

Synthesis and conductance measurement of periodic arrays of gold nanoparticles

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We report a formation method and an electrical characterization of aligned arrays of Au nanoparticles ($\sim 20\text{--}40\text{ nm}$). We synthesized the structure by immersing a substrate vertically into a solvent with nanoparticle and letting the solvent evaporate. The periodicity of the arrays has been controlled in $10\text{--}40\ \mu\text{m}$ range by tuning the evaporation rate of solvent. The resistivity shows a drastic decrease ($\sim 10^{-4}$) when annealed at $\sim 170\text{ }^\circ\text{C}$. While it is considerably due to a breakdown of ligands surrounding the Au particles, the large change in conductivity should be used for sensors to examine the interface molecules between Au nanoparticles. © 2008 American Institute of Physics. [DOI: 10.1063/1.3001938]

Nanoparticles have attracted significant recent attention, from the view points of both fundamental research as well as technological applications. Significant progress has been made in nanoparticle synthesis using solution-phase methods, which can control the size, shape, composition, and structure of the nanoparticles.^{1,2} At the same time, major efforts have been devoted toward forming ordered assemblies of nanoparticles into complex patterns and searching a novel function of nanoparticles for possible applications such as microsensors and photonic devices.³⁻⁷

Here in this study, we show a synthesis method and an electrical characterization of arrays of straight lines of nanoparticle with a monolayer thickness and a width of micrometer. We formed the structure by immersing a substrate vertically into a solvent containing dispersed nanoparticle and letting the solvent evaporate. Though the method is simple, it can precisely control the periodicity of the arrays by tuning the evaporation rate of solvent and particle densities. We have demonstrated fabrications of stripes with periodicity of $10\text{--}40\ \mu\text{m}$. The formation mechanism is a combination of attractive force between nanoparticles through lateral capillary force,⁸ and stick-slip motion of solvent.⁹⁻¹¹ An electrical conductivity measurement has been performed at 300 K in ultrahigh vacuum (UHV) condition with a four point probe method using novel microscale probes whose positions can be manipulated independently. The resistance versus the probe-distance shows a characteristic feature for a one-dimensional conductor. The resistivity shows a drastic decrease of 10^{-4} when annealed mildly at $\sim 170\text{ }^\circ\text{C}$. While it is considerably due to a breakdown of ligands surrounding the Au particles, the large change in conductivity should be a possible candidate for the use of sensors to examine the interface conditions between Au nanoparticles.

Experimentally GaAs(100), Si(100), and mica wafers were used as the substrates. No chemical treatment except acetone or ethanol cleaning was used; thus GaAs(100) and Si(100) surfaces were covered with native oxide. It is inter-

esting to notice that oxide surface of the former substrate is hydrophilic and that of the latter is hydrophobic. Gold nanoparticles of $\sim 20\text{ nm}$ in diameter (as purchased from BB International) were dispersed either in methanol or ethanol (density of nanoparticles $\sim 3.5 \times 10^{11}/\text{ml}$). The colloidal solution was kinetically stable at $\text{pH} \sim 7.0$ condition and no cohesion of the nanoparticles was observed.

Wire-arrays of the nanoparticles were fabricated using the following method. The substrates were inserted in a cylindrical glass container with a diameter of $\sim 1\text{ cm}$, and the gold colloidal solution ($\sim 0.5\text{ ml}$) was dropped in the container. Subsequently the solvent was dried naturally at room temperature ($\sim 291\text{ K}$) either under atmospheric or pumping conditions (pressure $\sim 1\text{--}0.1\text{ atm}$). The arrangement of the sample and the container is similar to that shown in previous reports of vertical colloidal deposition (VCD).^{12,13}

Fig. 1 shows optical and scanning electron microscope

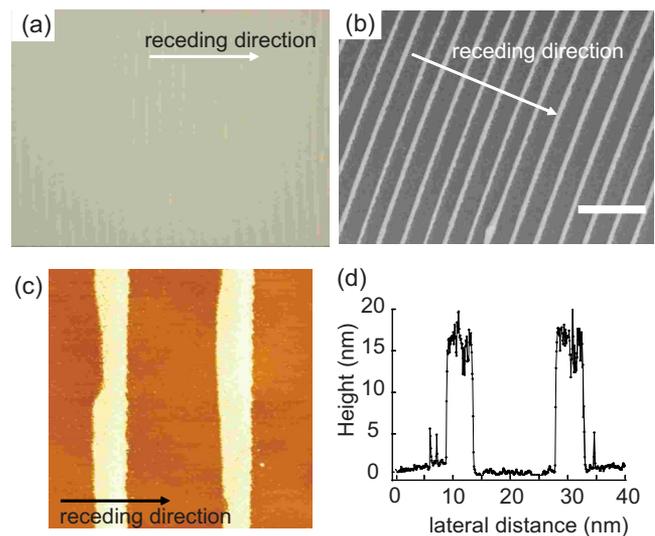


FIG. 1. (Color online) Au stripe array consisting of 20 nm gold nanoparticles obtained by evaporating methanol solvent. (a) optical micrograph ($420 \times 320\ \mu\text{m}^2$), (b) SEM image (scale bar = $50\ \mu\text{m}$), (c) AFM image ($40 \times 40\ \mu\text{m}^2$), and (d) line-profile of (c) along the horizontal direction.

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(SEM) images after the deposition of nanoparticles on the GaAs substrate using methanol as the solvent. In the optical microscope image shown in Fig. 1(a), well-ordered striped patterns can be observed, which are perpendicular to the receding direction of the solvent. The width and periodicity of the wires are estimated to be ~ 5 and ~ 20 μm , respectively. The color of the wires is light gold, indicating that they are assemblies of gold nanoparticles with small thickness.

The SEM images yield a higher contrast, and the bright lines in the SEM image correspond to the gold-colored wires in the optical micrographs. It should be noted that the length of the wire is typically more than 1 mm, which is limited only by the width of the substrate. Atomic force microscopy (AFM) images shown in Fig. 1(c) can provide height profile. As shown in Fig. 1(d), the average height is ~ 15 nm that is close to the diameter of the nanoparticles (~ 20 nm). We consider that a monolayer of 20 nm gold nanoparticles is formed in a self-assembled manner under the present condition.

Here we consider the formation mechanism of the straight arrays composed of Au nanoparticles. A meniscus line is formed along a liquid-air interface. The terminal point of this line is where solid, liquid, and air are merged, which is hereafter expressed as T . A thin layer of the solvent is formed on the substrate below point T . Gold nanoparticles, which diffuse into this thin solvent region, are trapped to become the nucleation sites for subsequent wire formation. One of the driving forces for the nucleation is the lateral capillary force, which works between the Au nanoparticles as an attractive force when the particles are arranged in a thin liquid layer.⁸

The wire grows in width while the solvent evaporates.^{12,13} A sudden recession of T occurs with a of 'stick-slip motion' of the solvent.¹⁴ The receding solvent is pinned at T due to a strong bonding between nanoparticles and solvent molecules. As the solvent evaporates, the contact angle between the substrate and solvent gradually decreases and the elastic energy stored at point T increases. When the stress exceeds the pinning energy, a slip motion would take place resulting in sudden recession of the solvent front.¹⁵

One of novelties of the deposition method shown in this article is that we can control the periodicity of the stripes by changing solvent and ambient pressure. Since the control of periodicity and width of the Au wires is critical, issues especially for a gridlike pattern formation should be a great advantage of this method.

First we have examined a variety of solvents and compared formed stripes. We have obtained no good stripes with the use of nonpolar solvents including toluene and hexane. This is mainly because a good mixture of nanoparticle colloids and nonpolar solvent cannot be obtained. Polar solvents of methanol and ethanol have shown good results. The width and periodicity of the formed stripes are, however, solvent dependent. We consider that this is due to the difference of their vapor pressures. Here we compare the stripes formed with methanol and ethanol containing the 20 nm nanoparticles. By drying both solvents with conditions of 1 atm and 293 K, we have obtained stripes with the periodicity of 20 and 40 μm for methanol and ethanol, respectively. We consider that the difference of the periodicity is due to their vapor pressures. The vapor pressures at 293 K are 12.3 and 5.33 kPa for methanol and ethanol, respectively. This indi-

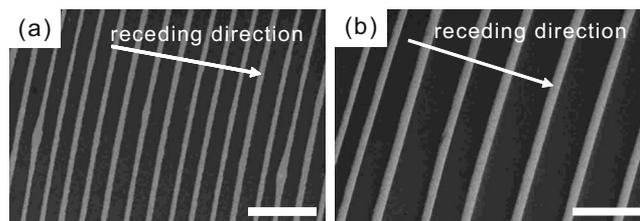


FIG. 2. SEM images of Au stripes (scale bar=50 μm). (a) and (b) are formed with solvents of methanol and ethanol, respectively. The difference of vapor pressures (12.3 and 5.33 kPa, respectively, at 20 $^{\circ}\text{C}$) considerably changes the periodicity.

cates that a rapid evaporation induces a shorter periodicity (Fig. 2).

We can further confirm the relation by pumping the vessel. When the pressure was maintained at 0.5 atm during evaporation, the periodicities of the stripes are 10 and 20 μm for methanol and ethanol, respectively. Interestingly the evaporation rate of ethanol at 0.5 atm is equal to the one of methanol at 1 atm. We obtained an exact same periodicity for these two cases, which indicates that the periodicity is mainly determined by the evaporation rate of solvents and supports above stated tendency of a shorter periodicity with a larger evaporation rate. The control of particle-deposition rate from the solvent with changing the vessel-pressure has been demonstrated previously.¹³ However, the technique shown here can form uniform stripe patterns not only in width and thickness but also in periodicity in the direction of receding direction over >0.4 mm.

Second, we also found that the periodicity and width of stripes can be changed by varying the particle size, a particle density and temperature of solvent, the mechanism of which is probably the difference of colloidal diffusion velocity. We have confirmed a stripe formation with larger nanoparticle of 30 and 40 nm. The versatility of the control of the periodicity is a characteristic feature of this formation method.

We switch to an electrical characterization of the Au stripes. The conductance measurement was executed with the four point probe method operated with independent four microprobes.^{16,17} The data were obtained in UHV condition at the temperature ~ 300 K. The spacing of the probes can be changed by manipulating the four probes independently. The SEM image of the wire and the four probes is shown in Fig. 3(a) and the image of the stripe is magnified in Fig. 3(b). We show the I - V plot in Fig. 3(c) that is linear in the voltage range of ± 0.02 V. In addition we show the resistance (R) versus the probe spacing Δd plot in Fig. 3(d), which can reveal the dimensionality of the conductor.¹⁸ The plot of Fig. 3(d) indicates a characteristic feature of one-dimensional conductor. This indicates that the current runs only through nanowires.

Assuming that a cross section of the stripe has a width of 5 μm and a height of 20 nm, the measured resistance can be calculated as ~ 0.2 Ω m. This should be compared with resistivities of a bulk Au 2.4×10^{-8} Ω m and VCD formed gold nanoparticles film 10^{-5} – 10^{-6} Ω m.¹³

To understand an origin of the high resistivity of the stripe, we have annealed the surface in UHV condition at 170 $^{\circ}\text{C}$ for 120 min. The I - V and R versus the Δd plot show a similar linear relation as are observed for a before-heating sample, the latter of which is superimposed in Fig. 3(d). However, we have to notice a drastic decrease in the resis-

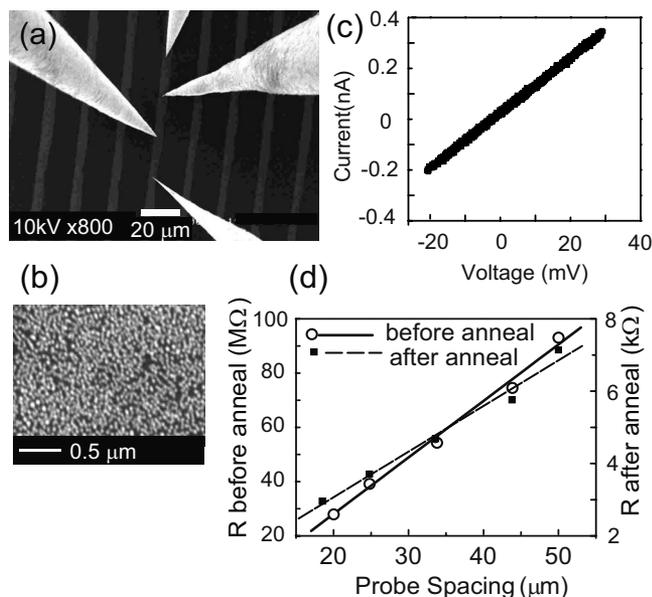


FIG. 3. SEM images of (a) the Au wire and the micro four point probes and (b) magnified image of the wire. (c) Current-voltage response of the single wire. Probe spacing is 50 μm . (d) Resistance of the wire as a function of probe spacing before and after annealing.

tivity, which changes to $1.6 \times 10^{-5} \Omega \text{ m}$ corresponding to a four order of magnitude smaller value. The resistivity is close to the one observed in the previous report of a nanoparticle film.¹³

We could not observe significant changes in the shape of the gold nanoparticles after the annealing in a magnified image such as Fig. 3(b). However, as has been proposed before,¹³ the functionality of the capping material may be lost by heating and Au–Au forms an electrical direct contact instead of sandwiching a ligand. We can speculate that the capping material is a citric acid, which has been used in the particle fabrication process.¹⁹ Though the decrease in the resistivity with a heating has been reported in the VCD report, the observed resistivity change was around ten. The difference is probably due to a monolayer nature of the synthesized stripes shown in this article, which is assumingly sensitive to an interface condition with neighboring particles. Similar large resistivity change is expected with a replacement of molecules in the interface between Au particles. Though we have not confirmed such gas sensitivity, the large resistivity change should be a potential candidate for gas sensors.

In summary, we have reported a formation method and an electrical characterization of aligned arrays of Au nanoparticles ($\sim 20\text{--}40 \text{ nm}$) on SiO_2 and GaAs substrates. Novel property of this method is that the periodicity of the arrays can be controlled by tuning the evaporation rate of solvent. The resistivity shows a drastic decrease ($\sim 10^{-5}$) when annealed at $\sim 170^\circ\text{C}$, which implies a high sensitivity to the interface conditions between Au nanoparticles and possible applications of molecule sensors.

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