Position Control of Metal Nanoparticles by Self-Assembly

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Bottom-up self-assembly has the capacity to overcome the limitation of top down nanofabrication. Recently, nanoparticles or molecules are expected to use as the building blocks. By using them it is desirable to place nanometer sized components such as nanoparticles in exact positions for nano-fabrication with high precision and reproducibility. In particular, gold (Au) nanoparticles, which covalently linked to biomolecules such as DNA, peptides, nucleic acids, proteins, and cell have attracted much attention for biosensing application, bioimaging application and so on. In this study, we present a novel and simple method of position control of Au nanoparticles on a nanopattern by self-assembly techniques such as block copolymer phase separation and self-assembled monolayers. Spherical Au nanoparticles were immobilized above the Au nanopatterns with a gap of a few nanometers. We believe this method will contribute to studies on the observation of single biomolecules such as DNA, peptides, nucleic acids, proteins, and so on.

Keywords: Au nanoparticles, self-assembly, block copolymer, self-assembled monolayers (SAMs), nanofabrication,

1. Introduction

Lithography technology continues to be the mainstream technology used in the semiconductor industry for the fabrication of silicon devices at less than 32 nm half-pitch. To improve performance of patterning, resists have been designed to optimize performance. However, feature sizes of sub 10 nm may not be easily obtained by lithography techniques. Thus, fundamental limitations associated with top-down lithographic techniques gradually have approached. Therefore, a new concept for scalable technologies is required to be developed and different novel techniques for nanolithography have been investigated [1, 2].

Bottom-up self-assembly has the capacity to overcome these limitations. Diblock copolymers are attractive in materials for nanofabrication applications because the diverse structures with tunable length scales are accessible [3, 4]. Diblock copolymer consists of two chemically different polymer chains which are covalently linked each other. Due to connectivity constraints and the incompatibility between the two blocks, diblock copolymers spontaneously self-assemble into microphase-separated nanometer-sized domains which exhibit ordered morphologies at equilibrium [5]. Depending on the degree of polymerization, the size of phase separated domains can be controlled so that it can be much smaller than features which can be printed by lithography technology [6-10]. This opens the door to applications in electronics, optics, and sensor technology and so on when using cylinder-forming materials.

Recently, a new nanofabrication uses nanoparticles or molecules as the building blocks to enter the nano-scale. In particular, it is desirable to place nanometer sized components such as nanoparticles in exact positions for nano-fabrication with high precision and reproducibility. One of the promising methods for constructing such ordered structures is to chemically attach nanoparticles onto a highly ordered layer of functional molecules such as self-assembled monolayers (SAMs), which are
formed by the spontaneous organization of thiolated molecules on a desired surface such as a metal, semiconductor, or insulator [11].

Nowadays, metal or semiconductor nanoparticles attract much interest because of their specific properties, which are different from the properties in their respective bulk materials [12, 13]. Therefore, they are expected as next generation electronic materials for display devices, LED, catalyst of solar cells, fluorescent marker in medical field, color material, optical limiter and so on [14]. In particular, gold (Au), which covalently linked to biomolecules such as DNA, peptides, nucleic acids, proteins and cell have been attracted much attention for biosensing and bioimaging application. Those properties can be controlled through the immobilization and the assembly of nanoparticles on an appropriate substrate. For example, the design of a practical plasmonic nanodevice relies on position of metal nanoparticles. Thus, it is desirable for many applications to place nanoparticles in exact positions, well separated from each other, and regularly.

As above-mentioned, one of the key challenges is the position control of nanoparticles on predefined areas in order to fabricate devices for practical purposes using nanoparticles. So far, a variety of techniques such as electron beam (EB) lithography [15], micro contact printing [16], scanning tunneling microscope lithography [17], dip-pen nanolithography [18], electrochemical etching and electrodeposition [19] have been used to fabricate arrays of nanoparticle on substrates with dimensions in the sub-100 nm. Also, progress has been made in the assembly of metal nanoparticles for the fabrication of nanoscale structures [20], and the EB patterning of nanoparticle monolayers has been demonstrated [21]. Although these techniques have brought a lot of impressive results, it is still fascinating to develop new preparation methods of nanoparticle arrays and improve these technologies. However, it is still difficult to precisely control the attachment of nanoparticles.

In previous study, we succeeded in a novel and simple method of fabricating patterned arrays of Au nanoparticles on a nanoscale reaction field by combining EB lithography and self-assembly techniques [22-24]. Also, we succeeded in controlled arrangement of Au nanoparticles capped with protecting ligand on Au nanopatterns [25]. In this study, we investigated position control of Au nanoparticles on a nanoscale reaction field by using self-assembly techniques.

2. Experimental

Si wafers were cleaned in piranha solution at 90 °C for 30 min and rinsed thoroughly with deionized water. Then, the substrates were modified with a neural layer by spin-coating followed by baking. Then, poly(styrene-block-methyl methacrylate) (PS-b-PMMA) was spin-coated from propylene glycol mono methyl ether acetate (PGMEA) solution on substrates modified with a neural layer. Dots patterns were fabricated on a Si substrate by self-assembly of diblock copolymer. PS-b-PMMA was purchased from Polymer Source, Inc. and used as received. Next, the samples were annealed at 180 °C for 24 hours at reduced pressure. Atomic force microscopy (AFM) measurements were conducted by SPM (N-3900/SPA-300HV) to examine the resulting microphase separation behavior of diblock copolymer thin films. Tapping mode AFM was performed with silicon tips (resonance frequency = 136 kHz). Also, the annealed film was treated with oxygen reactive ion etching (RIE) process in order to selectively remove the PMMA domains and form PS patterns on the substrate. After selective removal of one of the blocks, the remaining pattern can be obtained. The resulting morphology was recorded using field emission-scanning electron microscopy (FE-SEM, Hitachi-hitec S-5500). A thin layer of tungsten was sputter-coated on sample to restrain charge-up.

Using these remaining pattern of block-patterns, Au nano-patterns were fabricated on a Si substrate using lift-off process. The 15 nm thick Au layers on Ti layers was deposited by electron beam (EB) deposition. After electron beam deposition, the remained polymer film was dissolved by dipping the sample into a piranha solution for 10 min at 130 °C [26].

In self-assembly procedure, Au nano-patterns is exposed to a solution of dithiol linker compound in water. Au patterns were covered with SAMs by the immersion of the Au patterned substrate into water solutions of dithiol. We selected water-soluble SAM such as poly(ethylene glycol) dithiol because our purpose is biosensing such as single-molecular observation and plasmonics application. Finally, resulting SAMs patterns were immersed into the aqueous colloidal solution of citrate-stabilized Au nanoparticles in order to attach the nanoparticles onto them. In the sample
preparation for Au nanoparticles, an aqueous colloidal solution of citrate-stabilized gold nanoparticles was prepared following the method of Frens [27-29]. The structure obtained was imaged with a FE-SEM and the position control of Au nanoparticles was characterized.

3. Results and Discussion

Figure 1 shows a schematic process flow of our fabrication procedure of position control of Au nanoparticles on nanopattern structure. A preliminary experiment was carried out using phase separation of block copolymer PS-b-PMMA. At first, periodic dot patterns were fabricated on a neutral layers on Si substrate by self-assembly of diblock copolymer (step1). Secondarily, The PMMA block was selectively removed with O₂ RIE form PS patterns on the substrate. Also, the neutral layers was removed with O₂ RIE to make good adhesion between substrate and deposited metal (step2). The diameter of the cylinders was around 30 nm (Figure 3(a)). Then, Ti layers on Si substrate and Au layers on Ti layers is deposited by EB deposition (step3). After EB deposition, the remained polymer film of the block copolymer was dissolved by dipping the sample into a piranha solution for 10 min at 130 °C and leaving Au nano-pattern are unchanged (step4). Next, Au patterns were covered with SAMs by the immersion of the Au patterned substrate into aqueous solutions of dithiol (step5). Finally, SAMs patterns were immersed into the aqueous colloidal solution of citrate-stabilized Au nanoparticles in order to attach the nanoparticles onto them (step6).

Figure 2 shows tapping mode AFM phase image over 1 μm X 1 μm area of spin-coated PS-b-PMMA film on neutral layers on Si. The array of cylindrical domains was observed at the surface of film. The minor component PMMA forms cylindrical domains (dark area in AFM image). On the other hands, the major component PS constituted the matrix (light area in AFM image) as shown in Figure 2. The phase image shows highly ordered array of cylindrical domains.

Figure 3(a) shows a SEM micrograph of the nanopattern with self-assembled holes with the diameter of around 30 nm after O₂ RIE. (b) A SEM micrograph of the nanopatterns containing self-assembled holes and some lines after O₂ RIE.

Figure 3(a) shows a SEM micrograph of the nanopattern with self-assembled holes with the diameter of around 30 nm after O₂ RIE. It is reported that a thin film of asymmetric PS-b-PMMA with PMMA cylindrical domains was etched by O₂ RIE and nanopatterns with self-assembled line or holes are formed by selective removal of PMMA [30]. Although the SEM micrograph is not shown here, feature sizes of less than 30 nm and other shape of patterns could be easily achieved. Figure 3(b) shows a SEM
In this study, the position control of Au nanoparticles have been successfully fabricated by self-assembly such as block copolymer phase separation and SAMs. The diameter and the pitch of metal nanodots and line and pitch of line and space patterns can be controlled by using the block copolymer mask. Also, we can scale up or down the pitch by changing molecular weight ratios of the block copolymers. Furthermore we can scale down the pattern sizes of sub 10 nm below if we change other block copolymer with high Χ parameters such as polystyrene-block polyethylene oxide (PS-PEO) [31], polystyrene-block-poly(dimethylsiloxane) (PS-b-PDMS) [32], and poly (2-vinylpyridine-block-poly(dimethylsiloxane) (P2Vp-b-PDMS). Though only one example using a block copolymer phase separation was demonstrated, this method opens the door to various applications in electronics, optics, biosensing, bioimaging and so on.

4. Conclusion

We succeeded in position control of Au nanoparticles on nano-patterns using self-assembly. This method enables the position control of Au nanoparticles on the resulting water-soluble dithiol SAM nano-patterns. The diameter and the pitch of metal nanodots and line and pitch of line and space patterns can be controlled by using the block copolymer phase separation. In other words, we can scale up or down the pitch by changing molecular weight ratios of the block copolymers. This method is suitable for self-assembled nanolithography applications in electronics, optics, biosensing, bioimaging and so on.

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