Controlled Array of Silver Nanoparticles on Nanopatterns

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Nanoparticles have unique, size-dependent properties associated with magnetic, photonic, chemical, and electrical behavior, which are different from the properties in their respective bulk materials. Those properties can be controlled through the immobilization of nanoparticles on an appropriate substrate. Therefore, it is essential to construct ordered structure of the nanoparticles on solid substrate. We succeeded in the the controlled array of silver (Ag) nanoparticles on the resulting water-soluble dithiol self-assembled monolayer (SAM) nanopatterns such as line and space and dots. Spherical Ag nanoparticles were arrayed above gold nanopatterns with a gap distance of a few nanometers supported by water-soluble dithiol. The difference in attachment behavior of Ag nanoparticle between two kinds of dithiol SAMs was clearly observed.

Keywords: silver nano-particles, electron beam, self-assembled monolayers (SAMs), water-soluble dithiol, nano-fabrication,

1. Introduction

Metallic nanoparticles and their assemblies have unique, often size-dependent properties associated with magnetic, photonic, chemical, and electrical behavior, which are different from the properties in their respective bulk materials. [1, 2] Those properties can be controlled through the immobilization and the assembly of nanoparticles on an appropriate substrate or in a suitable medium. Interest in developing fabrication methods for metal nanoparticle arrays is expanded by their wide applications which includes surface-enhanced Raman spectroscopy (SERS) [3], Light-trapping applications in solar cells [4], fluorescent marker in medical field, color material, optical limiter and so on [5].

Recently, there has been considerable interest in developing methods for patterning nanoparticles because of their potential technological applications in molecular electronics, magnetic storage devices, and biosensors [6, 7]. In particular, gold (Au) and silver (Ag) nanoparticles, which covalently linked to biomolecules such as DNA, peptides, nucleic acids, proteins and cell have been attracted much attention for biosensing and bioimaging application. In particular, silver nanoparticles have been of interest for many years due to their optical, electronic and pharmacological properties.

Schatz et al. have discovered one and two dimensional array structures that produce remarkably narrow plasmon resonance spectra upon irradiation with light. [8] In order to investigate these interactions, precise control of nanoparticle orientation, size, shape and spacing is needed. Metal nanoparticles have been widely employed in SERS, since the aggregation of metal particles leads to the formation of aggregates with the roughness and fractal morphology necessary to produce intense Raman spectra. [9] Because the design of a practical plasmonic nanodevice relies on arrays of noble metal nanoparticles, the interactions between these nanoparticles is a crucial. Thus, it is desirable for many applications.
to place nanoparticles in exact positions, well separated from each other, and regularly. A promising method 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 [10]. The optical and electrical properties of layer-by-layer self-assembled films comprising Au or Ag nanoparticles and various organic compounds have been investigated [11-13].

As above-mentioned, one of the key challenges is the patterned deposition of nanoparticles on predefined areas in order to fabricate devices for practical purposes using nanoparticles. Various top-down and bottom-up techniques using sophisticated equipment and chemicals have been used to achieve the goal of nanostructure patterning. However, it is still difficult to precisely control the attachment of nanoparticles. A variety of techniques such as electron beam lithography [14], microcontact printing [15], scanning tunneling microscope lithography [16], dip-pen nanolithography [17], electrochemical etching, and electrodeposition [18] have been used to fabricate arrays of nanoparticles on substrates with the sub-100 nm dimensions. Also, progress has been made in the assembly of metal nanoparticles for the fabrication of nanoscale structures [19], and the electron beam patterning of nanoparticle monolayers has been demonstrated [20]. Although these techniques have produced many impressive results, it is still fascinating to develop new preparation methods for nanoparticle arrays and improve these technologies.

In previous study, we succeeded in location control of Au nanoparticles using combination of top-down and bottom-up nanofabrication. [21] Our purpose is single-molecular observation using combination of top-down and bottom-up techniques. For this purpose, we investigated the attachment of silver nanoparticles on Au nanopattern pattern. In this study, we investigated controlled arrays of silver nanoparticles on nano-patterns using combination of top-down and bottom-up nanofabrication. Also, we investigated the different in attachment of between Au and Ag on SAM patterns.

2. Experimental

Line and space patterns and dots patterns were fabricated on a Si substrate by electron beam lithography. ZEP 520A was used as a resist material. ZEP 520A was spin-coated onto silicon wafer at 3000 rpm and baked for 180 seconds at 180 °C. The resist is exposed at 75 kV using a dose of 200 μC/cm². Then the resist was developed in ZMD-N50 developer for 60s and rinsed with ZMD-B.

Using these resist 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 deposition. After electron beam deposition, the entire resist is dissolved by dipping the sample into a ZDMAC solution.

In the sample preparation for Ag nanoparticles, an aqueous colloidal solution of citrate-stabilized silver nanoparticles was prepared by the chemical reduction of silver nitrate by citrate produce [22, 23]. For the evaluation of Ag nanoparticles, UV-visible spectra of Ag nanoparticle were measured in 10 mm optical path length quartz cuvettes with a spectrophotometer. Also, samples for TEM were prepared by putting a drop of the colloidal solution on a copper grid coated with a thin amorphous carbon film. Then transmission electron microscopy images were obtained using a JEOL JEM-2010F transmission electron microscope (TEM,) at an acceleration voltage of 200 kV.

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 because our purpose is biosensing such as single-molecular observation and plasmonics application. Also, we used two different types of SAMs such as 3,6-dioxa-1,8-octanedi thiol and poly(ethylene glycol) dithiol. Finally, resulting SAMs patterns were immersed into the aqueous colloidal solution of citrate-stabilized Ag nanoparticles in order to attach the nanoparticles onto them. The structure obtained was imaged with a JEOL JSM-7400F field-emission scanning electron microscope (FE-SEM) at an acceleration of 5 kV, and the location control of nanoparticles was characterized. the controlled array of Ag nanoparticles was characterized.
3. Results and Discussion

Figure 1 shows a schematic illustration of our fabrication procedure of nanoparticle array on nanopattern structure. A preliminary experiment was carried out using line and space pattern construction. At first, line and space pattern is fabricated by EB lithography (step 1). Secondarily, Ti layers on Si substrate and Au layers on Ti layers is deposited by electron beam deposition (step 2). In step 3, the resist layer is removed in ZDMAC soak and leaving Au nano-pattern are unchanged. Au patterns were covered with SAMs by the immersion of the Au patterned substrate into aqueous solutions of dithiol (step 4). Finally, SAMs patterns were immersed into the aqueous colloidal solution of citrate-stabilized Ag nanoparticles in order to attach the nanoparticles onto them (step 5).

Although the SEM micrograph is not shown here, feature sizes of less than 100 nm and other shape of patterns can be easily achieved. As a result, defined areas on the Si surface remain protected by the patterned resist mask. After metal deposition and lift-off of the resist layer, metal semi-condensed line and space patterns remains on the surface.

The SAMs were fabricated by standard immersion procedure, resulting usually in the homogeneous and densely packed SAMs on Au. Patterning self-assembled material is typically achieved by covering the Au nano-patterns with SAM of organic molecules through the use of EB lithography. Two different length of SAMs such as 3,6-dioxa-1,8-octanedithiol and poly(ethylene glycol) dithiol were used in order to investigate attachment behavior of Ag nanoparticles on dithiol SAMs. The resulting patterned SAM is used as a binding layer for the spatially selective assembly of nanoparticles.

An aqueous colloidal solution of citrate-stabilized Ag nanoparticles was prepared. The size and shape of nanoparticles can be easily controlled by changing synthesis and process conditions in this method. Figure 2 shows UV-vis absorption spectrum of Ag nanoparticles. It is reported that the surface plasmon band of stable Ag nanoparticles is around 400 nm. [23] The yellow color of aqueous colloidal solution of Ag nanoparticles had a surface plasmon resonance absorption band at 430 nm. Its peak is a little broad. Ag nanoparticles preferred to attach to SAM on Au nanopattern. Figure 3 shows TEM image of aqueous colloidal solution of Ag nanoparticles. Ag nanoparticles were nearly spherical in shape and exhibited a relatively inhomogeneous distribution of Ag nanoparticles. These particles have a diameter between 10 and 50 nm. The mean particle size is around 30 nm, which is related to the absorption maximum at 430 nm. This inhomogeneous distribution of Ag nanoparticles was expected from the wider absorbance bands observed in the UV-visible spectra because the fwhh (full width at half-height) value of the absorbance bands can be used as estimation of the particle dispersion as already-reported. [24]

![Figure 2. UV-vis absorption spectrum of Ag nanoparticles.](image)

The controlled array of Ag nanoparticles was characterized by SEM. Figure 4 shows a typical SEM image of highly ordered nanoparticle immobilized above Ag nanopatterns with a gap distance of a few nanometers supported by dithiol SAM on Au nanopattern, corresponding to step 5 in Figure 1. Nanoparticles were anchored onto Au nano-pattern in both cases as shown in Figure 4. We succeeded in controlled array of Ag nanoparticles on the resulting dithiol SAM.
nano-patterns. Also, the difference in attachment behavior of Ag nanoparticle between 3,6-dioxa-1,8-octanediol and PEG dithiol were clearly observed as shown in Figure 4.

In this study, highly ordered nanoparticle structures with a diameter of 30 nm have been successfully fabricated by the combination of Top down nanofabrication such as EB lithography and bottom-up fabrication such as self-assembly. Similar trends in attachment of Au and Ag nanoparticle between 3,6-dioxa-1,8-octanediol and PEG dithiol SAM patterns were observed.

4. Conclusion
We succeeded in controlled arrays of silver nanoparticles on nano-patterns using combination of top-down and bottom-up nanofabrication as well as gold nanoparticles. Although the formation mechanism of the Au nanoparticles in our technique is not yet fully understood, a difference in the attachment behaviors of nanoparticles on dithiol SAMs with different lengths of the dithiol molecules was observed. This method enables the controlled arrays of Au and Ag nanoparticles on the resulting water-soluble dithiol SAM nano-patterns. This technique suggests interesting application such as novel devices and biosensing application.

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