Nanoparticle assembly on patterned “plus/minus” surfaces from electrospray of colloidal dispersion

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Abstract

Selective deposition of metal (Au) and oxide (SiO₂) nanoparticles with a size range of 10–30 nm on patterned silicon–silicon oxide substrate was performed using the electrospray method. Electrical charging characteristics of particles produced by the electrospray and patterned area created by contact charging of the electrical conductor with non- or semi-conductors were investigated. Colloidal droplets were electrosprayed and subsequently dried as individual nanoparticles which then were deposited on substrates, and observed using field emission-scanning electron microscopy. The number of elementary charge units on particles generated by the electrospray was 0.4–148, and patterned area created by contact charging contained sufficient negative charges to attract multiple charged particles. Locations where nanoparticles were (reversibly) deposited depended on voltage polarity applied to the spraying colloidal droplet and the substrate, and the existence of additional ions such as those from a stabilizer.

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1. Introduction

Nanoparticles with a size range of a few 100 nm show unprecedented chemical and physical behaviors, and have been extensively applied to electronic, magnetic, and optical industries. Application of nanoparticles to quantum devices, field emission display, single electron transistors, and data storage devices requires precise and accurate assembly of nanoparticles on desired patterns. Since recent electronic devices continue to be smaller, nanoscale patterning technology is absolutely necessary for the fabrication of tiny circuits for electrical control of small devices.

Gas jet deposition, ink jet printing, and self-assembly monolayer (SAM) can be applied to the deposition of nanoparticles on a plate with a specified pattern. In the gas jet deposition method, nanoparticles distributed in gas are ejected from a nozzle, and then are impacted and deposited on a plate. The ink jet route is also well-known technology. Droplets are dropped on a plate by continuously feeding suspensions with nanoparticles into a nozzle, and then particles in the droplets are deposited on a plate by evaporation of the droplets. For both gas jet deposition and ink jet printing, either the nozzle or the plate should be moved for drawing a pattern, therefore it is not easy to produce a clear pattern as only small vibrations occur, and the diameter of the nozzle is relatively too large (larger than 10 µm) to draw a line with a width of less than 10 µm. This is because resolution of the area depends on the diameter of the nozzle. SAM is useful to accurately array particles on a plate with specified patterns in few tens of seconds [1]. However, this process involves a liquid phase process, and therefore it is difficult to make particles deposit on a substrate in three dimensions. Moreover, several complicated steps such as a preparation of the substrate surface using a monomer, drawing of specified patterns on the prepared substrate using an electron beam, a UV lithography or an AFM (atomic force microscope), particle deposition on patterns in a suspension with particles, and rinse of the substrate with particles are required [2]. For a relatively simple drawing of nanoscale patterns with particles, additional improved methods using an aerosol phase process are required.
Electrospray is applicable to generate droplets with sizes in the order of 10–100 nm, and can be widely used in several applications such as electrospray ionization mass spectrometry for natural polymer (e.g., proteins, DNA) characterization [3], respiratory drug delivery [4], and microencapsulation [5]. In addition, since the generated droplets contain a number of charges, electrospray is useful for electrical control of single (individual) particles and for the production of well dispersed nanoparticles [6,7]. Therefore, it is expected that the electrospray method will be useful for positioning and arranging nanoparticles on a patterned substrate.

In this study, the electrospray route is used for gas-phase dispersion and direct deposition of nanoparticles on a solid substrate. Charging properties of particles generated in the gas phase by the electrospray were also investigated by an online measurement system. Electrified patterns are drawn with negative charges using a charge transfer across a conductive and non- or semi-conductor interface [8,9], and the electrical effects of the electrified pattern on the substrate are investigated. Finally, the nanoparticles will be deposited on the electrified pattern, and observed them by means of FE-SEM (field emission scanning electron microscopy) measurements.

2. Materials and methods

2.1. Electrospray system for generation of nanoparticles

Fig. 1 shows the schematic diagram for generation of nanoparticles, investigation of their electrical characteristics, and patterned deposition of particles on a silicon wafer (silicon–silicon oxidized substrate). The electrospray system consisted of a stainless steel capillary with an inner diameter of 100 µm, a substrate holder or a counter electrode made of a brass disk, and a chamber consisting of polyvinyl chloride and stainless steel for drying the generated colloidal droplets into nanoparticles. Suspension with nanoparticles was supplied into the capillary (with inner diameter of 0.1 mm) by a syringe pump (Model PHD 2000, Harvard Apparatus, Holliston). Polarity of particles generated by the electrospray was determined by voltage polarity applied to the capillary [7,10], therefore positive or negative voltages of a few kV could be applied to the spraying capillary through a DC high voltage supplier (Matsusada Precision, Kusatsu) for generating positively and negatively charged particles, respectively. The cone jet electrospray mode was used [6,7] as the proper condition for generation of stable and small droplets. The initial colloidal particles were dispersed in a mixture of water/methanol (50:50 vol%). The mixture ratio 50:50 of water/methanol has been widely used in electrospray studies especially in the field of mass-spectrometry. Scaling laws can be used to estimate the size of the droplets generated in the cone-jet mode [6,11]. It then can be predicted that it is necessary to prepare some conditions (e.g., liquid flow rate) in order to capture one particle in one droplet [6]. Experimental conditions based on multi-particles per one-droplet were also performed, however the results were not shown here. By increasing the feed rate of spraying solution, larger droplet can be formed and can transfer multi-particles [12]. When a positive voltage was applied to the capillary, N2 gas was fed into the spraying chamber. However, application of a negative voltage to the capillary did not allow the formation of a stable cone jet in N2 environment due to a discharge effect. Therefore, CO2 gas with a relatively high electrical breakdown threshold [13,14] was used as ambient gas for the cone jet mode of the electrospray when negative voltage was applied to the capillary. Distance from the end of the capillary to the counter electrode (i.e., the substrate) was fixed at approximately 10 mm. The counter electrode was connected to a digital electrometer (Model 6512, Keithley Instruments Inc., Cleveland) to confirm the cone jet mode of the...
electrospray through measurements of electric current carried by the electrospray [6,10,11]. Spray conditions were also precisely observed by an optical microscope and a CCD camera.

Sample nanoparticles consisted of SiO\textsubscript{2} particles with nominal diameters of 20–30 nm (suspension O-40) and 10–20 nm (suspension C) (Nissan Chemicals Industries, Ltd., Tokyo), and Au particles (20 nm, EY Laboratories, Inc., California). Suspensions with SiO\textsubscript{2} particles included a particular ion such as OH\textsuperscript{−} and Na\textsuperscript{+} to prevent particle coagulation, due to repulsive forces among particles (Nissan Chemical Industries, private communication). Besides, the fact shows that the additional ions play an important role in preventing nanoparticle coagulation, the liquid-phase ions probably affect not only the electrical characteristics of particles and gas-phase ions generated by the electrospray, but also the patterned deposition of particles on the substrate. Therefore, we investigated the electrical characteristics of electrosprayed particles and ions generated from the suspension C (SiO\textsubscript{2}) through a system of DMA (differential mobility analyzer; Model 3085, TSI, Inc., Shoreview, Minnesota)—CNC (condensation nucleus counter; Model 3022A, TSI, Inc.) and a DMA-FCE (Faraday cup electrometer) system [10,15], respectively. Particles and ions with opposite polarities to the voltage applied to the DMA can be classified, therefore the polarity of particles and ions generated from the electrospray can be identified by counting the number of classified particles and ions using the CNC and FCE systems, respectively. For some samples, zeta potentials, as an index of dispersion/aggregation of colloid particles, were measured using an electrophoretic light scattering spectrophotometer (ELS-8000 Photol, Otsuka Electronics, Co. Ltd., Osaka).

2.2. Electrified pattern on a substrate and its electrical properties

Fig. 2 illustrates the method for drawing a pattern of a silicon wafer/substrate with negative charges on an oxidized silicon surface. When a conductor comes into contact with a semi- or non-conductor, positive and negative charges are gathered in the conductor and semi- or non-conductor, respectively, due to their electrical potential difference [8,16]. Surface of the substrate should be hydrophilic (e.g., SiOH surface) to form patterns with charges [9]. In our study, the substrate was prepared by soninating them in NaOH solution for a few seconds, washing in ultra-pure water, and then drying under nitrogen atmosphere. The prepared substrate was mounted on a grounded brass plate, and areas (lines) of negative charge can be created by contact charging the solid surface by a grounded stainless steel needle. The needle was gliding over the substrate without applying pressure [17]. Another method to form the patterns of a substrate is using a stamp [1].

It is important to confirm the charges in the pattern, however the width of the patterned areas (lines) was too narrow to measure the charges. Here, charges in the patterned area were confirmed by comparing electrical potentials of a substrate (mm × mm) having area of few square millimeters with lots of patterned lines randomly prepared by gliding the stainless steel needle to substrates and a substrate without patterned lines. To measure non-contacting surface voltages, a high-sensitivity electrostatic voltmeter (Model 6000 B-7C, Trek, Inc., New York) was used.

2.3. Patterned deposition of nanoparticles on a substrate

The experimental system for patterned deposition of the particles is shown in Fig. 1. The substrate with a charged pattern attached on the end of the sampling rod was used instead of the counter electrode of brass ring. For deposition of particles generated by the electrospray on the substrate, the silicon–silicon oxidized substrate with a charged pattern was mounted on a brass plate that was attached to the end of a sampling rod, and positive or negative voltages and negative or positive voltages were applied to the capillary and the brass plate, respectively. Deposited particles on the substrate were observed using an FE-SEM (Field Emission-Scanning Electron Microscope; S-5000, Hitachi, Ltd.).

3. Results and discussion

3.1. Generation of particles using the electrospray method and their charging characteristics

Only charged particles with opposite polarity to that of the voltage applied to the DMA were classified by the DMA, so that mobility distributions of charged particles allowed the investigation of electrical characteristics of particles generated from the electrospray. Fig. 3 shows electrical mobility distributions of particles generated by feeding suspension C (with Na\textsuperscript{+} ions) into the capillary of electrospray while voltages of a particular polarity were applied to the capillary (\(V\textsubscript{1}\)) and the DMA (\(V\textsubscript{2}\)). It was clear that particles were not classified when polarities of \(V\textsubscript{1}\) and \(V\textsubscript{2}\) were identical, indicating that particles generated by the electrospray were charged with the same polarity as that of the voltage applied to the capillary, and additional ions (e.g., Na\textsuperscript{+}) for preventing particle coagulation had no effects on particle charging in the production of particles using the electrospray.

In a differential mobility analyzer, the number of elementary charge units on particles could be estimated by the ratio of measured electrical mobility to theoretical ones of particles with a specified diameter, \(Z_{\text{meas}}/Z_{\text{pth}}\) [18]. Diameter of SiO\textsubscript{2} particles in suspension C was 10–20 nm. \(Z_{\text{pth}}\) for singly charged particles

![Fig. 2. Method for patterning line with negative charges on a substrate.](image-url)
could be easily determined as 0.54–2.11 × 10⁻⁶ m² V⁻¹ s⁻¹ by the following equation:

\[ Z_p = \frac{peC_c}{3\pi\eta d_p^2}, \quad p = 1. \]  

Where, \( p \), \( e \), \( C_c \), and \( \eta \) are the number of elementary charge unit, the elementary unit of charge (1.6 × 10⁻¹⁹ C), the Cunningham correction factor, and the gas viscosity, respectively. The range of measured electrical mobility, \( Z_{\text{pme}} \) was 0.08–8 × 10⁻⁵ m² V⁻¹ s⁻¹, therefore, the number of unit charge on SiO₂ particles produced by the electrospray was estimated as 0.4–148. This indicated that particles produced by the electrospray had sufficient charges to enhance deposition efficiency and suppress the diffusion effect in the nanoparticle patterning process.

### 3.2. Electrified pattern on a substrate and its electrical properties

Fig. 4 shows surface potentials of patterned and non-patterned silicon–silicon oxidized substrates. Surface potential of a substrate with lots of patterns was lower than that without patterns. This observation results from the MOS (Metal Oxide Semiconductor) phenomena, i.e., contact of conductor to non- or semi-conductor allows electrons to transfer from the conductor to non- or semi-conductor and to remain on the pattern [8,9]. According to Krinke et al. [17], charge density could be estimated to be approximately 4000 elementary charges per square micrometers. Accordingly, it is believed that patterns of silicon/silicon-oxidized substrate written by a stainless steel needle have sufficient negative charges to deposit positively charged particles on the pattern of a substrate.

#### 3.3. Patterned deposition of nanoparticles on a substrate

In patterned deposition of Au nanoparticles with 20 nm diameter, a positive voltage of ∼2.4 kV and a negative voltage of ∼0.5 kV were applied to the capillary and the silicon–silicon oxidized substrate, respectively. Fig. 5 shows FE-SEM images of the substrate with patterns of Au particles. We clearly observed that Au particles were uniformly deposited on the patterned area (line), and the line of Au particles with a width of ∼100 nm and several millimeters in length formed on the substrate. Electrical potential of the patterned line (\( V_L \)) on silicon/silicon-oxidized substrate was lower than that of other parts (\( V_S \)), because negative charges have already attached and remained on the patterned line. Au particles produced by the electrospray were positively charged due to application of positive voltage to the capillary. Accordingly, the higher potential difference between the Au particles and the patterned line than that between the Au particles and other parts of the substrate resulted in a clear pattern of Au particles on the substrate.

Fig. 6 shows FE-SEM images for substrates with patterns of SiO₂ particles generated from suspension O-40. Since positive and negative voltages were applied to the capillary and the substrate, respectively, deposition of SiO₂ particles corresponded to the pattern applied with the stainless steel needle (Fig. 6a). However, when voltage polarities applied to the capillary and the substrate were reversed, the negatively charged SiO₂ particles were not deposited on the pattern but on the other parts of the substrate (Fig. 6b). These results were also shown in a previous research on nanoparticle patterned deposition from a gas phase [17]. In that reports, the authors explained that particle deposition on the other parts of the substrate was caused by negative charges on the patterned line of oxidized silicon substrate. Since negative charges were already deposited on the patterned line, application of positive voltage to the substrate caused a larger potential difference between the negatively charged SiO₂ particles and other parts of the substrate compared to that between particles and patterns. Thus, the other parts showed a
larger attractive force for negatively charged SiO\(_2\) particles than the patterned line with negative charges.

Similar experiments to those with suspension O-40 were performed for suspension C. In Fig. 7, it can be observed that deposition patterns of electrosprayed suspension-C were opposite to those obtained by suspension O-40. When applying negative and positive voltages to the capillary and the oxidized silicon substrate, respectively, negatively charged particles were deposited on the patterned line with negative charges (Fig. 7b); and when applying positive and negative voltages to the capillary and the substrate, respectively, they were deposited on other parts of the substrate (Fig. 7a).

According to the maker (Nissan Chemical Industries) Na\(^+\) ions were added in suspension O-40 for its stability. Since suspension C shows different results among the suspensions used in our study, one can suggest that Na\(^+\) ions affect patterned deposition of particles on the electrified substrate. We tried to compare electrical mobility distributions of ions produced from suspensions C and O-40. Fig. 8 shows measured electrical mobility distributions of ions generated from suspensions C and O-40. Suspension O-40 showed slightly higher detected ion currents than suspension C using FCE. However, it is difficult to conclude that this difference is caused by the presence of Na\(^+\) ions in suspension C because the difference was too small.

On the other hand, zeta potentials of the silica colloids were also investigated. It is well known that colloidal silica (e.g., products of Nissan Chemical Industries) has OH groups in the particle surface, and therefore is negatively charged in solvent/water. Silica C contains Na\(^+\) ions that are responsible for the formation of an electrical double layer. The as-received silica C has a pH of 8.6, which also indicates the existence of Na\(^+\) ions in the solution. Silica O-40, which has no Na\(^+\) ions, has a pH of 2.5. When measuring zeta potentials (Fig. 9), pH of silica (C and O-40, with a concentration of 20 wt\%) was changed by adding HCl, and pH at the isoelectric point could be determined. The isoelectric point of C
Fig. 7. FE-SEM images of substrate with patterns of SiO$_2$ particles for suspension C (initially has Na$^+$ ions); (a) for application of positive and negative voltages to the spraying-capillary (electrospray) and the substrate, respectively, (b) for application of negative and positive voltages to the spraying-capillary and the substrate, respectively.

Fig. 8. Electrical mobility distributions of ions produced from silica C (initially has Na$^+$ ions) and silica O-40, by their (a) positive and (b) negative electrosprays, respectively.

Fig. 9. Zeta potentials of silica C and O-40 colloidal solutions. (Concentration: 20 wt%. pH was changed by adding HCl.) (1.28) was higher than that of O-40 (0.79). These results indicated that in the case of silica C, some Na$^+$ ions were strongly attached to the OH group in the particle surface. Therefore, one would only need a small amount of H$^+$ ions (from HCl) for neutralizing the surface charge. In the case of O-40, since there is only one OH group in the particle surface, one would need more H$^+$ ions for neutralization, compared to silica C. In addition, we separately measured electrical conductivities of these silica solutions (20 wt%). Silica C and O-40 conductivities were $15.6 \times 10^{-2}$ S m$^{-1}$ and $4.43 \times 10^{-2}$ S m$^{-1}$, respectively. These results indicated that there were many ions (Na$^+$ ions) floating in the solution of silica C, compared with that of O-40.

Based on the existence of Na$^+$ ions, we investigated deposition patterns of SiO$_2$ particles by changing pH of suspension O-40 which was initially free of Na$^+$ ions, so that it reached the same pH as silica C. We added Na$^+$ ions (from NaOH) into O-40, and applied positive and negative voltages to the capillary and the substrate with a negatively charged pattern, respectively. Fig. 10 shows the FE-SEM microphotograph for the patterned deposition of SiO$_2$ particles on the substrate. Patterned deposition of SiO$_2$ particles in suspension O-40 with Na$^+$ ions was opposite to that for a suspension without Na$^+$. Accordingly, we suggest that ions consisting of Na$^+$ are probably produced when suspensions with Na$^+$ ions are electrosprayed, and electrical potential for the patterned line becomes larger than that for other parts of the substrate by pre-attachment of Na$^+$ ions on the patterned area/line.

4. Summary

Patterned deposition of nanoparticles on silicon/silicon-oxidized substrate was performed using the electrospray meth-
od. Particles produced by the electrospray and the patterned line created by contact charging contained sufficient unit charges to enhance deposition efficiency and suppress particle diffusion effect in the nanoparticle patterning process.

Clear patterns with particles produced by the electrospray formed on the oxidized silicon substrate. It was experimentally confirmed that not only voltage polarity applied to the capillary and the silicon/silicon-oxidized substrate, but also additional ions for suppressing particle coagulation in a suspension were important factors in the production of a desirable pattern by depositing particles on an silicon/silicon-oxidized substrate.

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