Selective deposition of gold nanoparticles on SiO$_2$/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 SiO$_2$ sample surface, then link amino function group only on SiO$_2$ surface by self-assembly mechanism. N-(2-Amino-ethyl)-3-aminopropyl-trimethoxysilane (AEAPTMS) pretreated sample was immersed in the gold colloidal solution such that the NH$_2$ group become protonated forming NH^{3+}. The NH^{3+} 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.
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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 (HS–C_2H_4–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 ($C_6H_8O_7Na_3 \cdot 2H_2O$) as a reductant was heated to boil, and 40 ml of 0.815 mM $HAuCl_4$ ($HAuCl_4 \cdot 4H_2O$) 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 (1 0 0)-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 (–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/cm^2.

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
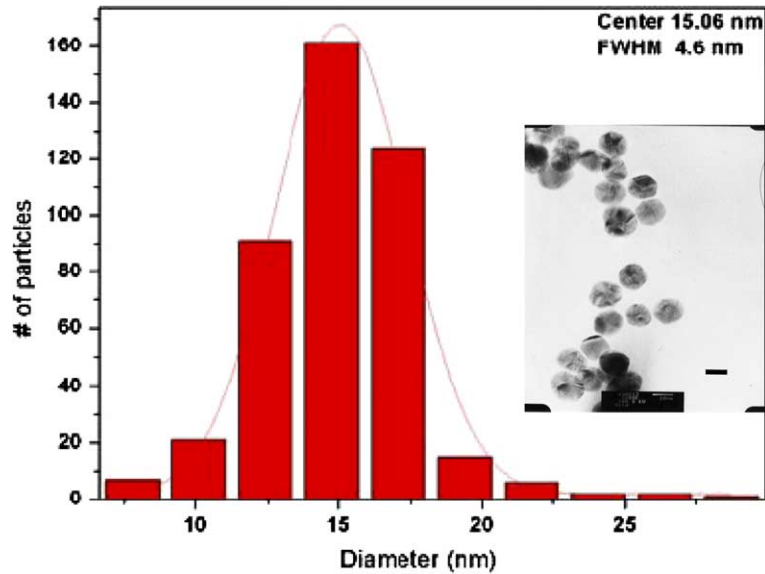
Fig. 1. (a) Histogram of gold nanoparticles with mean size measured using Image-Pro plus software from the SEM image. Inset shows TEM image of gold nanoparticles with diameter about 15 nm.

oxide patterns are patterned using standard optical lithography followed by BOE etching. The sample is cleaned with dilute HF (1%) solution to remove the native oxide on the silicon substrate. And, the hydrophilic surface is changed to hydrophobic by passivation the silicon surface with hydrogen-terminal groups. The sample was immersed into the AEAPTMS solution for 10 s to have amino alkoxysilane deposit on the oxide surface. During the immersing process, the silane only interact with hydroxyl [11] groups on the SiO_2 surface and thus form siloxane bond on the SiO_2 surface. The fabrication process sequence is illustrated in Fig. 2. Considering the hydrophobic nature of the
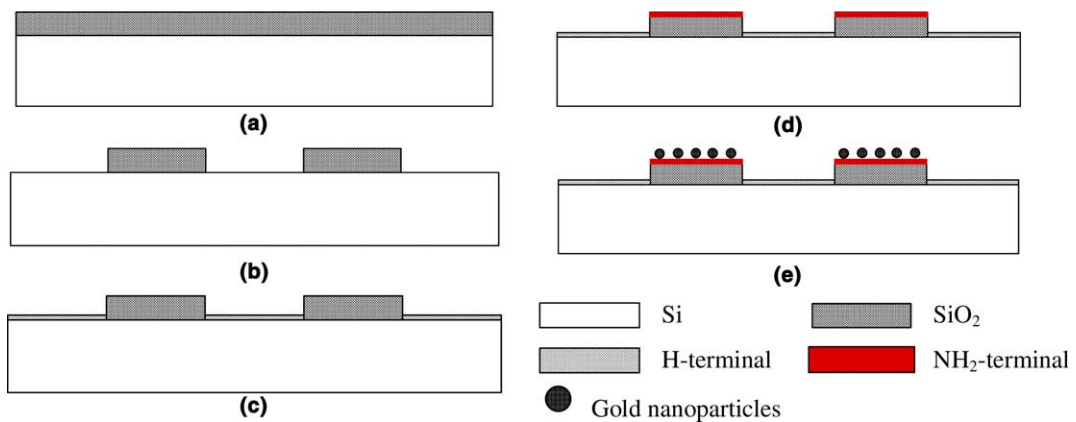

Fig. 2. Process flow of selective deposition of Au nanoparticles on thermal oxides: (a) Silicon dioxide thermally grown on silicon substrate; (b) SiO_2 patterns defined by photolithography and BOE wet-etching process; (c) HF dipping of sample for generation of H-terminated surface on silicon; (d) Functionalization on the surface of SiO_2 patterns by immersing samples in AEAPTMS water diluted solution; (e) Selective deposition of gold nanoparticles on SiO_2 patterns.

H-terminated [12] areas on the silicon substrate, it appears likely, however, that a water layer is absent or largely incomplete in these areas. Clearly, these chemical functionalities are missing on the H-terminated areas, such that amino-group only selectively appeared the SiO_2 patterns. Now, amino groups provide the surface with positive charges and also provide the electrostatic [10] interactions with citrate-passivated gold nanoparticles. In Fig. 3, the SEM images showed that regions terminated by the NH_2 groups clearly revealed a dense monolayer array of gold nanoparticles, while the H-terminal areas showed no gold nanoparticles deposition. When samples are immersed in the gold colloidal solution, the NH_2 groups become protonated forming NH^{3+}. The NH^{3+} groups are then electrostatically bindable to the negatively charged citrate-passivated gold nanoparticles, thus immobilizing them on the surface of silicon dioxide patterns. In contrast, such an assembly of gold nanoparticles is not formed on the H-terminated regions because H-terminated changed to hydroxyl group during the immobilizing, hydroxyl group lack of any strong affinity to citrate-passivated nanoparticles and easily washed away.

Impact of different AEAPTMS dilute solvents on performance of selective deposition is also investigated. Samples were immersed in both the water diluted AEAPTMS and the ethanol diluted AEAPTMS solutions. From Fig. 4(a) and (c), arrangement of gold nanoparticles shows sparser distribution in ethanol diluted AEAPTES solution. This is because that methoxy-group of amino alkoxysilane dissolved in the alcohol is easy alcoholysis [13] into ethoxy-group. This alcoholysis process slowed down the hydrolysis reaction such that amino alkoxysilane can not be easily formed on the SiO_2 surface and resulted in more dispersed deposition of gold nanoparticles. Nevertheless, Fig. 4(b) and (d) shows that gold nanoparticles still deposit on the silicon surface after a long immersion time. It is expected that the hydrolysis reaction still activated the surface of silicon and provide enough species of hydroxy groups for further binding. Based on the comparison of selective gold nanoparticles deposition experiment described, water was chosen as the AEAPTMS dilute solvent for selective deposition of Au nanoparticles in nanoscale.

Among several nanolithography techniques, scanning probe lithography is considered as one of the best lithographic techniques for fabricating nanostructures in experimental study. Scanning probe lithography uses a sharpened tip of an atomic force microscope with the highest spatial resolution. It is also well known that scanning probe lithography allows for routine generation of oxide nanopatterns on H-terminated Si samples [14]. After generation the oxide nanopatterns by SPL, the sample was immersed into TMAH wet etching solution to generated silicon nanowire (SiNW). Then, after dilute HF (1%) solution cleaning, the surface of silicon nanowire was
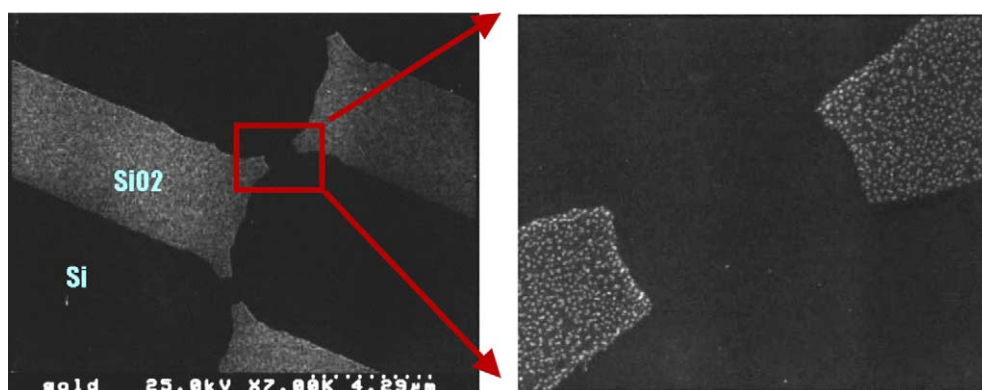

Fig. 3. The SEM images shows the selective deposition monolayer gold colloidal particles on the thermal grown SiO_2/Si surface.
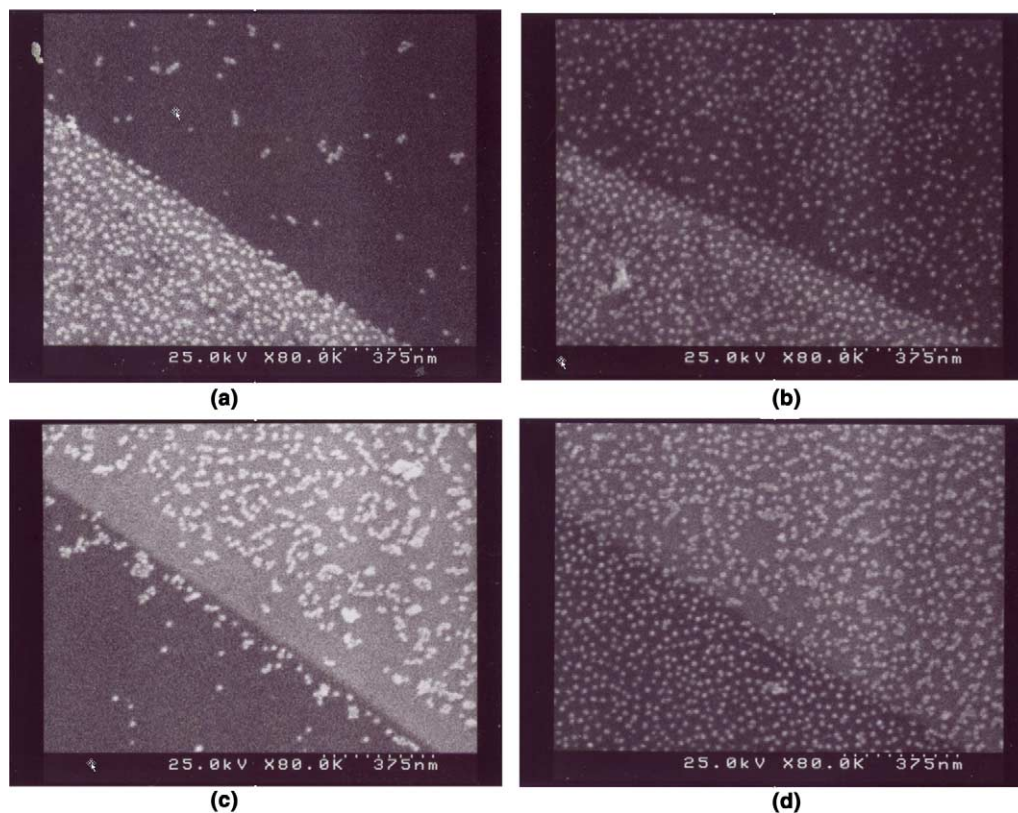
Fig. 4. SEM images of selective gold nanoparticles deposition after immersing samples in different dilute solutions for silane coupling agent (AEAPTMS). The SiO₂/Si patterns were functionalized with: (a) AEAPTMS/water for 5 s; (b) AEAPTMS/alcohol for 5 s; (c) AEAPTMS/water for 20 s; (d) AEAPTMS/alcohol for 20 s.

oxidized again with scanning probe lithography. The samples were again treated with a silanization procedure by immersing samples into *N*-(2-Aminoethyl)-3-aminopropyl-trimethoxysilane, which provides a surface bearing free amine (–NH₂) for selective gold nanoparticles deposition. Fig. 5 shows SEM image of gold colloidal particles deposited selectively on SPL-oxide patterns. The SiNW is about 100 nm wide in this demonstration.

3. Summary

Gold nanoparticles were prepared by trisodium citrate ($C_6H_8O_7Na_3 \cdot 2H_2O$) as a reductant for preparation of gold nanoparticles from $HAuCl_4$ ($HAuCl_4 \cdot 4H_2O$). The mean diameter of Au nano-particles is 15 nm. Selective deposition of Au nanoparticles on the *N*-(2-Aminoethyl)-3-amino-propyl-trimethoxysilane pretreated surface of thermal oxide patterns was then demonstrated. And, deposition of Au nanoparticles on SPL-oxided surface of a silicon nanowire is also achieved. During silanization treatment of oxide surface, immersion time plays important role in forming amino alkoxysilane on the surface of SiO₂ patterns. Different AEAPTMS dilute solvents result in different hydrolysis reaction rate which also affect the efficiency of forming amino alkoxysilane on the oxide surface such that different distribution patterns of Au nanoparticles occur. It is believed that the proposed technique in conjunction with top-down methods can be applied in both nanoelectronics and nanobiosensing applications.
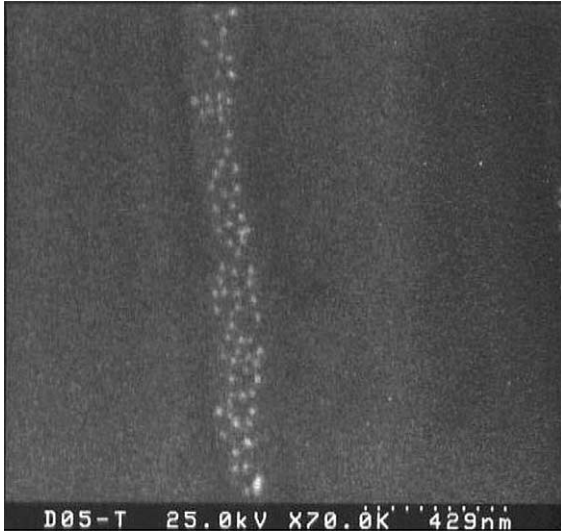
Fig. 5. The SEM image of gold colloidal particles deposited on the SPL-oxide surface of silicon nanowire. The feature size of silicon nanowire is about 100 nm.

Acknowledgement

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