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Microcontact Printing for Patterning Carbon Nanotube/Polymer Composite Films with Electrical Conductivity

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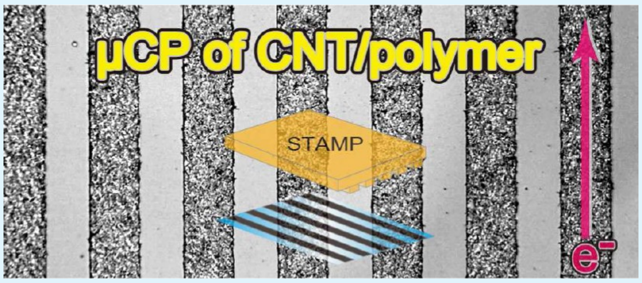

ABSTRACT: Patterned carbon nanotube (CNT)/acrylic resin composite films were prepared using microcontact printing (μCP). To prepare ink for μCP, CNTs were dispersed into propylene glycol monomethyl ether acetate (PGMEA) solution in which acrylic resin and a commercially available dispersant (Disperbyk-2001) dissolved. The resulting ink were spin-coated onto poly(dimethylsiloxane) (PDMS) stamps. By drying solvent components from the ink, CNT/polymer composite films were prepared over PDMS stamps. Contact between the stamps and glass substrates provided CNT/polymer composite patternings on the substrates. The transfer behavior of the CNT/polymer composite films depended on the thermal-treatment temperature during μCP; thermal treatment at temperatures near the glass-transition temperature (T_g) of the acrylic resin was effective to form uniform patternings on substrates. Moreover, contact area between polymer and substrates also affect the transfer behavior. The CNT/polymer composite films showed high electrical conductivity, despite the nonconductivity of polymer components, because CNTs in the films were interconnected. The electrical conductivity of the composite films increased as CNT content in the film became higher; as a result, the composite patternings showed almost as high electrical conductivity as previously reported CNT/polymer bulk composites.

KEYWORDS: *microcontact printing, carbon nanotube/polymer composite, patterning, electrical conductivity, dispersion, film*

1. INTRODUCTION

Carbon nanotube (CNT) films are expected to be useful devices, because of the excellent electrical, chemical, and physical properties of CNTs.[1] Polymer films containing CNTs (CNT/polymer composite films) are also promising materials; in some applications, the composite films are needed to be patterned in micrometer scale. For example, patterned CNT/polymer composites are potential organic light-emitting diodes (OLEDs).[2,3] Moreover, other applications of CNT/polymer composite patternings have been proposed, including use as sensors,[4,5] transparent electroactive materials,[6,7] and organic transistors.[8]

Photolithography is a well-known patterning method and widely used in industrial fields such as the fabrication of semiconductor devices and liquid crystal display (LCD) panels. Nevertheless, the development of alternative methods to photolithography has been desired,[9] because photolithography requires expensive instruments and is difficult to apply for substrates with complex structures. From this viewpoint, some nonconventional patterning techniques, such as nanoimprinting and inkjet printing, have been investigated.[10,11]

Microcontact printing (μCP) is a promising alternative to photolithography.[12−16] Its unique feature is to use stamps and inks to prepare patternings. Stamps (typically, poly(dimethylsiloxane) (PDMS)) with micrometer-sized relief patterns are immersed in or coated with inks containing a variety of materials; subsequently, the stamps are contacted with substrates. After peeling off the stamps, materials on the raised parts of the stamps form patternings over the substrates if they have stronger interaction and adhesion with substrates. The advantages of μCP are its simplicity (expensive instruments and severe reaction conditions are not necessary), applicability to curved substrates because of the flexibility of stamps, and a diversity of patternable materials. To date, numerous materials such as thiols,[12] CNTs,[17−19] DNA,[20−22] nanoparticles,[23−25] metal thin films,[26,27] and polymers[13] have been patterned via μCP.

Nevertheless, μCP of nanoparticle/polymer composites (including CNT/polymer composites) has been rarely reported, probably because of the following reasons. To prepare composite patternings by μCP, the composite particles must be highly dispersed in inks, but it is not easy to disperse nanomaterials, because they have high surface energy, which results in the aggregation of nanomaterials. Moreover, to transfer polymers via μCP, adhesion between polymer films and substrates should be suitably controlled (e.g., electrostatic interaction and physisorption of polymer for substrates, or thermal treatment to increase the adhesion of the polymer).[13]

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To date, there is very little research on μCP of CNT/polymer composites. Chang et al. reported that CNT/poly(3,4-ethylendioxythiophene)-poly(styrenesulfonate) composites ink stored in the recessed part of PDMS stamps could be transferred onto Si wafers.[28] The ink stored in the recessed part of PDMS stamp turned into parallel line-patternings through a gradually evaporating solvent. Their method is different from conventional μCP in which the raised part of stamps is used to form patternings and, therefore, might be preferable to preparing thin line-patternings but the morphological control of the patternings is limited, because of its peculiar process. Liu and Choi fabricated conductive composites through μCP of CNT/PDMS.[29] They transferred CNT/PDMS ink solution to substrates. Although this is a typical μCP process, the resolution of the patternings would be low, because of the use of solution-typed ink; indeed, only line-patternings with widths of several hundred micrometers were shown in their research.

In this study, we show CNT/polymer composite patternings can be simply prepared via conventional μCP. After spin-coating CNT/polymer composite dispersions over PDMS stamps, the volatile component was dried to form CNT/polymer composite films on the stamps. To transfer the CNT/polymer composite films from the stamps to substrates, we used thermal μCP methods that had been proposed to prepare polymer patternings.[30−34] This is the first study to transfer CNT/polymer solid films via μCP. Hereafter, effects of preparation process of inks, temperature of thermal μCP, pattern size, shapes of substrates, and CNT content in inks on μCP of CNT/polymer composites were examined. In addition, we investigated electrical conductivity of the CNT/polymer films.

2. EXPERIMENTAL DETAILS

2.1. Materials. Photoresist (PMER P-LA 900; Tokyo Ohka Kogyo Co., Ltd.), hexamethyldisilazane (Tokyo Ohka Kogyo Co., Ltd.), 2.38 wt % of tetramethylammonium hydroxide aqueous solution (NMD-W; Tokyo Ohka Kogyo Co., Ltd.), propylene glycol monomethyl ether acetate (PGMEA; Wako Chemical Co., Ltd.), acrylic resin dissolved in PGMEA (Acrycure, from Nippon Shokubai Co., Ltd.; the acrylic resin was 40 wt %), dispersant dissolved in PGMEA/butyl glycol/propylene glycol monomethyl ether solution (Disperbyk-2001; BYK Japan KK; nonvolatile content was 46 wt %), and CNTs (Showa Denko Co.) were used as received. Properties of the CNTs are as follows: average diameter = 150 nm; length = 10−20 μm; resistivity of bulk and individual CNTs = ca. 1×10^{-2} and 1×10^{-4} Ω cm, respectively. An SEM image of the CNTs is shown in Figure 1.

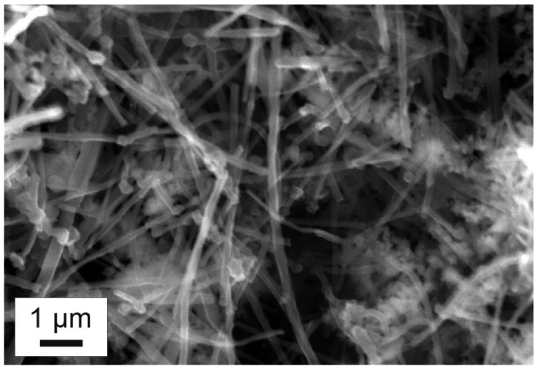

Figure 1. SEM image of carbon nanotubes (CNTs).

2.2. Preparation of PDMS Stamps. ITO plates (10 Ω, 2.5 cm × 2.5 cm; Geomatic Co., Inc.) were sonicated in acetone for 10 min and subsequently in ethanol for 10 min, followed by being dried in air. Hexamethyldisilazane was spin-coated on the ITO plates (1000 rpm, 5 s; 4000 rpm, 30 s). After baking the sample at 343 K for 3 min on a hot plate, photoresist was spin-coated on the samples (300 rpm, 10 s; 1000 rpm, 60 s). After baking the sample at 383 K for 5 min, the samples were kept at room temperature for 60 min. UV (1500 mJ/cm^2) was exposed on the samples through a photomask. The resulting samples were developed by immersing into tetramethylammonium hydroxide aqueous solution for 10 min, followed by being washed with water and dried at room temperature. The resulting micropatterned mold was replicated using Sylgard 184 (Dow Corning) with a PDMS/crosslinker ratio of 10/1. The obtained PDMS stamps were cut to be 20 mm × 20 mm. Prior to using them for μCP, their surfaces were exposed to oxygen plasma (SEDE-P; Meiwafosis Co., Ltd.) and they were stored in deionized water.

2.3. Preparation of CNT/Polymer Ink. The compositions of the CNT/polymer ink solutions are shown in Table 1. As an example, preparation procedures for 10 g of ink with 2.0 wt % CNTs will be described below. A mixture solution of dispersant (0.1 g) and PGMEA (3 mL) was stirred until the dispersant was dissolved (note that the amount of PGMEA was changed with content of CNTs). CNTs (0.2 g) were added into the solution and stirred with glass beads (2.5−3.5 ⌀mm) overnight. Polymer solution (1.5 g) dissolved in PGMEA (5.5 mL) was added into the CNTs−dispersant−PGMEA solution, followed by being stirred with the glass beads for 1 h.

Table 1. Composition of Ink Solution and Content of CNTs in the Composite Films

content of ink (wt %)				
CNTs	acrylic resin solution	dispersant solution	PGMEA	content of CNTs in composite films (wt %)
0.1	15	0.05	84.85	1.6
1.0	15	0.5	83.5	14
2.0	15	1.0	82	24
4.0	15	2.0	79	37
6.0	15	3.0	76	45

2.4. μCP of CNT/Polymer Films. The plasma-treated PDMS stamps stored in deionized water were dried using an air blower. The stamps were sonicated in PGMEA solution for 10 min and dried using an air blower. After the CNT/polymer ink solution was deposited dropwise over the PDMS stamps using a pasteur pipette, the ink solution was spin-coated (300 rpm for 10 s) on the stamps that were attached to glass plates using adhesive tape. The stamps spin-coated with ink were dried at 363 K on a hot plate to remove solvent component (i.e., solvents in the dispersant solution and the polymer solution, and PGMEA). Consequently, CNT/polymer films were formed on the PDMS stamps. The CNT content in the dried composite films is shown in Table 1 (CNT content in the film was estimated taking account of a process that PGMEA solvent and solvents in the commercially available dispersant and polymer were removed by heating). The PDMS stamps coated with CNT/polymer composite films were contacted with glass substrates, and a pressure (130 g/cm^2) was applied on them using metal blocks at 303, 333, 363, and 393 K for 5 min. When using glass tubes (outer diameter = ca. 0.72 cm) as substrates, the glass tubes were heated on a hot plate at 363 K for 5 min and the spin-coated stamps were contacted with the heated area of the glass tubes for 5 min. In this case, the stamps were manually contacted with the glass tubes, because the application of pressure using metal blocks was difficult due to columnar shapes of the glass tubes. After contacting, the stamps were carefully peeled from the substrates.

2.5. Characterization. Optical micrographs were taken using a digital microscope (Model VHX-200; Keyence). SEM images were recorded using a Model VE-8800 system (Keyence). A thin Au layer (ca. 15 nm) was deposited on specimens by magnetron sputtering prior to the SEM measurements. A conformal laser scanning microscope (VK-8500; Keyence) was used to measure three-dimensional (3D) images and height profiles. The film thickness (d) was estimated using a DEKTAK 3 system. Sheet resistances (R_s) of the films were measured by a four-point probe method, using a manual prober (Model HMP-200; HiSOL, Inc.). The electrical resistivities (ρ) were calculated on the basis of the following expression:

$$\rho = R_s d$$

The differential scanning calorimetry (DSC) measurements were performed using a differential scanning calorimeter (SII Nanotechnology, EXSTAR DSC7020) under a dry nitrogen flow at heating and cooling rates of 10 K/min, with 9.8 mg of samples, which were dried under vacuum before the measurements.

3. RESULTS AND DISCUSSION

3.1. Patterned CNT/Polymer Composites.

CNT/polymer composite patternings prepared by μCP at 363 K were characterized using SEM, optical microscopy, and conformal laser scanning microscopy. Figures 2a and 2b shows optical micrograph images of CNT/polymer composite patternings and a PDMS stamp after μCP. We can see that line-patterned CNT/polymer composites were uniformly formed on a glass substrate (Figure 2a) and the composite materials were completely removed from the raised parts of stamps; in contrast, the composite materials were present on their recessed parts (Figure 2b). The results indicate the successful transfer of CNT/polymer films from the raised parts of the stamps. Not only line-patternings but also circular-shaped CNT/polymer composite patternings could be prepared (Figure 2c). Film thickness of the composite films was estimated to be submicrometer from height profiles of 3D images (Figure 2d). The film thickness was almost the same in the patternings (except for their edge areas), because the spin coating provides uniform films on the PDMS stamps. The pattering method had repeatability; moreover, we could reuse the PDMS stamps by washing them in PGMEA under sonication after μCP.

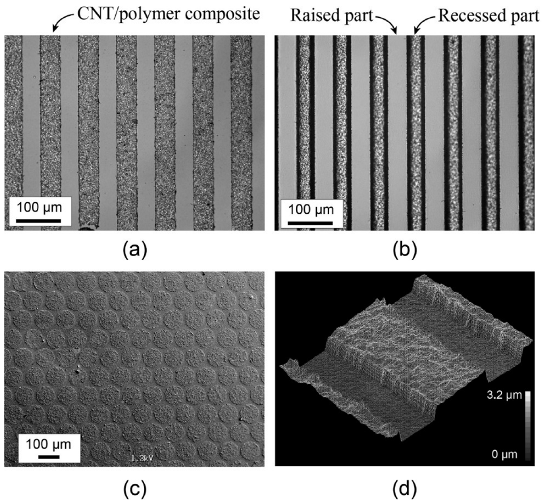

Figure 2. Optical micrograph images of (a) a line-patterned CNT/polymer composite and (b) a PDMS stamp after μCP. (c) SEM image of a circular-patterned CNT/polymer composite. (d) Three-dimensional (3D) image of a line-patterned CNT/polymer composite. Contact temperature: 363 K; CNT content in films: 24 wt %.

The transferable pattern size was limited by the length of CNTs. We tried to prepare line-patterned CNT/polymer composites 5 μm wide, but instead of forming line-patternings, all films on both raised parts and recessed parts were transferred over substrates. When preparing several micrometer-sized CNT/polymer composite patternings, CNTs present on raised parts possibly protrude to recessed parts or next raised parts of stamps. In this case, the protruded CNTs can act as glue; all the composite films on the stamps are transferred through μCP.

3.2. Effect of Thermal Treatment in μCP.

The glass-transition temperature (T_g) is the temperature at which some properties of polymers such as stiffness, heat capacity, and thermal expansion are drastically changed, and the value of T_g depends on several factors, such as chemical structure and film thickness of polymers.[35] As described earlier, some researchers reported that polymer films were transferred through μCP under heating at above their T_g, and they presume that the thermal treatments soften the polymer films, so that the films are removed from stamps.[30−34] However, the effect of the thermal-treatment temperature on μCP of polymer films has not been examined experimentally. Thus, we investigated whether thermal treatment at temperatures above T_g is necessary for μCP of CNT/polymer composite films. The T_g value of the acrylic resin used in this study measured from its DSC thermogram was 344 K (see Figure 3). Figure 4 shows optical images of CNT/polymer patternings transferred at different contact temperatures (303, 333, and 393 K). The optical image of patternings prepared at 363 K of contact temperature has already been shown in Figure 2a. From these images, it seems that the transfer behavior depended on the thermal-treatment temperature. Composite films were completely transferred at 363 and 393 K, while incomplete transfer of films was observed at 303 and 333 K. Taking account of T_g of the polymer in the film (344 K), it could be concluded that the CNT/polymer composite films are uniformly transferred when heating at higher temperature than the T_g of the polymer.

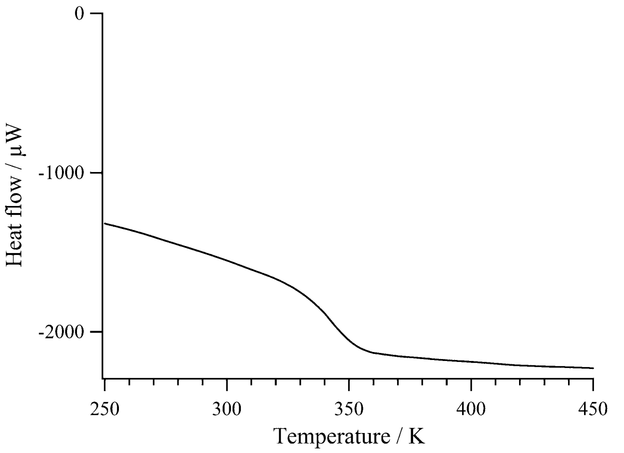

Figure 3. Differential scanning calorimetry (DSC) thermogram of acrylic resin used in this study.

3.3. Properties of Ink.

To prepare well-dispersed CNT/polymer ink solution, both the commercially available dispersant (modified acrylate block copolymer), which has been applied to disperse CNTs in solutions,[36−38] and stirring with glass beads, which brings about large shearing force, were necessary. Figure 5 shows optical micrograph images of CNT/polymer films that were prepared by spin-coating inks over glass substrates. The inks were prepared under four different

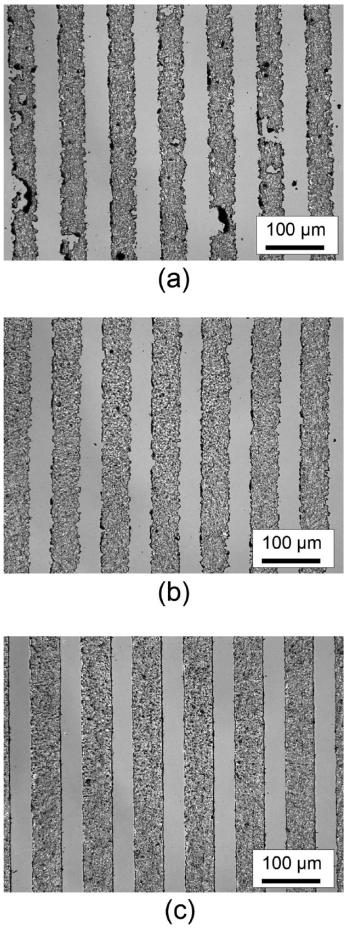

Figure 4. Optical micrograph images of CNT (24 wt %)/polymer composite patternings. Contact temperatures: (a) 303, (b) 333, and (c) 393 K.

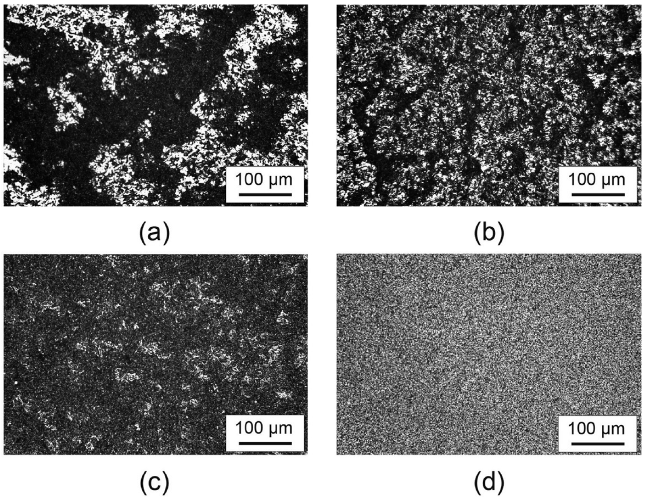

Figure 5. Optical micrograph images of CNT/polymer composite films. The films were prepared with spin-coating of inks (300 rpm for 5 s and 1000 rpm for 50 s), followed by being dried at 363 K. The inks were prepared in similar ways as in section 2.3 under four different stirring conditions: (a) without both the dispersant and the glass beads, (b) with the dispersant and without the glass beads, (c) without the dispersant and with the glass beads, and (d) with both the dispersant and the glass beads.

stirring conditions: (a) without both the dispersant and the glass beads, (b) with the dispersant and without the glass beads, (c) without the dispersant and with the glass beads, and (d) with both the dispersant and the glass beads. Clearly, large aggregates of CNTs are nonuniformly present on the substrate without the aid of the dispersant and the glass beads (Figure 5a). By stirring with either the dispersant or the glass beads (Figures 5b and 5c), the size of aggregates became small, but CNTs was not distributed evenly. In contrast, it seems that well-dispersed CNTs were uniformly deposited when the ink was prepared by stirring under both the dispersant and the glass beads. It is well-known that nanomaterials including CNTs are likely to aggregate, to reduce their high surface energy. The dispersant adsorbs onto CNTs and provides the steric hindrance, which prevents CNTs from aggregating. Stirring is also an important factor that affects the dispersed state of CNTs in the solutions.[39] In this study, large shear force induced by stirring under the glass beads broke the aggregation of CNTs.

Next, we will discuss the role of solvent in ink solutions. After spin-coating the ink over stamps, solvent in the ink was removed to prepare CNT/polymer films on the stamps; nevertheless, the presence of solvent is essential in this μCP process. Solvent lowers the viscosity of the ink, which facilitates homogeneous spread of ink over the stamps, and low viscosity allows excellent dispersion of CNTs in solutions. In this study, we used PGMEA (propylene glycol monomethyl ether acetate) as the solvent in ink because of the following reasons. The first reason is that polymer (i.e., acrylic resin) and the dispersant completely dissolve in PGMEA, but PDMS does not dissolve in PGMEA. Insolubility of PDMS stamps for the solvent is important to keep their patterned structure after spin-coating ink solution. Moreover, the extreme high boiling point is unfavorable for evaporating the solvent before μCP (boiling point of PGMEA = ca. 419 K).

Wettability between ink and stamps is also an important factor in μCP. When CNT/polymer composite ink was spin-coated over as-prepared PDMS stamps, the ink did not uniformly cover the stamps, because of poor wettability between them. Therefore, we treated the PDMS stamps with oxygen plasma to form many hydroxy groups on PDMS surface to increase their surface energy;[13] consequently, wettability between ink and PDMS stamps was significantly improved.

3.4. CNT Content in Composite Patternings.

Figure 6 shows optical micrographs after μCP of CNT (1.6, 14, 37, and 45 wt %)/polymer films. We can see line-patternings of CNT (1.6, 14, and 37 wt %)/polymer films but CNT (45 wt %)/polymer film was not transferred to substrates. Such transfer behavior would be explained by changing the contact area between the polymer component of films and substrates. As the amount of CNTs in films increases, the polymer content in films relatively decreases, which indicates that the contact area between the polymer and substrates decreases. In μCP of the CNT/polymer composite films, it is likely that adhesion between polymer and substrates contributes to transfer the films. Therefore, a decrease in the amount of polymer component (i.e., increase in CNT component) of composite films would be unfavorable for transferring the films.

Comparing optical images of CNT (1.6, 14, and 37 wt %)/polymer patternings shown in Figure 6, their appearances were slightly different. Even though CNT (37 wt %)/polymer films were transferred on substrates, the resulting patterning was not as good quality as CNT (1.6 and 14 wt %)/polymer

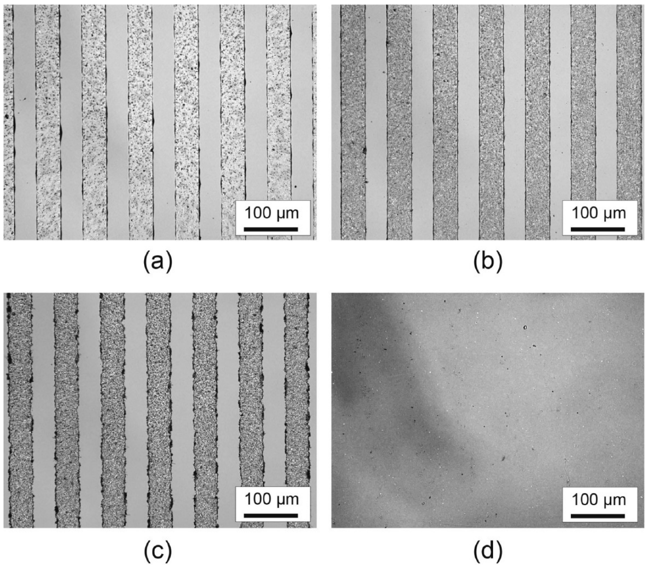

Figure 6. Optical micrograph images of CNT/polymer composite patternings ((a) 1.6 wt % CNT, (b) 14 wt % CNT, (c) 37 wt % CNT, and (d) 45 wt % CNT). The contact temperature was 363 K.

patternings; the edge of the CNT (37 wt %)/polymer patternings was not sharp. In these cases, μCP was performed at 363 K, and interestingly, sharp line-patternings of CNT (37 wt %)/polymer were formed when being transferred at 393 K (data not shown). Probably, the polymer films were softened with increasing contact temperature, resulting in better adhesion between the film and the substrate. However, CNT (45 wt %)/polymer composite films were not transferred, even at 393 K, implying that the decrease in the contact area between polymer and substrate would prevail over the increase in adhesion via thermal treatment at 393 K.

3.5. Conductivity of CNT/Polymer Films. CNTs used in this study have high electrical conductivity, because post-treatment (i.e., heating under inert atmosphere) increases their crystallinity. It is well-known that CNT/polymer bulk composite shows electrical conductivity if a sufficient amount of CNT is present in the composite.[39,40] Thus, electrical resistivity of CNT/polymer films was measured using a standard four-probe method. The results are shown in Figure 7. Note that the electrical resistivity of CNT (1.6 wt %)/polymer film could not be measured, because of its low conductivity. As the CNT content in the composite films increased (from 14 wt % to 37 wt %), their electrical resistivity decreased, which is accord with previous studies on CNT/polymer bulk composites.[39] Comparing CNT/polymer composite patternings to CNT/polymer bulk composites,[39] the patterning was comparable in conductivity to the bulk composites. Taking account of the fact that it is more difficult to prepare CNT/polymer patternings than CNT/polymer bulks, the high conductivity of the patternings is noticeable.

Figure 8 shows surface SEM images of CNT/polymer composite patternings. Generally, in order to make CNT composite materials conductive, interconnection among a sufficient amount of CNTs is essential.[39,40] For CNT (1.6 wt %)/polymer patterning, its surface was relatively smooth and CNTs were sparsely dispersed in polymer films. In such case, current hardly flows, even though voltage is applied at opposite sides of films, because each CNTs rarely connected. Indeed, for only the CNT (1.6 wt %)/polymer patterning, sputtering of thin Au layer was indispensable to obtain SEM images, which also indicates its low electrical conductivity. At much higher CNT content (37 wt %), larger amount of CNTs was observed in the films and it is seems that CNTs are interconnected each other, which results in high electrical conductivity. Even though CNT (37 wt %)/polymer patterning was sputtered with an Au thin layer to obtain clearer SEM images, we could measure their SEM images without the Au layer, because of its conductivity. According to numerous studies, electrical conductivity of CNT/polymer composites depends on various factors of CNTs such as aspect ratio, conductivity, dispersion, and distribution.[40] The high aspect ratio of CNTs is favorable for their interconnection, and poor dispersion prohibit the formation of CNT networks. As mentioned above, CNTs are well-dispersed in inks with the aid of the glass beads and the

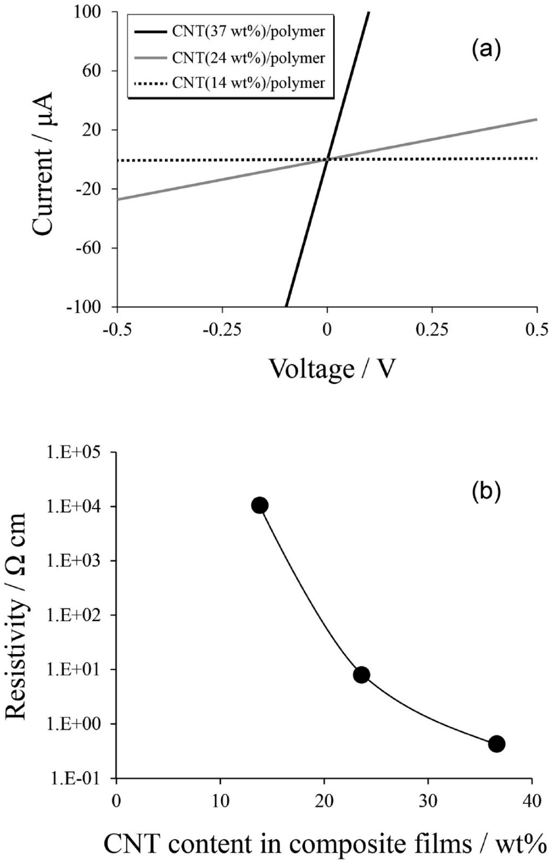

Figure 7. (a) Current−voltage characteristics and (b) resistivity of CNT/polymer films.

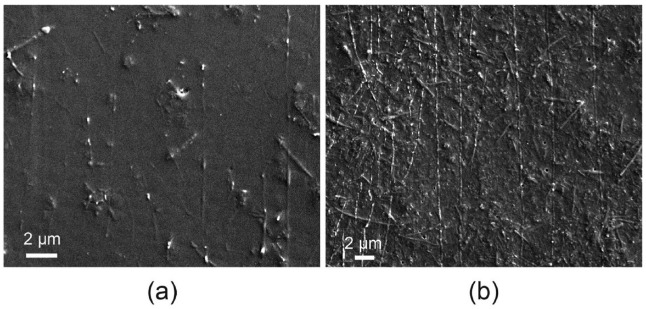

Figure 8. SEM images of CNT ((a) 1.6 and (b) 37 wt %)/polymer composite patternings.

dispersant, which allows CNTs to interconnect in the composite films to be high electrical conductive films.

3.6. μCP of CNT/Polymer Films over Curved Substrates. An advantage of μCP is the flexibility of PDMS stamps; flexible stamps enable films to transfer on substrates with a complex surface structure. Thus, as a demonstration, we prepared CNT/polymer composite patternings onto glass tubes. The results are shown in Figure 9. In the photograph, a thin gray film was uniformly present on the glass tubes, and in the optical micrographs of the gray films, line-patternings were observed. This result suggests that μCP of CNT/polymer composite is applicable for curved surface.

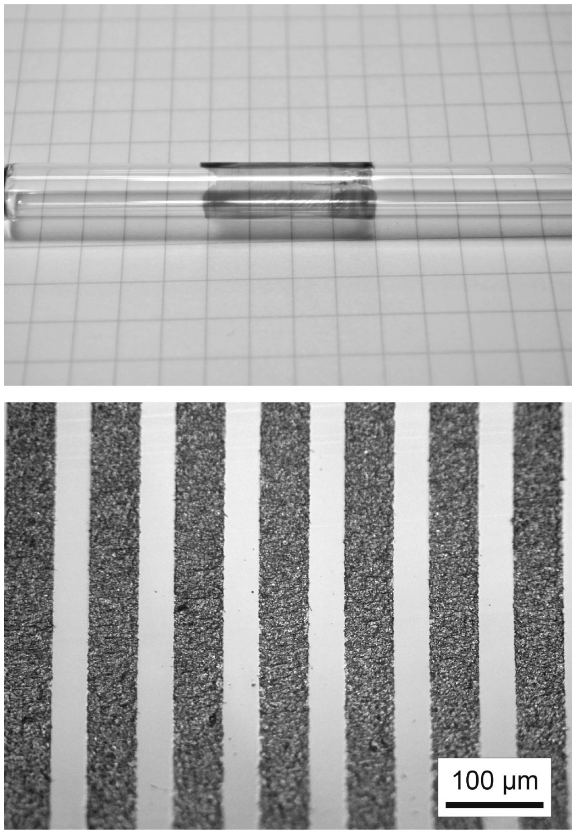

Figure 9. Photograph and optical micrograph image of CNT/polymer composite patternings on a glass tube.

4. CONCLUSION

CNT/acrylic resin composite films were patterned via μCP. In ink solutions, CNTs were highly dispersed, because of the stirring with glass beads and a dispersant. After the ink was spin-coated over PDMS stamps, CNT/polymer composite films were prepared over the stamps by evaporating solvent from the ink. By contacting them onto glass substrates, CNT/polymer composite films present on the raised parts of the stamps were transferred to the substrate to form patternings. The patternings were formed, even on curved glass substrates (glass tubes). In the μCP, thermal treatment at temperatures higher than T_g of the polymer component was indispensable to complete transfer of the composite films, because the thermal treatment helps remove the films from the PDMS stamps, because of softening of the polymer component. In addition to the thermal treatment, the contact area between the polymer and substrates was also important: high CNT content (i.e., low polymer content) was unsuitable to transfer the films, because of poor adhesion between the polymer and substrates. Since the CNTs in the films were interconnected, the CNT/polymer composite films showed almost as same electrical conductivity as CNT/polymer bulk composites.

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Notes

The authors declare no competing financial interest.

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