

Controlled two-dimensional distribution of nanoparticles by spin-coating method

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We demonstrate that the controlled distribution of nanoparticles can be achieved by employing the spin-coating method. The Co and Ag nanoparticles were uniformly distributed on the Si and SiO₂ substrates with this method. The particle density was controllable by varying the concentration of colloids. The spatial distribution of the nanoparticles within the patterned area was also shown to be uniform with small boundary effect, which is favorable for current microelectronics technology. We propose that the spin-coating method can be utilized in developing mass production processes for future nanodevices. © 2002 American Institute of Physics. [DOI: 10.1063/1.1445811]

Nanoparticles have attracted much attention due to their potential application for various future high-performance devices, especially for the electronic devices such as single electron transistor¹ or floating-gate field effect transistor.² In these days, semiconductor and metal nanoparticles of the length scale ≤ 10 nm can be chemically synthesized³⁻⁷ with precise control of the size.⁸ Semiconductor nanoparticles may be placed easily on substrates of wider band gap semiconductors to form quantum dot arrays with better qualities than the heteroepitaxially grown structures.^{9,10} Metal nanoparticles can be used as catalysts to grow nanowires^{11,12} and as etch masks in nanolithographic processes to fabricate nanopillars¹³ and quantum dots.¹⁴ Transition-metal nanoparticles are also useful in fabricating high density magnetic recording media.¹⁵

In utilizing nanoparticles for device technology, one of the fundamental issues is how to distribute nanoparticles uniformly on patterned surfaces with precise control of density. In most studies, the self-assembly scheme has been employed using the chemical interaction between the nanoparticles and the substrate.¹⁶⁻¹⁹ This method is effective in achieving a dense layer of nanoparticles. However, the control of the particle density is difficult at submonolayer regime. Moreover, special chemical treatments are needed on the substrate surface, and the results are sensitive to the local chemical environment with enhanced defect susceptibility.

In this letter, we demonstrate that uniform distribution of nanoparticles with controllable density can be achieved using the conventional spin-coating method. We have spread colloidal Co and Ag nanoparticles on Si and SiO₂ wafers using the spin-coating method. The resulting particle distribution was uniform and the density was found to be controllable by varying the molar concentration of the colloids. On the pat-

terned surfaces, we observed that the nanoparticle density is slightly higher at the edge.

Co and Ag nanoparticles were prepared by chemical synthesis. Co nanoparticles were synthesized by a thermal decomposition process where 4 ml of 0.5 mol (M) Co₂(CO)₈ toluene solution was injected into hot toluene solution with 0.089 g of NaAOT [sodium bis(2-ethylhexyl) sulfosuccinate]. After refluxing for 6 h at 380 K and following centrifuge separation process, black colored Co nanoparticles were obtained in powder form. The AOT-stabilized Co nanoparticles were dispersed in toluene.²⁰ As compared to other methods,^{21,22} this hot injection process takes advantage of fast formation of monodisperse nuclei. The following growth process is slow and homogeneous to assure narrow size distribution and good crystallinity. Ag nanoparticles were obtained by alcohol reduction of silver acetate (AgAc) in the presence of polyvinyl pyrrolidone (PVP).²³ AgAc and PVP (0.167 g and 3.0 g, respectively) were dissolved in 20 ml of ethanol and then refluxed for 5 h. The resulting Ag nanoparticles were separated by centrifuge after the addition of acetone, and dispersed in ethanol. Figures 1(a) and 1(b) show the transmission electron microscopy (TEM) images of the prepared Co and Ag nanoparticles with average diameters of 8 nm ($\sigma=0.7$) and 20 nm ($\sigma=3.0$), respectively. X-ray dif-

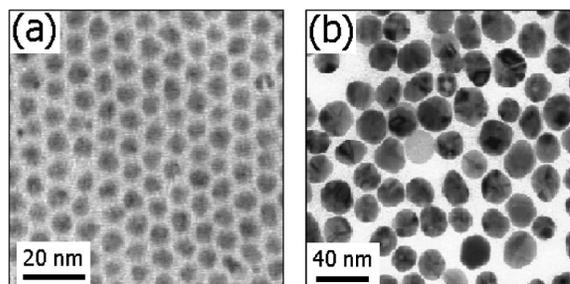


FIG. 1. The TEM images of the synthesized nanoparticles on TEM grid. (a) Co and (b) Ag particles with diameters of 8 nm and 20 nm, respectively.

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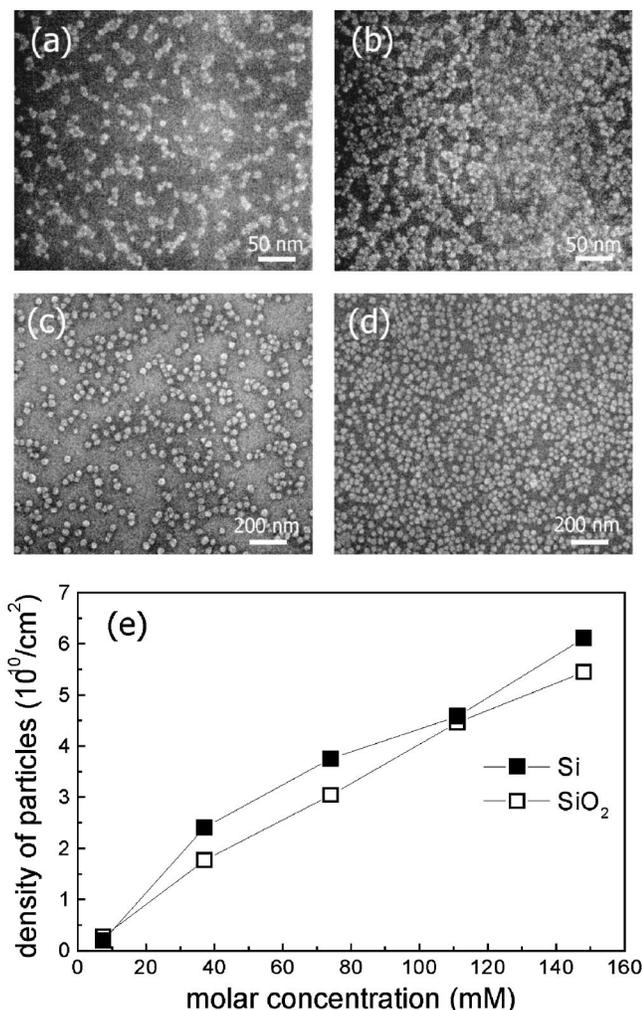


FIG. 2. The FESEM images of Co and Ag nanoparticles distributed on Si and SiO₂ wafers, respectively. The molar concentrations of the colloids used are (a) Co 5 mM, (b) Co 30 mM, (c) Ag 37 mM, and (d) Ag 148 mM. (e) The relation between the particle density of 20 nm Ag nanoparticles and the molar concentration of the colloids on the Si and SiO₂ wafers.

fraction analysis showed that these particles have face-centered-cubic structure.

We used the spin-coating method to spread the colloidal nanoparticles on wide areas of Si and SiO₂ wafers. One of the conditions to guarantee the uniform distribution of the nanoparticles is that the colloidal solution wets the substrate surface. Toluene and ethanol used as the solvents wet both Si and SiO₂ wafers. The Si surface was prepared by etching the native surface oxide of the Si wafer in diluted HF solution, and the SiO₂ surface was used as produced in factory. For easy control of the nanoparticle density on the surface, we fixed the rotational speed of the spin coater at 5000 rpm but varied the molar concentration of the colloids by dilution.

Figures 2(a)–2(d) show the field emission scanning electron microscopy (FESEM) images of the 8 nm Co [Figs. 2(a) and 2(b)] and 20 nm Ag [Figs. 2(c) and 2(d)] nanoparticles distributed by the spin-coating method on Si and SiO₂ wafers, respectively. The molar concentrations of the colloids were (a) 5 mM, (b) 30 mM, (c) 37 mM, and (d) 148 mM. The FESEM images show that the Co and Ag nanoparticles were uniformly distributed for all concentrations apart from some aggregation. The particle densities estimated from the images were Fig. 2(a) 2.5×10^{11} , Fig. 2(b) 8.2×10^{11} , Fig. 2(c) 2.3×10^{10} , and Fig. 2(d) 5.6×10^{10} particles/cm². Shown in Fig. 2(e) is the relation between the molar concentration and the resultant densities of the 20 nm Ag nanoparticle on the Si and SiO₂ wafers. The particle density monotonically increases with the molar concentration on both surfaces. More importantly, the particle density was reproducibly obtained for a given colloidal concentration.

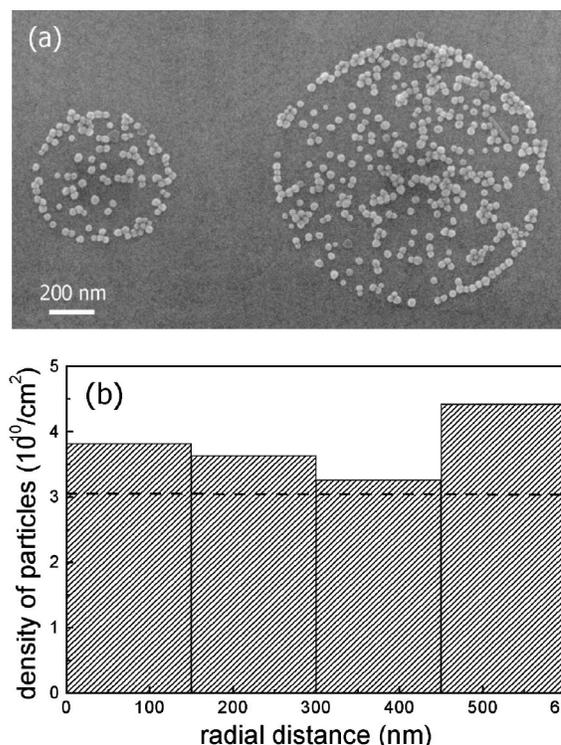


FIG. 3. (a) The FESEM images of Ag particles distributed within circular patterns with diameters of 0.6 (left-hand side) and 1.2 (right-hand side) μm formed on SiO₂ surface. The molar concentration of the colloid is 74 mM. (b) The density of Ag nanoparticles as a function of distance from the center of the 1.2 μm diameter circle. The broken line represents the average particle density on unpatterned surfaces at the same condition.

The densities of nanoparticles on the Si and the SiO₂ wafers were varied using the spin-coating method from below 1×10^9 particles/cm² up to saturation density near 1 monolayer. At low densities, the distribution was *random and uniform* over a wide area of the wafer. At higher densities, the nanoparticle interacts with neighboring particles and form two-dimensional clusters with local order. Below the saturation density, piling up of the nanoparticles to thicker layers was not observed. These observations were common to both Si and SiO₂ substrates.

To investigate the behavior of nanoparticles on patterned surfaces, we made circular patterns on the poly(methyl-methacrylate) (PMMA) resist by electron-beam lithography and distributed nanoparticles using the spin-coating method. The substrate was then baked at 400 K at ambient environment to burn the surfactant surrounding the nanoparticles and fix the nanoparticles on the substrate. Finally, the PMMA resist was removed in the lift-off process by acetone, leaving nanoparticles only within the exposed area.

Figure 3(a) shows a typical FESEM image of 20 nm Ag nanoparticles distributed within circular patterns from the 74 mM colloid. The radial distribution of the nanoparticles inside the pattern of 1.2 μm diameter [right-hand side circle in Fig. 3(b)] is shown in Fig. 3(b). The density of nanoparticles is relatively constant around 3.0×10^{10} particles/cm² until approximately 450 nm from the center, where it increases to about 4.5×10^{10} particles/cm². The broken line represents the average particle density on unpatterned surfaces at the same condition.

Figure 3(a) shows a typical FESEM image of 20 nm Ag nanoparticles distributed within circular patterns from the 74 mM colloid. The radial distribution of the nanoparticles inside the pattern of 1.2 μm diameter [right-hand side circle in Fig. 3(b)] is shown in Fig. 3(b). The density of nanoparticles is relatively constant around 3.0×10^{10} particles/cm² until approximately 450 nm from the center, where it increases to about 4.5×10^{10} particles/cm². The broken line represents the average particle density on unpatterned surfaces at the same condition.

Fig. 3(a)] is shown in Fig. 3(b). The average particle density was around 4.0×10^{10} particles/cm², higher than that on the unpatterned surface of the substrate [3.0×10^{10} particles/cm², dotted line in Fig. 3(b)]. Due to the bounding effect caused by the PMMA pattern, the local density of the particles is higher near the edge than near the center. It is interesting to find depleted region right inside the high-density boundary region.

The FESEM images in Figs. 2 and 3 show uniformity down to micrometer scale, but also indicate that the nanoparticles tend to aggregate preventing nanometer-scale uniformity. This aggregation might be due to some attractive interaction between the surfactant shells of the nanoparticles in the solvent. To achieve uniform two-dimensional distribution at nanometer scale, this tendency of aggregation should be effectively prohibited by introducing interparticle repulsion. One possible way is charging the nanoparticles, which will keep the nanoparticles apart from each other and prevent from gathering.¹⁶

The results of our study suggest that the simple spin-coating method can be applied efficiently to nanoparticle-related processes for the future nanodevice technologies. The mechanical nature of the spin-coating method enables the uniform distribution of nanoparticles over wide area once the proper solvent wetting the substrate surface are chosen. No chemical treatments on the surface is needed, unlike the self-assembly methods. The particle density on the surface is easily controllable by varying the concentration of nanoparticle colloids with the fixed rotational speed of the spin coater. This method is fully compatible with the conventional mass production techniques.

In conclusion, we have demonstrated that nanoparticles can be uniformly distributed on various substrates using the simple spin-coating method. We propose that the presented method is applicable in developing the practical mass production processes for the future nanodevice technologies.

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