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Planar Array of 1D Gold Nanoparticles on Ridge-and-Valley Structured Carbon

Toshiharu Teranishi,*[†,‡] Akira Sugawara,[†] Takami Shimizu,[†] and Mikio Miyake[†]

School of Materials Science, Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Tatsunokuchi, Nomi, Ishikawa 923-1292, Japan, and "Organization and Function", PRESTO, Japan Science and Technology Corporation, 2-1 Hibikino, Wakamatsu, Kitakyushu, Fukuoka 808-0135, Japan

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Patterning the building blocks of materials into special periodic structures will provide us interesting and useful electronic,[1] optical[2] and magnetic[3] properties originated not only from the constituent material but also from the long-range order of these structures. The formation of two-dimensional (2D) superlattices of metal nanoparticles has been vigorously investigated,[1−4] while the fabrication of one-dimensional (1D) chains is the most challenging subject, because it is quite difficult to arrange metal nanoparticles in low symmetry. For further miniatuarization of microelectronic devices, ordering nanoparticle building blocks in 1D configuration to produce one-dimensional chains is required to make use of single-electron tunneling effect at room temperature. If we are able to organize them into 1D configuration, the tunneling behavior of electrons between nanoparticles can be investigated in detail, and the resolution of integrated circuits will be drastically improved beyond the resolution of the current photolithography technique, even though desirable 2D patterning of nanoparticles would be required. Template methods are the effective ways to form the long-range 1D chains of metal nanoparticles.[5] For example, 1D chains of gold (Au) nanoparticles have been successfully fabricated by using the pore channels of alumina membranes,[5a] the step edges of amorphous carbon thin films,[5b] and biopolymers.[5c] However, the formation of long-range 1D chains of metal nanoparticles in planar structure has not been achieved with these template methods. Here we show a novel method to fabricate a planar array of 1D chains of size-controlled Au nanoparticles prepared by our original chemical process[4g] in combination with a specially developed technique to produce nanoscale ridge-and-valley structured substrates using a vacuum process.[6] The faceted (110) planes of sodium chloride crystals were used as templates to produce nanoscale ridge-and-valley structured carbon layers with a vacuum process. When these carbon layers loaded on copper grids were dipped in toluene solution of dodecanethiol-protected Au nanoparticles of 3.4 nm in Au core diameter followed by natural evaporation, a planar array of 1D chains of Au nanoparticles was formed predominantly in valleys and on ridges of carbon layers, where the assembly mechanism may be somewhat unique.

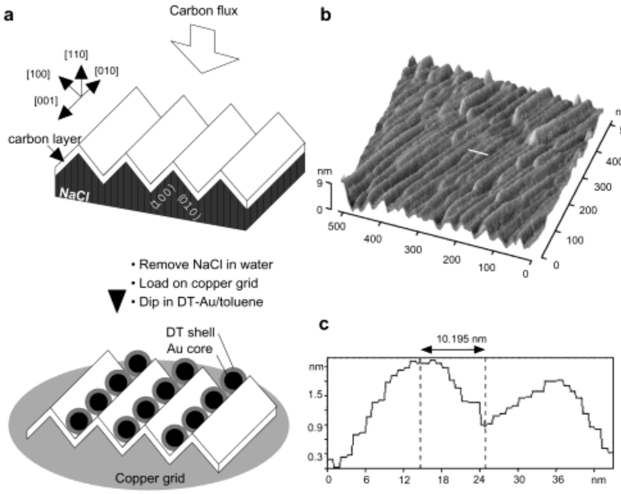

Figure 1. (a) Schematic illustration of a preparation of the carbon layer with ridge-and-valley structure and the formation of planar 1D chains of dodecanethiol-protected gold nanoparticles (DT−Au). (b) AFM image of a ridge-and-valley carbon layer on copper grid. (c) A line profile along the white line indicated in (b).

The nanoscale carbon gratings were prepared in an ultrahigh vacuum chamber equipped with NaCl and carbon evaporators and reflection high-energy electron diffraction (RHEED) apparatus. Optical-grade (110) polished NaCl single crystals (muscut angle <3°, purchased from CASIX, Inc.) were used as templates. These crystals were etched in deionized water for a few seconds to remove surface contamination prior to loading into the UHV chamber. The 20-nm-thick NaCl overlayers were deposited by thermal evaporation onto the NaCl templates at 250 °C. Since NaCl(110) is an unstable plane, the film surface becomes faceted with low-energy (100) and (010) planes during the homoepitaxial growth of NaCl. The facet formation tilted by 45° with respect to the surface normal was confirmed in situ by RHEED. A 30-nm-thick carbon replica layer was deposited directly on the NaCl surface, as shown in Figure 1a. The carbon layer was floated off from the NaCl substrate in water and was then loaded onto 400-mesh copper grids. As seen in Figure 1b presenting an AFM image of the carbon replica layer, it preserved ridge-and-valley surface topography with long and straight in-plane macrosteps along [001] of the NaCl epilayer. It was found from the line profile in Figure 1c that the valley depth and its period are a few nm and ca. 20 nm, respectively.

A method to control the size of dodecanethiol-protected Au nanoparticles (DT−Au) was totally different from those in the liquid phase[7] and described elsewhere.[4g] The Au nanoparticles of 3.4 ± 0.3 and 5.4 ± 0.7 nm were obtained by the heat-treatment of 1.5 nm DT−Au nanoparticles in the solid state, which were prepared by the Brust's two-phase reaction procedure.[8] The 1D chains of gold nanoparticles on the carbon layer-loaded copper grid were prepared either by placing a drop of 5 mM toluene solution of DT−Au nanoparticles onto a carbon layer-loaded copper grid (a drop method) or by dipping a carbon layer-loaded copper grid perpendicular into the toluene solution for 3 s with a valley direction kept to a dipping direction (a dip method), followed by naturally evaporating toluene.

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* To whom correspondence should be addressed. E-mail: tosiharu@jaist.ac.jp.
[†] Japan Advanced Institute of Science and Technology.
[‡] PRESTO, Japan Science and Technology Corporation.

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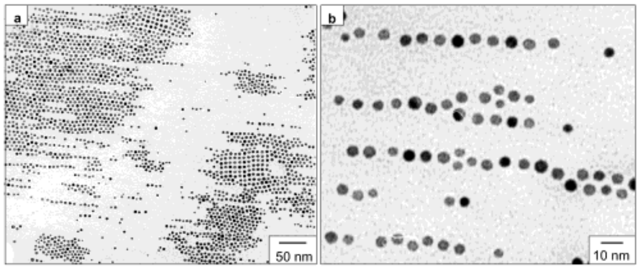

Figure 2. (a) Low magnification TEM image of 5.4 nm DT−Au nanoparticles on a ridge-and-valley carbon layer prepared by a drop method. (b) Magnified TEM image of 1D chains of DT−Au nanoparticles.

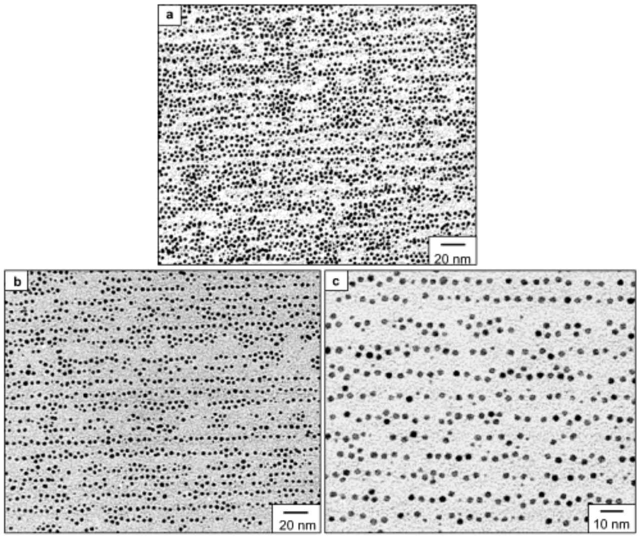

Figure 3. TEM images of 3.4 nm DT−Au nanoparticles on ridge-and-valley carbon layers. (a) Prepared by a drop method. (b) Prepared by a dip method. (c) A magnified image of (b).

Figure 2 shows TEM images of 5.4 nm DT−Au nanoparticles on a carbon layer with ridge-and-valley structure obtained by a drop method. As seen in Figure 2a, the 2D superlattices of hexagonal and square packings were predominantly formed, but these structures are likely to reflect the direction of valleys. In some parts, we observed the formation of 1D chains of gold nanoparticles, as shown in Figure 2b. The chains heading for the similar direction are composed of a few 10 gold nanoparticles. Most of chains have irregular interparticle spacings, and nanoparticles are not arranged in a line. Moreover, a regular planar array of 1D chains was not obtained, probably because the size of DT−Au including the DT length, 9.0 nm,[9] is too large to sensitively distinguish between a ridge and a valley of carbon layer.

The smaller DT−Au nanoparticles could distinguish them to form a planar array of 1D chains. DT−Au nanoparticles (3.4 nm), whose size including the DT length is 7.0 nm, prepared by the heat-treatment at 150 °C were used in place of 5.4 nm ones. Adoption of a drop method to 3.4 nm DT−Au nanoparticles led to both a drastic reduction of the formation of 2D superlattices and the fabrication of a planar array of 1D chains of DT−Au nanoparticles, as shown in Figure 3a. However, almost all the 1D chains were bundles of a few chains. To avoid the production of such aggregated structures, a dip method was applied to the colloidal solution of 3.4 nm DT−Au nanoparticles. As seen in Figure 3b and c (magnified one), the number of bundles of chains was decreased, and the planar array of 1D chains of Au nanoparticles ordering in a line was formed throughout a few mm^2 of the carbon substrate. The 1D chains formed an array at a distance of $\sim$20 or $\sim$10 nm , which corresponds to one or one-half valley period, respectively. From AFM measurement of this sample, there is likely to be one line of nanoparticles between two ridges, indicating that the Au nanoparticles were predominantly immobilized in valleys and partly on ridges. One explanation of the formation mechanism may be as follows: When the substrate is withdrawn from the toluene, the Au nanoparticles are adsorbed and assembled mainly in valleys at the upper edge of the substrate by the adhesive[5b] and attractive capillary forces,[10a] respectively. Then the growth of 1D chains of nanoparticles is caused through convective particle flux by solvent evaporation from the already ordered chains.[10b] Now an investigation on electronic property of 1D chains of DT−Au nanoparticles is in progress.

Our studies demonstrate an approach for building planar arrays of 1D chains of Au nanoparticles aiming future nanoelectronic devices. Not only the interchain distances but also the symmetrically complex patterns of many kinds of nanoparticles, such as metal, semiconductor, and organic nanoparticles could be tuned by using various faceted surfaces of inorganic crystals. For the production of future ULSI, the combination of this method with a special patterning technique of nanoparticles by the protective ligands may be necessary and is under consideration.

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Supporting Information Available: A method to control the size of DT−Au nanoparticles in the solid state (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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