Aldrich) was used as a solvent to dissolve OTS. Copper solution was prepared with sulfate pentahydrate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , Junsei), sulfuric acid ( $\text{H}_2\text{SO}_4$ , Junsei) and thiourea ( $\text{CH}_4\text{N}_2\text{S}$ , Sigma).  $\text{H}_2\text{O}$  was purified to above  $18 \text{ M}\Omega\text{cm}$  using an aquaMAX<sup>TM</sup>-ultra system.

OTS was deposited on the B-doped *p*-type silicon (100) wafers. Before using the Si wafer, it was treated with piranha solution ( $\text{H}_2\text{SO}_4 : \text{H}_2\text{O}_2 = 7:3 \text{ v/v}$ ) at  $130^\circ\text{C}$  for 50 min, followed by rinsing with DI water, acetone and ethanol, and then dried by  $\text{N}_2$  gas. The cleaned Si substrates were then immersed for 48 hr at room temperature in a solution of 5 mM OTS in anhydrous toluene [4]. The substrate was treated by sonication in pure toluene, acetone, and ethanol for removing excess OTS molecules. Thickness of OTS monolayer was determined by the ellipsometry measurement (L116B,

On the OTS deposited substrate, only the area contacted by the tip was modified locally by AFM anodic oxidation. 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).

A schematic diagram for the site-defined modification is shown in Fig. 1. Pattern inscription was carried out using a pre-programmed time-to-voltage signal for each point of the pattern. AFM patterning was performed under ambient conditions (23~25°C, 50~60% relative humidity). Threshold voltage ( $V_0$ ) was measured by oxidation extents of surface according to applied voltage change. Locally modified surface has an affinity to metal ion. For the  $\text{Cu}^{2+}$  adsorption, drops containing 0.6 M  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , 0.5 M  $\text{H}_2\text{SO}_4$ , and 0.025 M thiourea were placed on the modified region for 5 min [5]. For the  $\text{Cu}^{2+}$  reduction, inverse bias voltage of anodic oxidation was applied. Then the final image of copper island was obtained by the AFM.

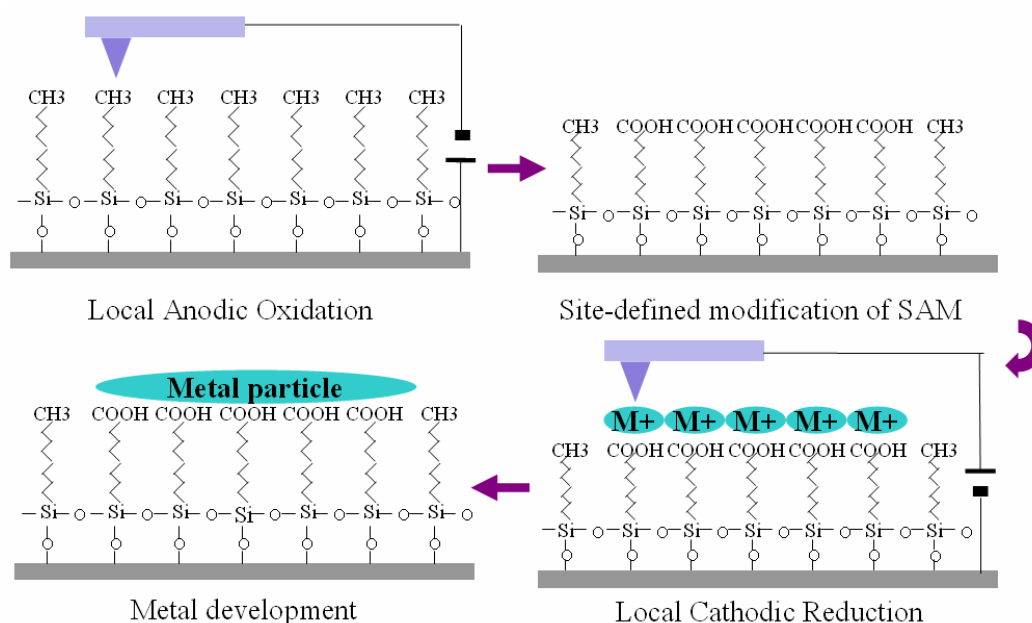


Fig. 1. Schematic diagram of the site-defined self-assembly of metal particle on the pre-patterned organosilane template

The regularity of OTS monolayer was confirmed by results of AFM (SPA-400, Seiko Instrument, Japan), ellipsometry and contact angle analysis. AFM images of OTS monolayer display near complete flatness, and water contact angle was increased from  $11.8^\circ$  to  $105.4^\circ$  due to the increase of hydrophobicity (Fig. 2). The high hydrophobicity, which is derived from methyl groups contributed by OTS, allows one to prevent the aqueous drops from spreading over the substrate. Monolayer thickness is 2.2 nm, while reported thickness of OTS is varied from 1.6 to 2.5 nm [6].

According to Carim *et al.* [7], the piranha solution treatment transforms the surface oxide into silanol group (*ca.*, 5 per nm<sup>2</sup>). This concentration of OH groups is approximately equivalent to the number of alkyl chains that can be fully packed in nm<sup>2</sup>. It should be noted that densely packed and defect-free self-assembled monolayer is an essential part for high coverage by tip-induced electrochemical reduction of the surface-bound metal ion.

By AFM local anodic oxidation, terminal groups ( $-\text{CH}_3$ ) of organic resist changed into carboxyl groups ( $-\text{COOH}$ ) as shown in Fig.1. At the point of the threshold voltage, no topographic image appears, while lateral image appears. This implied surface composition was changed. These locally modified monolayer surface then was used to induce site-selective self-assembly of number of

different materials (organic, metal, and semiconductor), according to a pre-defined pattern. Absorbed metal ions on the pre-patterned organosilane templates are reduced to metal nanoparticles by the inverse process of the AFM anodic oxidation.

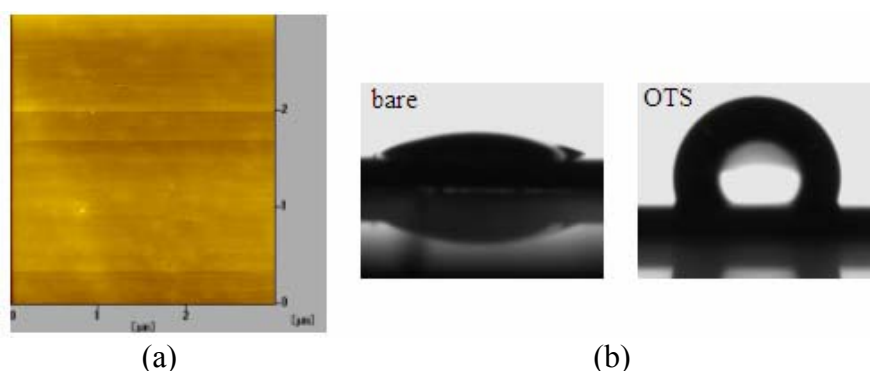


Fig. 2. Characterizations of OTS monolayer a) AFM topography image (image size is  $3\text{ }\mu\text{m}\times 3\text{ }\mu\text{m}$ ) b) water contact angle analysis

Site-selective chemical growth of noble metal such as silver and gold had been studied by Maoz *et al.* [1,8]. They provide a conclusive evidence for the possibility of site-defined self-assembly of silver metal ion both chemically and nanoelectrochemically on patterned monolayer templates with sulfur-containing outer groups. In this study, selective adsorption capability of carboxyl functional group to copper ions was applied as a target metal.

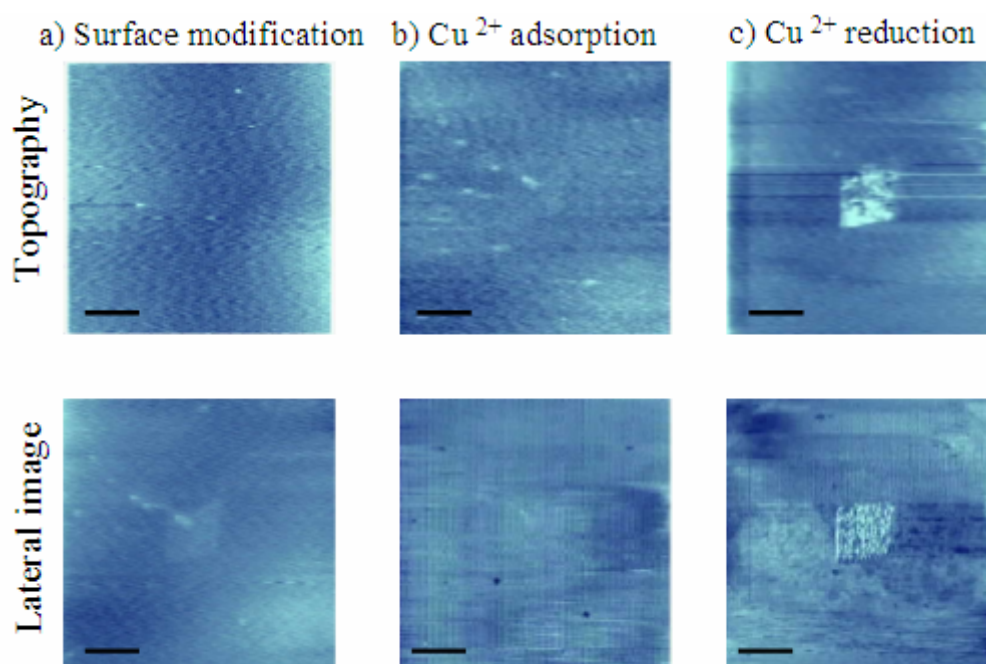


Fig. 3. Contact-mode AFM images of copper nanoparticles generated by tip-induced electrochemical patterning (upper ones are topographic images and lower ones are lateral images, in all images, 1 bar= $5.4\text{ }\mu\text{m}$ ). a) locally modified SAM by AFM anodic oxidation, b) copper ion absorption on the prepatterned monolayer template, and c) copper ion reduction by inverse bias of anodic oxidation

Fig. 3 shows images taken by AFM at each step after surface modification, copper ion adsorption and reduction by AFM tip. Results show that copper microstructure was fabricated on the pre-patterned shape. As shown in Fig. 4, copper island was formed on the square shaped area. The

size of copper-deposited area is  $5.4\ \mu\text{m} \times 5.4\ \mu\text{m}$ , and the height is approximately 4 nm. The average surface roughness of copper island was measured by the variance of the line ( $R_a$ ).

$$R_a = \frac{1}{N} \sum_i^N |Z_i - Z_{avg}|$$

The  $R_a$  values of copper-free and copper-deposited area are about 0.40 and 2.58 nm, respectively. It is noted that the surface roughness was changed by the reduction of copper. The height or thickness of copper island was controlled by the repeated adsorption and reduction process, which consisted of additional adsorption and reduction process and improved the coverage and thickness of copper structure. The area size of Cu-pattern was adjusted by controlling the pattern magnification (X1~X20) and the pre-patterning size.

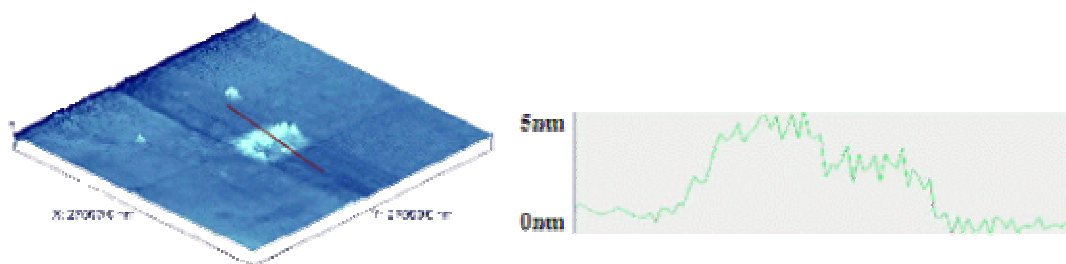


Fig. 4. 3D topographic image of site-defined copper island (pattern size is  $5.4\ \mu\text{m} \times 5.4\ \mu\text{m}$  and height is approximately 4 nm)

The size of patterns should be smaller than these reported results for future applications, particularly in the field of nanoelectronics. For such applications, the ability to assemble complex functional structures with precisely defined nanoscale dimensions is critical. Further research on miniaturizing and increasing the complexity of the site-defined metal patterns are currently in progress.

## Conclusions

Conventional wet chemical reduction can be used to deposit macroscopic surface layers, whereas site-defined reduction can be achieved from the micro- down to nanometer size due to the sharpness of AFM tip. In summary, experimental results reported here provide a clear evidence for the feasibility of site-defined self-assembled nano- and/or micro-patterning. This method can be a basis for the development of surface self-assembled electronic circuits of nanometer dimensions. Spatially defined metal structure on organic monolayer templates can be manufactured by precise control of experimental conditions, such as the composition of monolayer template and target metal ion.

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