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Designable formation of metal nanoparticle array with the deposition of negatively charged nanoparticles

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Abstract

Ultrafine gold and platinum nanoparticles (NPs) were fabricated by pulsed laser ablation in helium gas and the NPs 2–15 nm in diameter were selectively classified by an electrostatic size-selection technique employing a low-pressure differential mobility analyzer (LP-DMA). The spherical NPs obtained showed a narrower distribution of diameters of anionic NPs over cationic NPs. With this knowledge, the anionic NPs were deposited onto silicon substrates designed by electron beam lithography processing, and designable patterns of arrayed NPs were produced by removing the photoresist layer.

Keywords: Pulsed laser ablation; Nanoparticles; LP-DMA; Nanodevices

1. Introduction

The drive towards greater microminiaturization entails further development in nanodevices, because nanometer scale materials exhibit unique properties which differ considerably from those in the bulk. Above all, nanoparticles (NPs) show a variety of size-dependent properties due to the dramatic changes in the ratio of surface area to volume as a function of a NP size [1–7]. Examples include catalytic activity of gold (Au) nanostructures for the oxidation of carbon monoxide [1], surface enhanced Raman scattering in coinage NPs [2], a quantum dot effect in semiconductor NPs [3,4], the electric resistance of an Au nanorod [5], and size-dependent magnetic [7] and structural evolution [8]. It is also noteworthy that single-crystalline chemical growth has been reported in nanorods and nanowires [9,10]. Thus, the study of size-dependent effects in NPs and nanorods is crucial not only for basic science, but also for industrial applications.

For these studies, it is an important issue to develop a methodology for the preparation of well-defined nanostructured materials, and electrical mobility analysis methods as typified by a differential mobility analyzer (DMA) [11] have recently provided an effective tool to control the size of NPs [12–15]. In particular, a low pressure differential mobility analyzer (LP-DMA) is beneficial when classifying monodispersed ‘‘naked’’ metal NPs, charged negatively or positively, in the range of 1–100 nm in diameter in the gas-phase. However, the LP-DMA has been applied to select the size of only NPs that are spherical in shape [12], and furthermore, the NPs classified in this manner have been usually randomly deposited on a substrate in order to characterize their electronic and magnetic properties.

In order to utilize the characteristics of metal NPs, it is ideal to assemble them on a substrate in a designed manner, rather than randomly. The proper 2D arrangement of NPs is expected to exhibit new magnetic properties due to an exchange interaction of electron spin mediated by the substrate [16,17], as well as collective electronic/optical behavior by dipole–dipole interaction [18,19]. Moreover, a regular pattern is technologically crucial to define the coordinate of the NP positions, when the NPs are functionalized as, for instance, magnetic memory units. One of the ways to regularly arrange NPs is to couple the NP deposition with a template substrate patterned by electron beam lithography.

In this work, we report a new way to make use of the LP-DMA with a laser ablation source to isolate well-defined

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negatively charged NPs, which are then deposited in a regular array on a designed silicon substrate, patterned by electron beam lithography. From the evaluation of diameter dependence of the NPs, the deposition mechanism involved in the formation of the NPs assembly has been proposed.

2. Experimental

The experimental details have been described previously [20], and therefore only a brief description will be given here. The apparatus is composed of the ablation chamber, the LP-DMA chamber, and the deposition chamber. High purity helium gas (99.9999%) was introduced into the ablation chamber by controlling the flow rate (Q_a) at 0.4–1.0 standard liters per minute (SLM) using a mass flow controller. A rotating target disk of gold (Au) or platinum (Pt) (diameter 50 mm, 2 mm thickness, purity 99.95%) was vaporized with the second harmonic (wavelength of 532 nm, 20–40 mJ/pulse) of a Nd^{3+}:YAG laser in an ambient He pressure of 1.5–3 kPa. Metal NPs produced in the ablation chamber were transported through a stainless tube (length: 300 mm and bore diameter: 10 mm) to the LP-DMA chamber by a He flow.

In the LP-DMA illustrated schematically in Fig. 1, charged NPs were classified by a helium sheath gas flow denoted as "Q_c" (flow rate of 2.0–5.0 SLM) and an electric field generated by applying voltage (V_{dc} = 0–150 V) to an inside cylinder, where the direction of the sheath gas flow is perpendicular to that of the electric field, V_{dc}. In this study, Q_c was varied from 2.0 to 5.0 SLM which was set to be five times larger than the helium gas flow rate into the ablation chamber, Q_a (from 0.4 to 1.0 SLM), which provides a good classification performance [21].

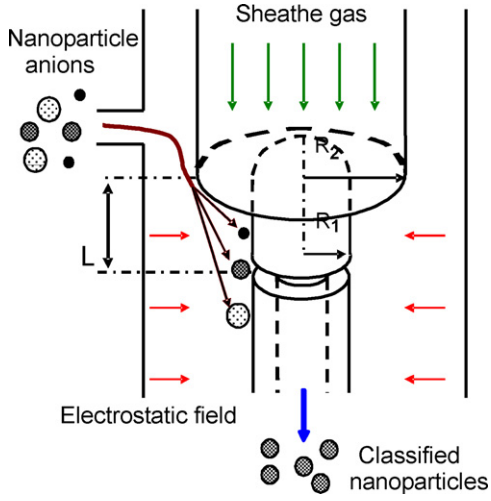

Fig. 1. A schematic illustration of a low-pressure differential mobility analyzer (LP-DMA). Metal NPs produced by laser abalation were transported through a stainless tube on the side wall to the LP-DMA chamber by a He flow, and the classified NPs are deposited onto a substrate at the bottom. In general, the median value of the electric mobility distribution of the classified NPs, Z_{PC}, is dictated by the applied voltage, V_{dc} (0–150 V), the sheath gas flow rate, Q_c (2.0–5.0 SLM), and the three dimensions of L, R_1, and R_2 in the DMA. The dimensions of the DMA were L = 10 mm, R_1 = 11 mm, and R_2 = 18 mm in this apparatus, which are short enough to classify the NPs of 1–20 nm in diameter.

In general, the median value of the electric mobility distribution of the classified NPs, Z_{PC}, is found by using the applied voltage, V_{dc}, the sheath gas flow rate, Q_c, and the three dimensions of L, R_1, and R_2 in the DMA [11] in the following equation;

$$Z_{PC} = \frac{Q_c \ln(R_2/R_1)}{2\pi L V_{dc}} \quad (1)$$

The dimensions of the DMA were L = 10 mm, R_1 = 11 mm, and R_2 = 18 mm in this apparatus, dimensions which are short enough to classify NPs of 1–20 nm in diameter. The sheath gas flow (Q_c) and electrical field (V_{dc}) are crucial factors for the classification of NP diameter (d_{NP}) together with an instrumental DMA's shape, and their relationship is simply expressed as

$$V_{dc} = Q_c \times d_{NP}^2 \times C_{DMA} \quad (2)$$

where C_{DMA} in this work is 0.332 for singly charged NPs (q = 1) in helium. For example, an applied voltage of 20 V is required for the selection of NPs whose diameter is 3.5 nm when Q_c is 5.0 SLM. When Q_c is 2.0 SLM, NPs of 15.0 nm in diameter are classified by setting the voltage at 150 V.

In the deposition chamber, a Faraday cup was set below the outlet nozzle of the LP-DMA (inner diameter: 4.0 mm). The amount of classified NPs was measured as electric current by the Faraday cup before deposition, and classified NPs were deposited onto a grid for transmission electron microscope (TEM) after optimizing the NP amount to be about 1×10^{10} min^{-1} (~30 pA). The kinetic energy of the deposited NPs were governed by the gas flow speed, and it was typically around 100 meV. After the deposition onto a grid (deposition time ~30 min), the morphology of the NPs was characterized by a field emission-transmission electron microscope (TEM) and by scanning electron microscope (SEM). The size distributions of the NPs were measured from the TEM images and were fitted by a log-normal function to evaluate the efficiency of the classification, as it is known that the logarithm of the NP diameter has a Gaussian distribution [22].

With this method of classification, anionic NPs were deposited onto silicon substrates (phosphor (P) doped n-type: 3–5 Ω cm resistivity) with features designed by electron beam lithography processing. Extra NPs deposited on the photoresist were removed by dissolving the resist, resulting in designable patterns of arrayed NPs that could be produced and observed by SEM and atomic force microscopy (AFM).

3. Results and discussion

3.1. Classification of Au nanoparticles

Fig. 2 shows TEM images and the size distributions of ~5.8 nm anionic Au NPs in diameter as classified by the LP-DMA. Most of the classified NPs have a spherical shape, and the histograms of the size distributions were fit by a log-normal