

Controlled Deposition of Silicon Nanowires on Chemically Patterned Substrate by Capillary Force Using a Blade-Coating Method

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We demonstrate a new method for depositing silicon nanowires (NWs) on selected areas of large-scale substrates with a high deposition yield. The method is based on blade-coating, which takes advantage of capillary force. First, water is blade-coated onto the chemically patterned substrate surface on which hydrophilic areas are surrounded by a hydrophobic self-assembled monolayer, selectively depositing water onto those areas. Second, before the water evaporates, a silicon NW dispersion is blade-coated onto the same surface, and in this step, the dispersion comes into contact with the water. An NW dispersion consists of water-insoluble solvent and NWs that have been chemically modified such that they tend to be adsorbed at the water/solvent interface due to capillary force or to minimize the free energy. Thus, in the second step, NWs position themselves on the hydrophilic areas after the water and dispersion solvent have evaporated. Using this method, NWs were selectively deposited on $2 \times 15 \mu\text{m}^2$ hydrophilic areas on a substrate with an area of 20 cm^2 with a probability over 0.9. We investigated the mechanism of NW deposition on the hydrophilic areas by the free energy calculation with the interfacial tension between NW and water, between NW and the solvent of the NW dispersion, and between water and the solvent. The energy calculation showed that the NWs are stabilized in the state where roughly half of the NWs sink into the water on the hydrophilic areas in the blade-coating process.

I. Introduction

Semiconductor nanowires (NWs) and carbon nanotubes (CNTs) have been intensively studied in the field of pure science and technical applications because of their unique electrical properties and diverse device behaviors.^{1–7} They are also promising candidates for components of electronic devices fabricated on flexible substrates, since they can be dispersed in a solution and deposited onto the substrates by solution processes at ambient temperature, at which the substrates do not degenerate. It is necessary to develop techniques for placing these materials in specific areas with desired configurations to be able to build useful devices using these materials. Many methods for depositing NWs or CNTs have been developed, including aligning NWs with the direction of an applied electric field,⁸ aligning NWs using fluidic flow,⁹ depositing CNTs on chemically patterned areas by electrostatic forces or van der Waals interaction,^{10–13} and aligning NWs using the Langmuir–Blodgett method.^{14–16}

In this paper, we present a new method for depositing silicon NWs on specific areas with a high deposition yield, applicable to depositing NWs or CNTs on large-scale substrates and useful for the mass production of devices. Our method is based on a blade-coating method that takes advantage of capillary force. Figure 1 shows our method in schematic form. First, water is blade-coated onto the chemically patterned substrate surface, on which hydrophilic areas are surrounded by a hydrophobic

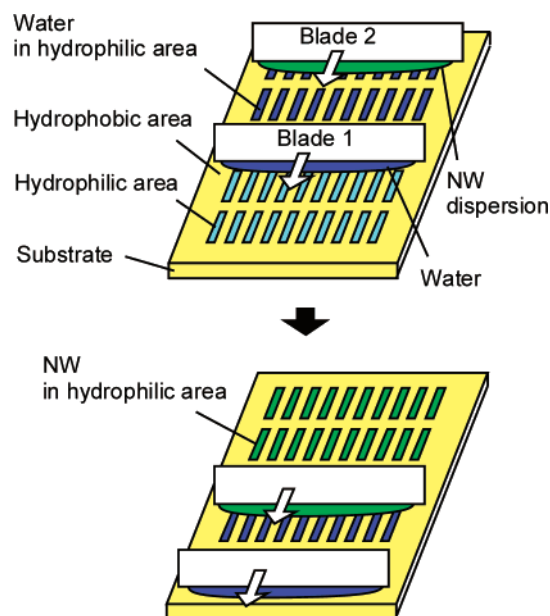


Figure 1. Schematic images of the NW deposition method, comprising two steps: (a) first, water is coated by blade 1 onto the chemically patterned substrate surface where hydrophilic areas are surrounded by a hydrophobic self-assembled monolayer, selectively depositing water on the hydrophilic areas, (b) second, before the evaporation of the water, silicon NWs dispersion is coated by blade 2 onto the same surface and in this step, the dispersion comes into contact with the water.

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self-assembled monolayer. In this step, water is selectively deposited on the hydrophilic areas. Second, before the water evaporates, a silicon NW dispersion is blade-coated onto the same surface, and in this step, the dispersion comes into contact

with the water. In our method, we chose a water-insoluble solvent for dispersing NWs and chemically modified the NWs such that they tend to be adsorbed at the water/solvent interface by capillary force or in order to minimize the free energy. Thus, in the second step, the NW dispersion solvent initially coats the water to prevent it from evaporating, after which the NWs are adsorbed onto the water/solvent interface. After the blade-coating of the NW dispersion, the NWs remain at the water/solvent interface and congregate in the hydrophilic areas during the evaporation of the water and solvent. Capillary force acting on a liquid/liquid interface has previously been used in assembling micro-structures, such as a variety of sizes of plates, micro devices, and cylindrical LEDs in hydrophobic areas with set configurations.^{17–23} However, to our knowledge, there are no reports on the use of capillary force acting on a liquid/liquid interface for the deposition of nanostructures such as NWs and CNTs, although the capillary force acting on a liquid/vapor interface has been used for deposition of CNTs and nanoparticles.^{24–26} Our studies of NW deposition on substrates have shown that NWs can be efficiently deposited on specific areas by a blade-coating method with the assistance of capillary force. Since the capillary force pulls the NWs into specific areas from the dispersion solvent, our method does not require NW dispersions with high concentrations, which are unstable and tend to precipitate. In addition, since the blade-coating method is widely used for coating various films onto large-scale substrates, our method is likely to be feasible for fabricating large-scale devices such as large flexible displays. In this work, we present our results on the deposition of silicon NWs on selected areas of a substrate with an area exceeding 20 cm² with high deposition yield and discuss the mechanism of NW deposition on the hydrophilic areas from the viewpoint of free energy calculations.

II. Experimental Section

Silicon NWs were synthesized by employing gold particles as a catalyst via vapor–liquid–solid growth.³ The gold particles with an average diameter of 100 nm were adsorbed onto a thermally oxidized, 6-in. silicon wafer whose surface had been chemically modified with 3,5-diaminopentyltrimethoxysilane. The wafer was placed in a cold-wall chemical vapor deposition chamber, and its temperature was held at 450 °C. A mixture of Si₂H₆ and H₂ was introduced into the chamber at 450 °C with a total pressure of 0.3 Torr for the prescribed time to synthesize NWs on the substrate. The silicon wafer was then annealed in oxygen gas at 1100 °C for 4 min to oxidize the NW surfaces. The average length and diameter of the NWs, viewed by SEM or TEM, were estimated to be 15 μm and 100 nm, respectively.

The NWs on the silicon wafer were chemically modified by dipping the wafer in 1 vol % 1-chloroethyltrichlorosilane in hexadecane and chloroform solution (4:1 in volume) for 3 h, followed by rinsing in chloroform in a dry nitrogen atmosphere. We chose 1,4-dichlorobutane as the solvent for NW dispersion, since its solubility in water is very low.²⁷ The dispersion of the chemically modified NWs was prepared by sonicating the wafers in 70 mL of 1,4-dichlorobutane for 15 min. The concentration of NW in the dispersion was estimated to be 0.002 wt % from inductively coupled plasma-atomic emission spectrometry. The NWs dispersion was stable, showing no precipitation over 6 months.

The 4 in.-diameter silicon wafers, covered with silicon nitride, were cleaned by oxygen plasma, and a photomicrographic process was applied to the wafer to make posi-resist patterns in the form of rectangles whose longitudinal side lengths were 15

μm and horizontal side lengths varied from 2 to 20 μm, lined up with a prescribed sideways spacing and lengthways spacing of 200 μm. The wafers were dipped in 1 vol % 2-perfluorooctylethyltrichlorosilane solution in perfluorooctane for 2 h, then rinsed with perfluorooctane in a dry nitrogen atmosphere. The resist film was removed from the wafer by dipping it in acetone. During these procedures, the 2-perfluorooctylethyltrichlorosilane adsorbs onto only the surfaces that are not coated with the resist films. Because the silicon nitride surface is hydrophilic and the self-assembled monolayer from 2-perfluorooctylethyltrichlorosilane is hydrophobic, the hydrophilic rectangle areas were surrounded by hydrophobic areas on the wafers.

For depositing NWs on the chemically patterned substrate, the water and NW dispersion layers were applied using a homemade blade-coater with one stainless steel plate and one glass plate. Both plates measured 50-mm long by 30-mm wide by 1-mm thick. Each blade was set with its surface facing a 2-mm spacing, and their edges faced the substrate at a distance of 0.2 mm. Water and NW dispersion were injected with glass pipettes between the plate edges and the surface so as to allow the meniscus to create a liquid curtain. The plates were moved at a velocity ranging from 2 to 35 mm/s in the direction parallel to the longitudinal side of the hydrophilic rectangle areas on the surface.

The interfacial tension between NW and water, $\gamma_{N/W}$, and between NW and dichlorobutane, $\gamma_{N/d}$, and between water and dichlorobutane, $\gamma_{W/d}$, were obtained experimentally to calculate the free energy change of the NWs and water/ dichlorobutane system, as follows. The $\gamma_{W/d}$ was estimated to be 45.0 mJ/m² by the drop weight method. To obtain $\gamma_{N/W}$ and $\gamma_{N/d}$, we assume that the surface energy of chemically modified NW, γ_N , is the same as that of the silicon substrate, γ_S , which was chemically modified using the same method as that for the NW, and thus $\gamma_{N/W}$ and $\gamma_{N/d}$ are the same as the interfacial tension between the chemically modified silicon substrate and water, $\gamma_{S/W}$, and between the chemically modified silicon substrate and dichlorobutane, $\gamma_{S/d}$, respectively. The values of $\gamma_{S/W}$ and $\gamma_{S/d}$ are respectively calculated from eqs 1 and 2,

$$\gamma_S = \gamma_W \cos \theta_W + \gamma_{S/W} \quad (1)$$

$$\gamma_S = \gamma_d \cos \theta_d + \gamma_{S/d} \quad (2)$$

where γ_W , γ_d , and θ_W , θ_d are the surface tension of water, dichlorobutane, and the static contact angle of water, dichlorobutane on the chemically modified silicon substrate, respectively. The values of θ_W and θ_d were estimated, respectively, to be 66.4° and 17.9° using an auto contact angle meter (Kyowa Interface Science: CA-Z). The values of γ_W and γ_d were estimated, respectively, to be 72.8 mJ/m² and 35.5 mJ/m² by the ring method. The value of γ_S is calculated by the Van Oss–Chaudhury–Good eqs 3 and 4,^{28–30}

$$\gamma_L(1 + \cos \theta) = 2(\gamma_S^{LW} \gamma_L^{LW})^{1/2} + 2(\gamma_S^+ \gamma_L^-)^{1/2} + 2(\gamma_S^- \gamma_L^+)^{1/2} \quad (3)$$

$$\gamma_S = \gamma_S^{LW} + 2(\gamma_S^+ \gamma_S^-)^{1/2} \quad (4)$$

where the γ_i is the surface tension, the superscripts S and L represent the chemically modified silicon substrate and liquid, respectively, the superscripts LW, +, and – refer to the apolar (Lifshitz-van der Waals) component, the electron-acceptor (Lewis acid) component, and the electron-donor (Lewis base) component, respectively, and θ is the static contact angle of

the liquid on the silicon substrate. The value of γ_s was obtained to be 40.5 mJ/m² by measuring the contact angle of three different liquids, water, ethylene glycol, and diiodomethane, whose γ_L^{LW} , γ_L^+ , and γ_L^- are known.³⁰ Using the value of γ_s , $\gamma_{s/w}$, and $\gamma_{s/d}$ were calculated, respectively, to be 11.4 mJ/m² and 6.7 mJ/m² from eq 1 and (2).

III. Results and Discussions

Figure 2 shows dark-field optical micrographic and secondary electron microscopic images of the substrate, on which $2 \times 15 \mu\text{m}^2$ hydrophilic areas are patterned, after one cycle of coating water and NW dispersion of 0.002 wt % at a velocity of 10 mm/s. Figure 3 shows a dark-field optical micrograph of the reference substrate on which only the NW dispersion was blade-coated, without the water-blade. Although the synthesizing conditions of NWs were set to grow rod-shaped NWs $15 \mu\text{m}$ in length, we also obtained NWs with other shapes, such as rod-shaped NWs with lengths greater or less than $15 \mu\text{m}$, particle-shaped NWs, or curved NWs. Thus in these microscopic images, a variety of shapes and sizes of NWs were observed on the substrate. The density of NWs on the substrate with water-blade coating was much greater than that without water-blade coating. Water-blade coating plays a crucial role in depositing NWs on the substrate. Even if water-blade coating is not employed, NWs might be deposited selectively on the hydrophilic areas with high yield. In this process, the NW dispersion is selectively deposited on the hydrophilic areas by blade-coating, followed by the adsorption of NWs onto the areas after the evaporation of the solvent carrying the dispersion. However, a dispersion with high concentration would be required. In this case, the NW concentration of the dispersion should be greater than that required for the volume of dispersion deposited on the hydrophilic area to include one or more NWs. A rough calculation indicates that it needs dispersions with NW concentrations of at least 1 wt % to deposit one NW per $2 \times 15 \mu\text{m}^2$ hydrophilic area.³¹ Although an NW dispersion with such a high concentration can be made up, it is unstable and tends to precipitate, and thus the blade-coating method using the NW dispersion is not reproducible and inadequate for the application to mass production of devices.

On the substrates with water blade-coating, one or more individual NWs formed an aggregation, and each aggregation lined up with an average sideways spacing of $7 \mu\text{m}$ and lengthways spacing of $200 \mu\text{m}$, as shown in Figure 2, parts a and b. Since the configuration of the aggregations is the same as that of hydrophilic areas, the NWs in each aggregation are likely to be positioned in hydrophilic areas. The selective deposition of NWs on the hydrophilic areas was also confirmed by the secondary electron microscopy image. Five $2 \times 15 \mu\text{m}^2$ hydrophilic areas surrounded by a self-assembled monolayer were imaged, as shown in Figure 2c. This image contrast results from the difference in secondary electron emission between the monolayer and the silicon nitride.³² In this image, rod-shaped NWs, particle-shaped NWs, and curved NWs are placed in each hydrophilic area, and the rod-shaped NWs are aligned parallel to the longitudinal side of the hydrophilic areas. A comparison of the configuration of NWs with that of the hydrophilic areas reveals that almost all of the NWs stayed within the hydrophilic areas and did not protrude from the areas, with some exceptions. These results demonstrate that our method is suitable for making electronic devices with NWs, since their position and alignment can be specifically decided by the hydrophilic shape, and thus they can be precisely connected to electrodes.

The alignment and number of NWs in a hydrophilic area should be affected by the shape of the area. To examine this

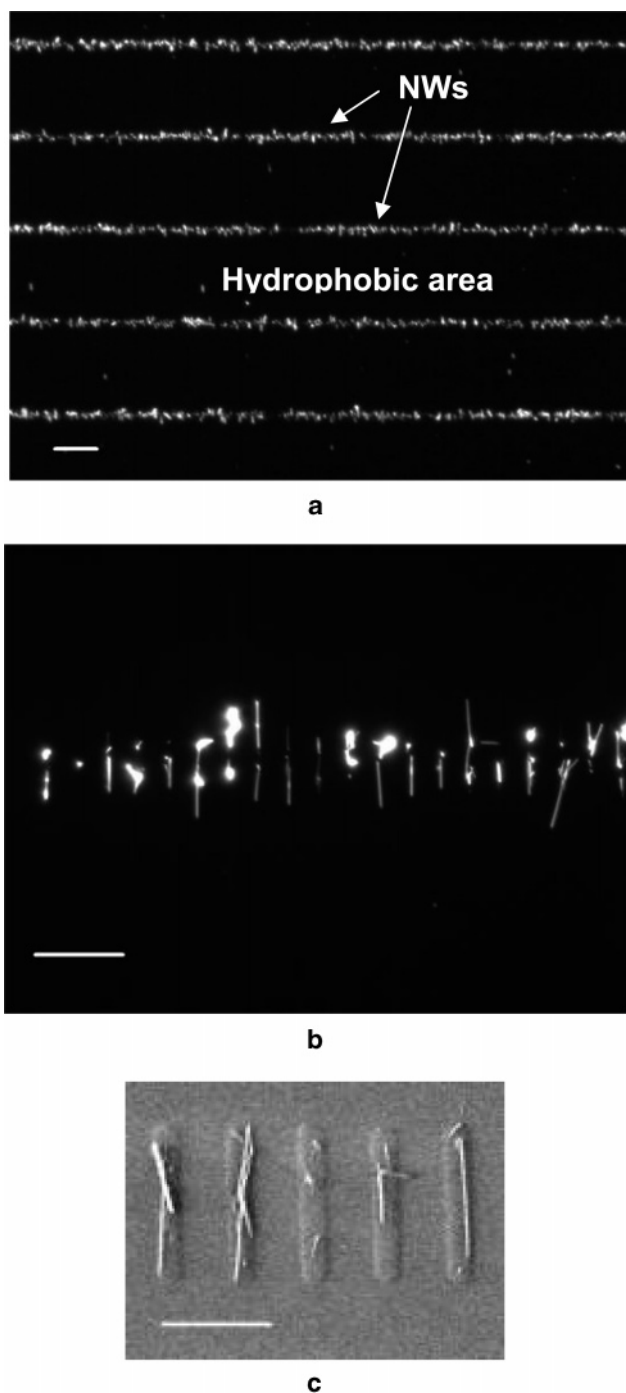


Figure 2. (a),(b) Optical dark-field microscopy images and (c) secondary electron microscopy image of the chemically patterned substrates after one cycle of the blade-coating of water and NW dispersion of 0.002 wt % at a velocity of 10 mm/s. The hydrophilic $2 \times 15 \mu\text{m}^2$ areas on the substrate line up with a sideways spacing of $7 \mu\text{m}$ and lengthways spacing of $200 \mu\text{m}$. The white areas correspond to NWs. The lengths of the white bars at the lower left of the images are (a) $100 \mu\text{m}$, (b) $20 \mu\text{m}$, and (c) $10 \mu\text{m}$ respectively. In these images, the blade-coating direction of NW dispersion corresponds to the longitudinal direction.

effect, an NW dispersion was blade-coated on the substrates whose surface had five kinds of hydrophilic rectangular areas with a longitudinal side length of $15 \mu\text{m}$ and various horizontal side lengths, W , of 2, 5, 10, 15, and $20 \mu\text{m}$. Figure 4, parts a, b, c, and d, shows typical dark-field optical micrograph images on the substrate at $W = 2, 5, 10$, and $20 \mu\text{m}$, respectively, after blade-coating with water and NW dispersion of 0.002 wt % at a velocity of 10 mm/s. The direction of the rod-shaped NWs

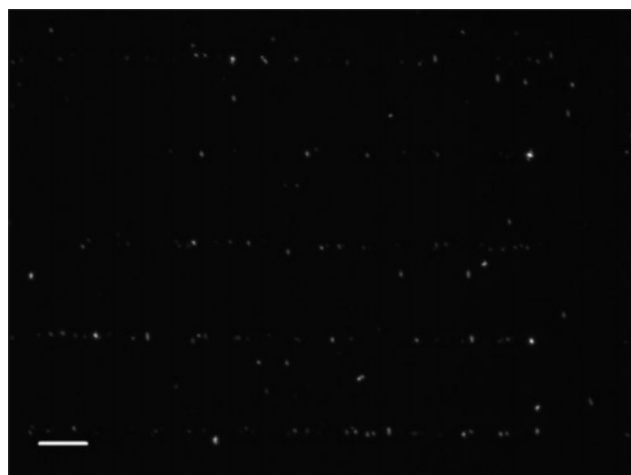


Figure 3. Optical dark-field microscopy image on the chemically patterned substrates after one cycle of the blade-coating of NW dispersion of 0.002 wt % at a velocity of 10 mm/s. The pattern of the hydrophilic areas on the substrate is the same as that of the substrate used for Figure 2. The white areas correspond to NWs. The white bar at the lower left of the image represents 100 μm . In this image, the blade-coating direction of NW dispersion corresponds to the longitudinal direction.

corresponds to the longitudinal direction of the image at $W = 2$, while they depart from the longitudinal direction at $W = 5$ and are almost random at $W = 10$ and 20. The direction of the rod-shaped NWs is likely to be restricted by the W value when the NW length is greater than W , and the angle between the NW and longitudinal direction becomes smaller as the difference between the NW length and W becomes larger. The NWs tend to gather at the periphery of the rectangular areas at $W = 10$ and 20, as shown in Figure 4, parts c and d. This gathering of NWs is likely to be caused by the entrainment of NWs by the water or solvent flow traveling to the periphery of the rectangular areas during their evaporation in these areas after blade-coating.³³ The average number of NWs in a hydrophilic area was estimated by counting the number of rod-shaped NWs with a length exceeding 5 μm in each hydrophilic area. Although differently shaped NWs, such as shorter rod-shaped NWs, particle-shaped NWs and curved NWs, were also placed in the areas and should be counted to arrive at an accurate number, we can get a rough estimate of the numbers in hydrophilic areas by counting only by the rod-shaped NWs. Figure 5 shows the relationship between the average number of NWs in a hydrophilic area and W , indicating that the number is proportional to W . NWs are deposited at the hydrophilic areas after they come into contact with the water on these areas during blade-coating. Because the probability of the contact should be proportional to the hydrophilic areas, which is itself proportional to W , the number of NWs was proportional to W .

To permit the mass production of devices with NWs, it is necessary for any NW deposition method to place NWs in the selected areas with a high deposition yield. The deposition probability of NWs onto a hydrophilic area was thus investigated. The NW dispersion was blade-coated onto substrates over 20 cm^2 in area whose surfaces had $2 \times 15 \mu\text{m}$ hydrophilic areas lined up with a sideways spacing of 7 μm and lengthways spacing of 200 μm . After blade-coating, 500 to 1500 hydrophilic areas, randomly selected from the substrates, were observed by optical microscopy. The deposition probability of NWs was deduced by dividing the total number of hydrophilic areas in which NWs were present by the number of hydrophilic areas observed. Our deposition method cannot discriminate the shape of NWs so long as the size of the NWs is small enough to be

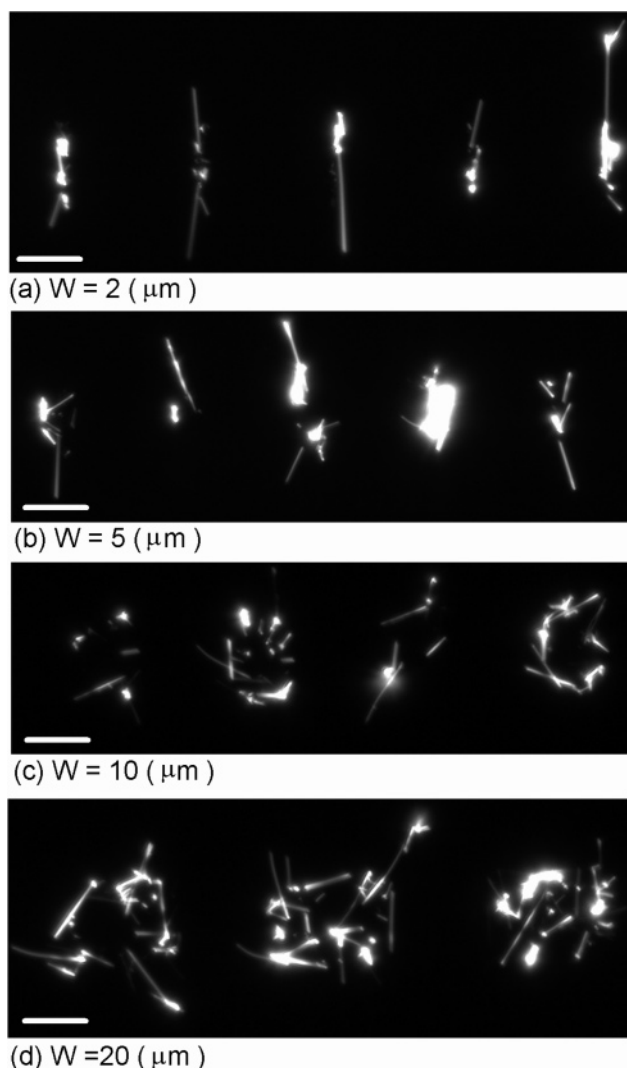


Figure 4. Optical dark-field microscopy images on the chemically patterned substrates whose surfaces have hydrophilic areas with a variety of shapes after one cycle of blade-coating with water and NW dispersion of 0.002 wt % at a velocity of 10 mm/s. The images show NWs (white areas) deposited at (a) five $2 \times 15 \mu\text{m}^2$, (b) five $5 \times 15 \mu\text{m}^2$, (c) four $10 \times 15 \mu\text{m}^2$, and (d) three $20 \times 15 \mu\text{m}^2$ hydrophilic areas. The white bars at the lower left of the images represent 10 μm . In this image, the blade-coating direction of NW dispersion corresponds to the longitudinal direction.

placed within the hydrophilic areas. Thus, in our estimation, we counted not only rod-shaped NWs 15 μm in length, but also other-shaped NWs to clarify the potential for high deposition yield of NWs using our method although this estimation method might overestimate the probability, which reflects on the process yield in fabricating devices. It is noted that our estimation did not count NWs which cannot be discriminated by optical microscopy, thus the probability deduced by our method might be smaller than that deduced by scanning electron microscopy images.

Figure 6a shows the probability dependence of the concentration of NW dispersion after blade-coating at a velocity of 10 mm/s. The probability increased with an increase in the concentration below around 0.003 wt % and levels off at around 0.003 wt %. Because the probability of the contact of an NW with the water in a hydrophilic area increases with an increase in the concentration, the deposition probability of NWs increased at concentrations below around 0.003 wt %. Concentrations above around 0.003 wt % should thus be large enough for NWs to deposit on almost all of the hydrophilic areas. After the

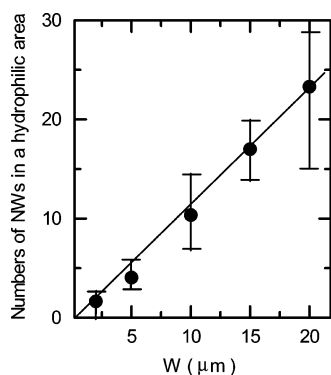


Figure 5. Relationship between the horizontal side length W of the hydrophilic areas and the average number of rod-shaped NWs with a length greater than 5 in a hydrophilic area. Each data item in the graph represents an average of the numbers of NWs at each of the 20 hydrophilic areas, and the error bar ranges between the maximum and minimum number in these areas.

saturation of the probability around 0.003 wt %, the number of NWs in the hydrophilic areas tended to increase with concentration. Figure 6b shows the probability dependence of the blade-coating velocity using the NW dispersion of 0.0018 wt %. The probability was almost constant below around 10 mm/s and decreased with velocities above around 10 mm/s. The decrease in probability above around 10 mm/s is likely to be caused by the decrease in the exposure period of NW dispersion to the hydrophilic areas during blade-coating. The water in the hydrophilic areas is likely to evaporate before the coating of NW dispersion over the water if the blade-coating velocity is too low, which decreases the deposition probability of the NWs. We speculate that two effects, water evaporation and increased exposure period of NW dispersion to the water with a decrease in the blade-coating velocity, compete with each other at velocities below around 10 mm/s, resulting in a constant probability. Figure 6c shows the probability dependence of blade-coating cycles with an NW dispersion of 0.002 wt % at a velocity of 10 mm/s. The probability was 0.94 for the first cycle, and increased with more cycles to reach 0.99 at the fourth cycle. Although the probabilities at second and fourth cycles were almost the same, the number of NWs in a hydrophilic area increased with an increase in the cycles (data are not shown). As one cycle of the coating was complete within 30 s in our method, it takes only 2 min for NWs to be placed on selective areas with a probability of 0.99. It is noteworthy that a high probability of deposition can be achieved using a dispersion with a low NW concentration of 0.002 wt %. These results indicate that a NW deposition probability of over 0.9 in the hydrophilic areas can be achieved by using NW dispersion with a concentration greater than 0.004 wt % or repeating blade-coating cycles at a suitable blade-coating velocity.

In our NW deposition method, the water-blade coating plays a crucial role in depositing NWs. We postulate that NWs are adsorbed at the water/solvent interface due to capillary force or to minimize the free energy. However, it was difficult to observe the adsorption process experimentally, since it occurs on a micrometer scale and within 1 s. However, we can confirm the validity of our postulation from free energy calculations. Figure 7a shows schematic sectional images of two states of the NW and water/solvent system. In this system, a column-shaped NW with a length of D and a radius of R is placed parallel to the water/solvent interface. The free energy difference E between the two states is a function of Z , the distance between

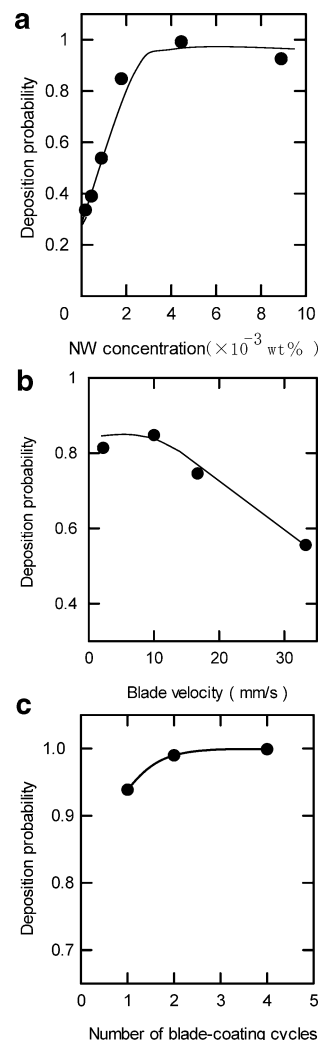


Figure 6. Dependence of the deposition probability of NWs onto $2 \times 15 \mu\text{m}^2$ hydrophilic areas on (a) concentration of NW dispersion, (b) blade-coating velocity, and (c) blade-coating cycle. (a) The NWs were deposited by blade-coating water and NW dispersion at a velocity of 10 mm/s. The probability was deduced from 500 hydrophilic areas on a substrate. The concentration of the NW dispersion was adjusted by the condensation or dilution of the NW dispersion with a concentration of 0.002 wt %. (b) The NWs were deposited by blade-coating water and NW dispersion with a concentration of 0.0018 wt %. The probability was deduced from 500 hydrophilic areas on a substrate. (c) The NWs were deposited by blade-coating water and NW dispersion with a concentration of 0.002 wt % at a velocity of 10 mm/s. The probability was deduced from 1500 hydrophilic areas on three substrates.

the water/solvent interface and bottom of NWs in the water. The value of E can be deduced from the eq 5,

$$E = LD(\gamma_{N/w} - \gamma_{N/d}) - DX\gamma_{w/d} \quad (5)$$

where L and X are the contact line length between water and solvent, and the distance of two points of a water/solvent/NW interface (see Figure 7a), respectively. The values of L and X are functions of Z and R , as shown in Figure 7a. The values of $\gamma_{N/w}$, $\gamma_{N/d}$, and $\gamma_{w/d}$ were experimentally deduced to be 11.4 mJ/m², 6.7 mJ/m², and 45.0 mJ/m², respectively. The relationship between E and Z/R is shown in Figure 7b for a NW of 100 nm in diameter and 15- μm length. The value of E falls to a minimum in the state where roughly half of the NWs sink into the water. This result supports our postulation that NWs are adsorbed onto the water/solvent interface so as to minimize the

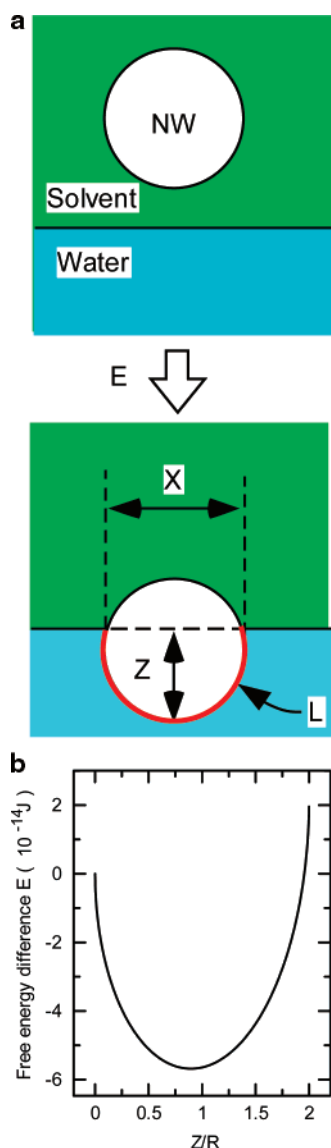


Figure 7. (a) Schematic sectional images of the two states around the solvent/water interface, NW dispersed in solvent (upper), or NW in contact with water (lower). The variable E indicates the difference in the free energy between the two states. In this image, a column-shaped NW is placed parallel to a water/solvent interface. The variables L , X , and Z are the contact line length of the water and solvent (red line length), the distance of two points of a water/solvent/NW interface (dashed line length in NW), and the distance between the water/solvent interface and the NW bottom in the water, respectively. (b) Free energy difference dependence of Z/R for a NW of radius 50 nm R and length $15 \text{ }\mu\text{m}$.

free energy. Capillary force acts on the NWs and minimizes the free energy. After the blade-coating of water and NW dispersion, the water and NW dispersion remain in the hydrophilic areas where NWs are adsorbed onto the water/solvent interface. The NWs migrate to hydrophilic areas during the evaporation of the water and solvent.

CNTs have been selectively deposited on amino group-modified surface areas by electrostatic interaction between the negatively charged CNT and positively charged amino-groups.^{10–12} Liu et al. reported that by using this method, CNTs could be selectively deposited on amino-group modified areas at a probability of about 0.7.¹¹ Our method is similar to that for CNT deposition in the sense that both methods use chemically patterned substrates. However, the driving force for bringing NWs into hydrophilic areas in our method is not electrostatic

force, since the water on the hydrophilic areas plays a crucial role in the deposition of NWs. In our early studies in NW deposition, we expected that NWs could be effectively deposited onto aminosilane-modified surfaces, because the NW surface has negatively chargeable silanol groups, and amino groups on the substrate can be positively charged. However, no critical differences were found between NW densities on the chemically modified substrate and the unmodified substrate after coating NW dispersion onto these substrates. We assume that the different adsorption behavior between NWs and CNTs is caused by their volume difference: NWs are about $1000\times$ larger than CNTs, and the larger the volume, the smaller the electrostatic effect. However, more detailed analysis is needed, which will be reported elsewhere.

IV. Conclusions

We have demonstrated a new method for depositing NWs on selected areas with a high deposition probability. Using this method, NWs were selectively deposited and aligned on $2 \times 15 \text{ }\mu\text{m}^2$ hydrophilic areas on the substrate over 20 cm^2 areas with a probability exceeding 0.9. The mechanism of NWs deposition onto the hydrophilic areas were investigated from the viewpoint of free energy calculation. The calculation showed that the NWs are stabilized in the state where roughly half of the NWs sink into the water on the hydrophilic areas in the blade coating process.

Since our method is based on a blade-coating method that is widely used for printing various inks onto large-scale substrates, it has potential for application to the manufacture of large devices with NWs and scaling up for mass production. To confirm the potential of our method, it is important to clarify the relationship between the deposition probability and the number of rod-shaped NWs with a defined length in a hydrophilic area and to find out the factor controlling the numbers of NWs because the electronic properties of the devices with NWs, such as field effect transistors, vary with the number. However, it was difficult in our experiment to deduce a meaningful relationship using our NW dispersion, which includes a variety of shapes of NWs; it is not clear whether the deposition probability of rod-shaped NWs with $15 \text{ }\mu\text{m}$ and the other-shaped NWs are the same, or whether other-shaped NWs present at the hydrophilic area disturb the deposition of rod-shaped NWs into the same area, or vice versa. To deduce the dependence of the deposition probability on the number of the NWs in a hydrophilic area, NW synthesizing conditions should be optimized so as to grow only the rod-shaped NWs and use the dispersion including only rod-shaped NWs for NW deposition. This is in progress in our laboratory.

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