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Selective deposition of gold nanoparticles on SiO₂/Si nanowire

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Abstract

We demonstrate selective deposition of citrate-passivated gold nanoparticles onto silicon dioxide patterns. Further, selective deposition of gold nanoparticles on the oxides, generated by scanning probe lithography (SPL), surface of silicon nanowire is achieved. Main methodology is to form H-terminated silicon surface and hydroxyl group on SiO₂ sample surface, then link amino function group only on SiO₂ surface by self-assembly mechanism. *N*-(2-Aminoethyl)-3-aminopropyl-trimethoxysilane (AEAPTMS) pretreated sample was immersed in the gold colloidal solution such that the NH₂ group become protonated forming NH³⁺. The NH³⁺ groups provide a negative charge bindable environment for citrate-passivated gold nanoparticles. Impact on different AEAPTMS dilute solvents is also investigated for the performance of selective deposition of gold nanoparticles. It is found that H-terminated sample surface effectively eliminated nonspecific reaction during silanization such that microscale or nanoscale selective deposition of gold nanoparticles is obtainable. The proposed method can be applied in both nanoelectronics and nanobiosensors. © 2005 Elsevier B.V. All rights reserved.

Keywords: Gold nanoparticles; Scanning probe lithography; Self-assembly; AEAPTMS

1. Introduction

In the past decade, one of the major needs in nanotechnology is searching techniques for assembling nanoparticles into architectures on a solid surface; Patterning of the building blocks like

nanoparticles into special nanostructures provides the basis for applications such as photonic devices [1,2] and sensors [3] and electronic devices [4]. So far, many low-dimensional assemblies of colloidal nanoparticles techniques have been examined. Cui et al. [4] report that assemble nanoparticles effectively into nanostructures by capillary force; Evaporation of the solvent leads to the three-phase contact line moving slowly across the substrate, the solution–vapor interface deforms, and the

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resulting capillary force slides the nanostructure toward the thicker part of the solution and pushes the particle toward the substrate. Using this method, particles are selectively forced into the lithographically defined nano-fillister with very high efficiency. Zhang et al. [5] developed a method for fabricating arrays of Au nanostructures on a solid surface based on Dip-pen nanolithography and wet chemical etching. A 16-mercaptohexadecanoic acid (MHA)-coated tip was prepared by immersing a commercial Si_3N_4 tip. Each pattern was generated by holding the MHA-coated tip in contact with an Au surface. Thiol functionalized molecules, 2-aminoethanethiol ($\text{HS}-\text{C}_2\text{H}_4-\text{NH}_2$) (AET), were used to modify these nanopatterns. After immersing the AET-modified nanostructures into a solution of citrate-stabilized gold nanoparticles, a monolayer of Au particles localized on each of the nanopatterns. Santhanam et al. [6] proposed that uniform, close-packed monolayer and bilayer arrays of alkanethiol-coated gold nanoparticles used as “ink” for microcontact printing [7] (μCP). In the study, a uniform monolayer of the nanoparticles is self-assembled on a wafer surface and is transferred intact onto a patterned poly(dimethylsiloxane) (PDMS) stamp pad by the Langmuir–Schaefer (LS) method. After contacting the substrate with PDMS stamp, a patterned close-packed array of nanoparticles is deposited on the substrate. Zheng et al. [8] showed that the OTS self-assembled monolayer (SAM) was formed on silicon by immersing the silicon substrate in OTS solution. Localized oxidation of the OTS-covered silicon substrate was performed with a commercial AFM. The amino-terminating APTES monolayer was selectively formed on the lithographically created silicon oxide regions by soaking the substrate in APTES solution.

In this work, we demonstrate firstly selective deposition of gold nanoparticles on surface of thermal SiO_2 of a silicon sample. Then, scanning probe lithography and self-assembly techniques were adopted for realizing local deposition of gold nanoparticles on the nanoscale silicon dioxide surface by blocking on the other silicon surface with HF treatment. Different AEAPTMS dilute solvents are also investigated for better selective deposition of gold nanoparticles.

2. Experiments and results

The synthesis methodology of gold nanoparticles is based on Frens’s method [9]. A starting solution of 100 ml of 2.2 mM trisodium citrate ($\text{C}_6\text{H}_8\text{O}_7\text{Na}_3 \cdot 2\text{H}_2\text{O}$) as a reductant was heated to boil, and 40 ml of 0.815 mM HAuCl_4 ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$) was added with rapidly mixing. The solution was then heated to boil for 15 min, solution initially developed a pale yellow color and then a gray color, which changed to lavender and then transformed into red in 1–3 min. A p-type (100)-oriented bare silicon wafer with, before coating processing, standard RCA cleaning was employed and followed by 950 °C dry oxidation for 30 min; the thickness of the oxide is about 300 Å. Hydroxyl-terminal surface of SiO_2 are further modified by a silanization procedure involving *N*-(2-Aminoethyl)-3-aminopropyl-trimethoxysilane [10] (AEAPTMS), which provides a surface bearing free amine ($-\text{NH}_2$). Sample immersed in AEAPTMS dilute solution in water for 5 min, the samples were dried with N_2 and baked at 120 °C for 30 min with hotplate after samples cleaning. After aqueous amino silane modification, the amino-terminal samples were then immersed in gold nanoparticles solution for 1 h. After immersion, the samples were rinsed with DI water and dried with N_2 . This process led to the deposition of a monolayer of gold nanoparticles which repell each other due to the formation of negative citrate ions on the surface of the Au particles. Fig. 1 shows histogram of particle diameters with fairly narrow peak distribution, and the mean diameter of gold nanoparticles was about 15 nm. Inset shows the TEM image of gold nanoparticles. It was found that the gold nanoparticles were dispersed homogeneously on the surface of silicon dioxide. The particle coverage on the amino-terminated SiO_2 surface was estimated to be 1.3×10^{11} particles/cm².

Based on above experimental results, it is convinced that the citrate-passivated gold nanoparticles were dispersed homogeneously on the surface of amino-terminal samples. Consequently, another samples were prepared to justify the feasibility of selective deposition of gold nanoparticles. The process starts with the thermal oxidation. The

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