Toward Large-Scale Integration of Carbon Nanotubes

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This paper presents a large-scale assembly method to deposit discrete multiwalled carbon nanotubes (MWCNTs) across gaps present in an electrode array. A parametric study showed that MWCNTs dispersed in a liquid could be deposited to individually span gaps by combining an alternating current (ac) and a direct current (dc) electric field in a given ratio; it was shown that the ac field (5 MHz) serves to selectively attract and the dc field to guide individual deposition. Repeated trials demonstrated accurate, discrete, and aligned deposition at room temperature with 90% yield over an electrode array having 100 gaps.

Introduction

Carbon nanotubes (CNTs) have been intensively studied since their discovery in 1991.[1] Due to their electrical transport and mechanical properties,[2,3] applications such as in molecular electronic devices[4] have been proposed using single- or multiwalled carbon nanotubes (SWCNTs or MWCNTs).[5−8] For these applications, CNTs must be properly positioned on electrodes by either direct growth,[5,6] manual manipulation,[7] or random spreading.[8]

The direct growth method has been used for the integration of CNTs on electrodes; for example, thermal chemical vapor deposition has been used to grow a single SWCNT across a pair of electrodes with a high yield.[9] Growth was achieved, however, at a temperature of 900 °C, which may be prohibitively high for making fully integrated devices. Furthermore, SWCNT spacing of 500 μm or greater was necessary to avoid growth in unwanted directions. A chemical patterning method has been demonstrated to deposit discrete SWCNTs by electrostatic interaction.[10−12] The processing steps, however, are sensitive to the chemical functionalization of both the SWCNT and the substrate, which could be an issue both in processing and performance.

Here, we report an electric field-guided method to assemble discrete MWCNTs across 100 opposing electrode pairs, a method which lends itself to mass production. There have been various approaches to exploiting "electrokinetic" effects for depositing nanoscale and microscale components.[13−15] None of the methods, however, have deliberately mixed alternating current (ac) and direct current (dc) electric field components for achieving deposition of individual components in an array; here, a composite electric field with a particular ratio of the magnitudes of ac:dc electric fields was used to place a single MWCNT spanning a pair of opposing electrodes separated by a gap. This approach eventually led to the demonstration of individual MWCNTs assembled across what we will henceforth refer to as a "gap array".

Experimental Section

The dielectrophoretic force exerted by a nonuniform ac electric field can selectively attract and orient MWCNTs from a mixture of MWCNTs and other particles.[16] SWCNTs were deposited with an ac electric field, but the deposition consistently resulted in multiple SWCNTs deposited in bundles.[17] The composite electric field was used here to take advantage of the influence of both ac and dc electric fields during deposition.

Figure 1a shows a schematic of a circuit that combines ac and dc electric fields in a controllable way. The ratio of a dc (E_{dc}) to an ac electric field (E_{ac}) was varied along the equivalent constant strength electric field line, $E_{rms} = [E_{ac}^2/(2 + E_{dc}^2)]^{1/2}$ (Figure 1b).

An aluminum electrode pair (gap distance, ~4 μm; width, 300 μm) was lithographically patterned on a thermally oxidized wafer (p-type, PCA silicon, CA). The electrodes were used to investigate the influence on deposition of MWCNTs by the composite electric field. We used MWCNTs[18] grown with an arc-discharge method whose average diameter was 22 nm and average length was 7 μm as determined by scanning electron microscopy (SEM; Hitachi S-4500) observation and transmission electron microscopy (TEM; Hitachi HF2000; Figure 2). The MWCNTs were sonicated (Sonicator: no. 08849-00, Cole-Parmer, IL) in an ethanol solution for 12 h; this sonication raised the temperature of the MWCNT/ethanol mixture to ~60 °C. Following sonication, the mixture was left at room temperature for 30 min until it cooled. An aliquot of this solution (~6 μL) was placed on the gap while the composite electric field was being applied across the electrodes. The particular ac/dc ratio of the electric field was determined through the parametric study described later in this paper. The electric field was continuously applied until the solution completely dried out. The sample was then imaged by SEM. Variation of the field

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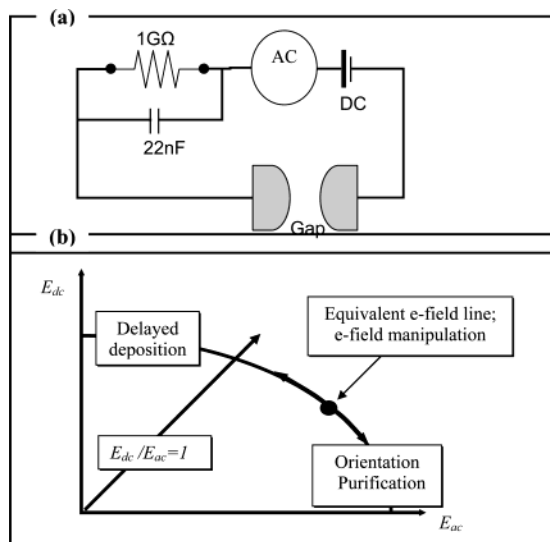
Figure 1. Schematic diagram for a single MWCNT deposition. (a) The composite electric field is created by combining an ac and a dc voltage source in series to deposit a single MWCNT on a gap. A 22-nF capacitor is inserted parallel to a high (1 GΩ) resistance to manipulate the composite electric field; the capacitor allows for ac current with negligible amplitude loss, and the resistance is used to induce a high electric field strength at a gap before MWCNT deposition. However, when a MWCNT is deposited, the electric field was not completely reduced to zero because of the large contact resistance (>1 GΩ) between the deposited MWCNT and the metal layer. (b) An electric field equivalent line is defined for the ratio E_{dc}/E_{ac}, as a guide to when individual MWCNT deposition can be achieved. If the ratio becomes small, both orientation and purification can be obtained because an ac field dominates. The short circuit mechanism is more effective in the opposite case because only a dc field decreases when a MWCNT is deposited.
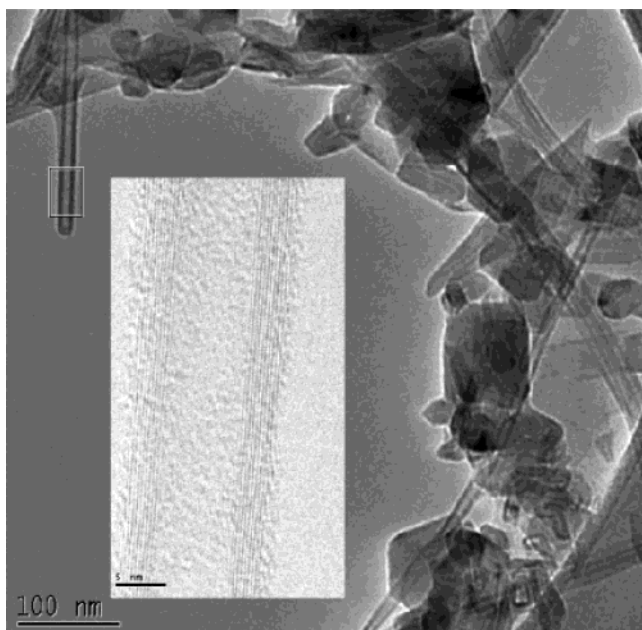

Figure 2. TEM image of MWCNTs[18] used in this experiment. MWCNTs composed of multiple shells were covered with amorphous carbon. High electrical resistance (>1 GΩ) was measured between the MWCNTs and the metal electrodes owing to this amorphous carbon surface layer.

strength showed that a few MWCNTs were attracted around the gap when the composite field strength was 0.544 $V_{rms}/\mu m$. The frequency of the ac component was set at 5 MHz, a value shown to selectively attract SWCNTs.[19]

Results and Discussion

Single Gap Experiments. The deposition across the Al electrodes demonstrated the distinct functions of the ac and the dc components of the electric field (Figure 3). When the dc electric field was dominant ($E_{dc}/E_{ac} > 1$), unwanted particles deposited between the electrodes and only a few poorly oriented MWCNTs were attracted to the electrode (Figure 3a,b). When a pure ac field was applied ($E_{dc}/E_{ac} = 0$), particles were rarely deposited and several MWCNTs were attracted (Figure 3c). Most MWCNTs attracted in this case were shorter than the 4-μm gap (with a few exceptions) and oriented between the two Al electrodes. When the ratio (E_{dc}/E_{ac}) varied between 0 and 1, the deposition showed a particular type of pattern dependent on the ratio (E_{dc}/E_{ac}; Figure 3d–f). Although this pattern is not entirely regular, it shows a strong correlation with the ratio (E_{dc}/E_{ac}); as the ratio decreased, the average spacing between the deposited MWCNTs increased and the number of deposited particles (non-MWCNT material) decreased. When the ratio was 0.41, ordered MWCNTs were deposited across the gap with an average spacing of 0.76 μm, and a small number of particles were also deposited (Figure 3d). For a ratio of 0.32, the average spacing between MWCNTs increased to 0.84 μm as shown in Figure 3e. For a ratio of 0.22, the average spacing increased to 1.7 μm and even fewer particles were deposited (Figure 3f). Through such a parametric study, we found that the deposition of MWCNTs across a gap with a desired spacing could be tuned by varying the ratio (E_{dc}/E_{ac}) for 5-MHz ac.

The deposited pattern of MWCNTs and other particles is interpreted as being the combined result of a dielectrophoretic force, an electrophoretic force, and an electrokinetic force generating a mechanical flow. A dielectrophoretic force on a particle, induced by polarization in a nonuniform oscillating electric field, is related to the geometry of the particle, its material properties, and the spatial distribution of the ac electric field. The induced force is proportional to both a polarized length cubed (a^3, i.e., geometry) and the gradient of the electric field squared (∇E^2, i.e., spatial distribution of the ac field).[20] The dielectrophoretic force is also dependent on the complex, frequency-dependent permittivity. Here, the ac frequency (fixed at 5 MHz), the electric field distribution, the ratio E_{dc}/E_{ac}, and the electrode shape were used to control the deposition pattern.

In the case of the parallel electrodes as shown in Figure 3, the ac electric field gradient is almost negligible (i.e., $\nabla E^2 \simeq 0$) along the vertical direction and so the dielectrophoretic force in this direction is close to zero; in contrast, the electric field rapidly changes in the horizontal direction, across the electrodes. The field changes particularly abruptly near the electrodes. Particles much larger than the gap size are expelled by the large dielectrophoretic force arising from the large field gradient at the electrode edges (see ref 21 for TEM image details).[14,21]
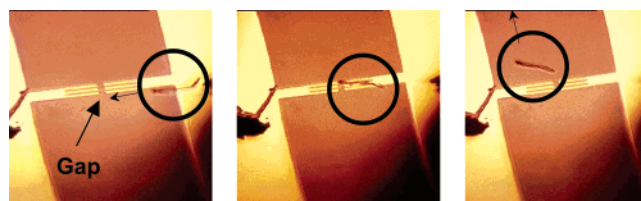
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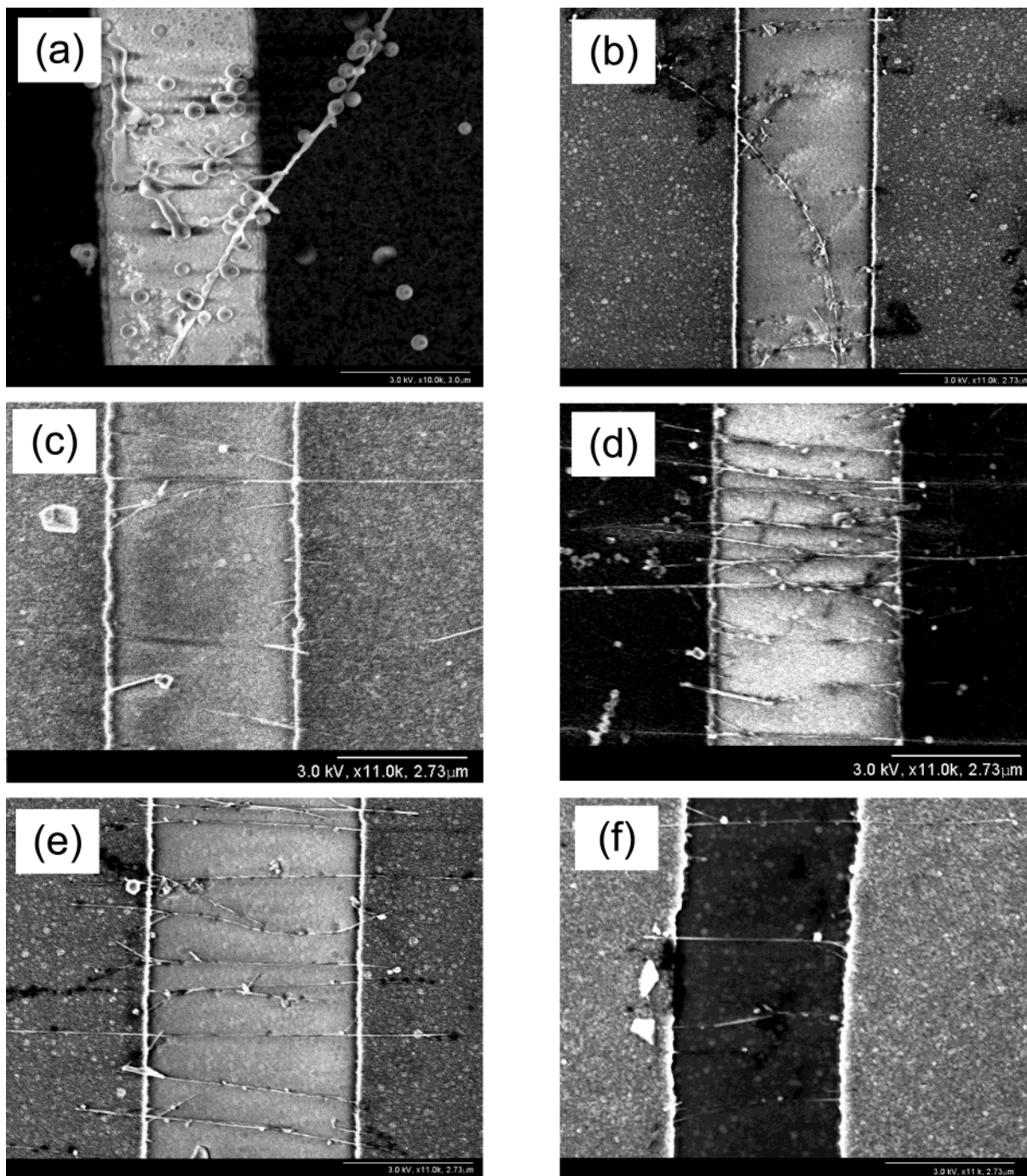
As a result, most of the attracted MWCNTs under the

Figure 3. SEM images of MWCNT deposition as a function of the varying ratio E_{dc}/E_{ac}. The strength of the electric field is 0.544 $V_{rms}/\mu m$ (ac at 5 MHz) between two Al electrodes patterned on a silicon nitride surface. When the ratio is between 0 and 1, a regularly patterned deposition was observed, in addition to filtering and orientation. (a) A dc electric field ($E_{dc}/E_{ac} = \infty$). (b) A biased ac field ($E_{dc}/E_{ac} = 1.22$). (c) A pure ac field ($E_{dc}/E_{ac} = 0$). (d) A biased ac field ($E_{dc}/E_{ac} = 0.41$). (e) A biased ac field ($E_{dc}/E_{ac} = 0.32$). (f) A biased ac field ($E_{dc}/E_{ac} = 0.22$).

pure ac electric field are smaller than the gap size, as shown in Figure 3c.

Under the effect of a pure dc electric field, the electrophoretic force acts to attract any charged particles including charged MWCNTs. The MWCNTs could be

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(21) A large DNA cluster was deposited in a water solution on the basis of an ac electric field (5 MHz). The DNA finally stayed at the left edge of the electrodes because it was pushed by the high gradient of the electric field on both electrodes. These phenomena were repeatedly observed. (Photographed by Kristina Korosi.)

covered with ions such as carboxylate generated by electrolysis of solvent ethanol.[16] By using a very strong electrophoretic force (over 5 V/μm), InP nanowires have been deposited across a pair of electrodes,[15] but in bent or twisted shapes seemingly because of the lack of directionality in the electric field. On the basis of our observations, when only a dc field was used, CNTs with particles were randomly attracted between electrodes and showed very little directed orientation (Figure 3a).

On the other hand, the use of the composite electric field allowed for control of attraction, orientation, and spacing, which we were eventually able to exploit for the
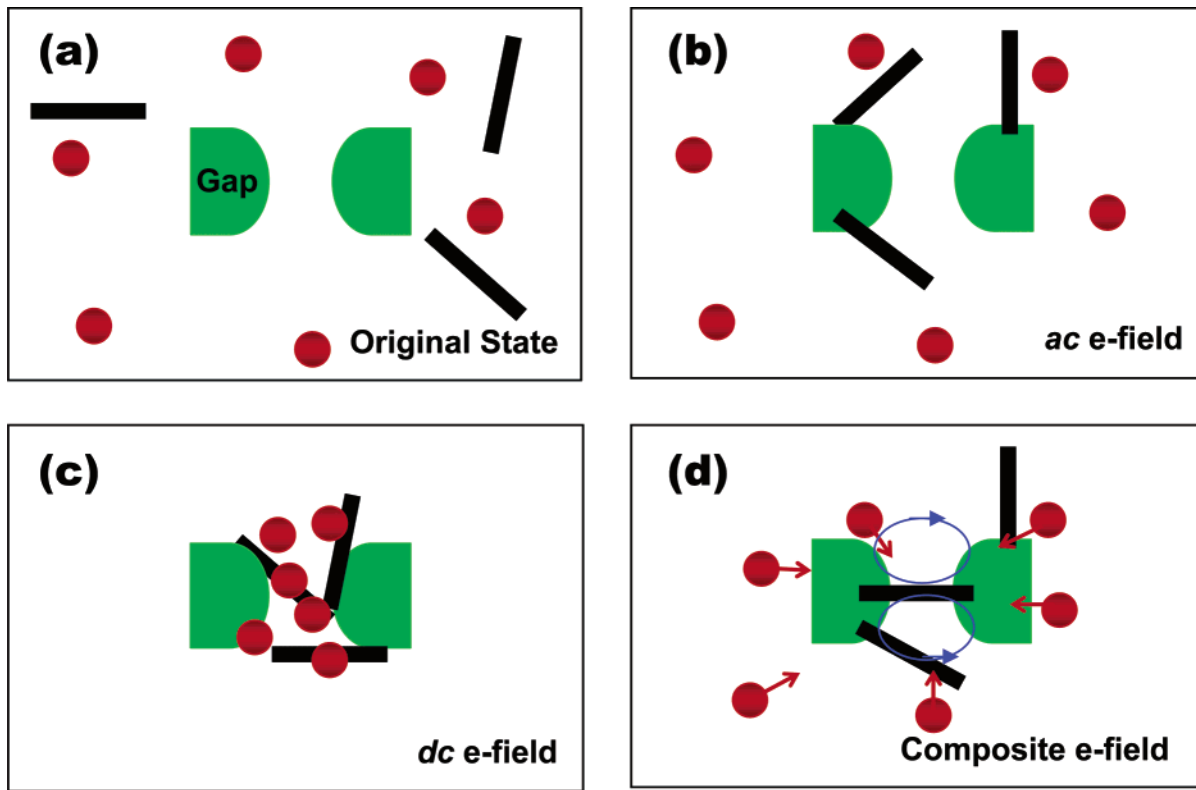
Figure 4. Schematic of deposition with ac only, dc only, and composite electric fields. (a) Before applying an electric field. (b) At an ac electric field of 5 MHz, only MWCNTs are attracted no matter how long the deposition time is, but deposition across the gap rarely happened, especially for when the MWCNT length was much larger than the gap size. (c) For a dc electric field, MWCNTs and particles are randomly attracted without orientation. (d) For the composite electric field, MWCNTs are quickly attracted and placed across the gap and particles are sluggish in their movement. Vortex flows are expected as a result of a dc electric field and its electroosmotic flow.
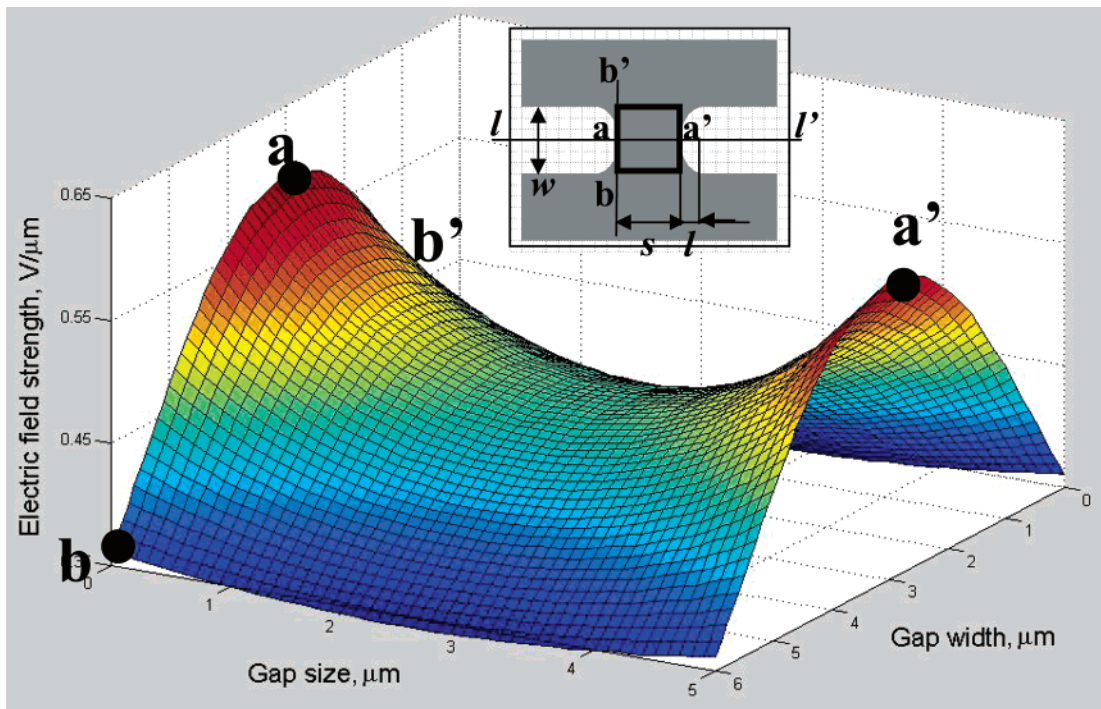

Figure 5. Simulation of an electric field on a semi-elliptical-shaped gap ($s = 5$ μm, $l = 3$ μm, and $w = 6$ μm). The electric field across the gap is 0.5 V/μm. At a high frequency (5 MHz) ac electric field, a metastable point is located in the middle of cross section $a-a'$ because the dielectrophoretic force becomes 0 ($\nabla E^2 = 0$). In the case of a highly tapered gap (e.g., $s = 5$ μm, $l = 8$ μm, and $w = 2$ μm), the electric field gradient is large enough to repel the attracted MWCNTs because a singular point is found at points a and a'. It was experimentally found that SWCNTs would not stay between two highly tapered electrodes.[26]

individual deposition of MWCNTs by the combined field method (Figure 3d−f). We suggest that the controlled

patterning of deposited MWCNTs is due to a fluid dynamic effect in which vortices are created near the deposited
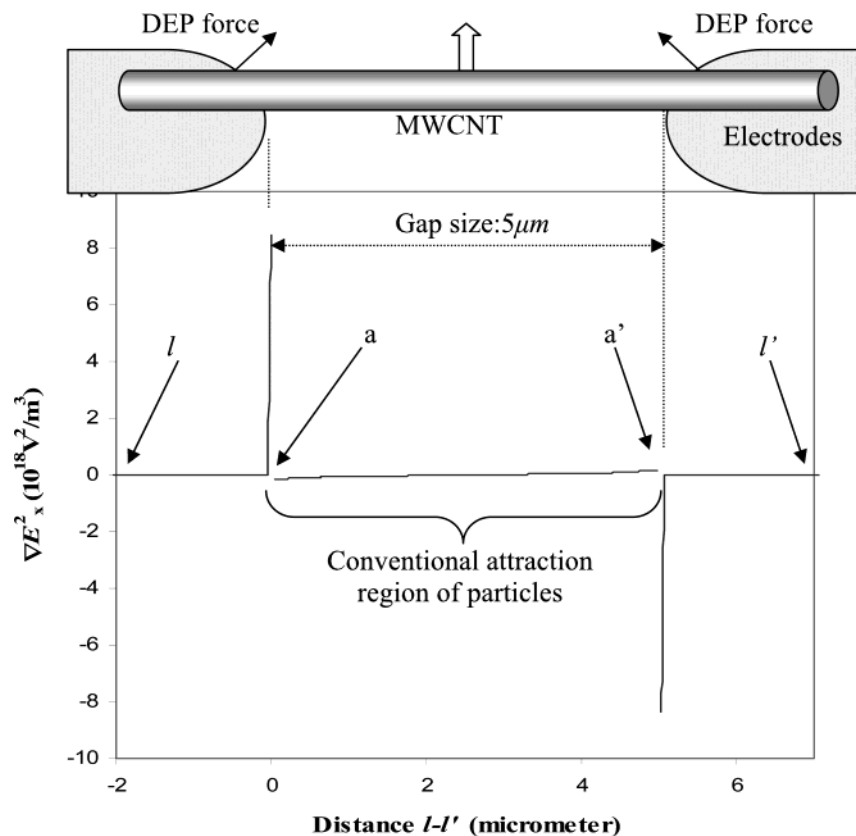
Figure 6. Computational result (by FEMLAB) of the x component of $\nabla|E|^2$, that is, $\nabla|E|^2_x$ at a certain moment of time under a pure ac field. There are huge positive and negative peaks and discontinuities at the sharp edges as a result of the rapid change of the electric field along the x direction. Thus, the dielectrophoretic (DEP) forces from both electrodes will always "push" the MWCNT out of the overlapped region ($a-l$ or $a'-l'$). As a result, the MWCNT does not deposit between the round-shaped electrodes because of these forces. It should be noted that this phenomenon occurs because the MWCNT, unlike the gold nanowires used in ref 14, has poor contact resistance on the metal electrode (gold; contact resistance was measured to be >1 GΩ) and does not eliminate the electric potential when deposited. Also, this situation is different from the general situation in dielectrophoresis because the length of the MWCNT is bigger than the size of the gap.

MWCNT. We further speculate that this is an electroosmotic flow generated by the dc component of the composite electric field. An electroosmotic flow is generated by the motion of ions between the two parallel electrodes as a result of a uniform dc potential gradient.[22] Before a MWCNT approaches the electrodes, a uniform electroosmotic flow is present from the positive to the negative electrodes; the oxide layer present on the surface of the silicon wafer is negatively charged because of the partial deprotonation of Si−OH groups. When a MWCNT enters and spans the electrodes, the electric field is distorted as a result of its presence; we have modeled this using FEMLAB, and the results will be published elsewhere. The FEMLAB modeling shows that the distorted electric field generates a component orthogonal to the initial uniform flow, and this leads to the generation of vortex flows near the deposited MWCNT. We speculate that these (as modeled) flows prevent other MWCNTs from entering the region near where the first MWCNT is deposited. As a result, the deposition occurs with the MWCNTs well-spaced and nearly equidistant from each other. In previous experiments with colloidal particles, an electrokinetic flow was observed to form periodic patterns between electrodes spaced 200 μm apart.[23] Although colloidal particles may themselves alter the flow patterns that we speculate are present, it is possible that quantum

dots (which are a few nanometers in diameter) might be introduced into the ethanol as a means of observing this flow via their fluorescence. This is a suggested topic for future study.

We have recently obtained supporting evidence for the presence of this electroosmotic flow by the stretched deposition of λ-DNA using a composite electric field.[24] Unlike other results,[22,25] one end of the DNA was not fixed by chemical attachment in our case; thus, it was not the dielectrophoretic force that stretched the DNA. In our experiment, a DNA molecule was always deposited in a coiled form in a pure ac field (5 MHz) whereas all types of particles were deposited in a pure dc field. When the dc field was combined with the ac field, a single DNA molecule was deposited in a stretched form. We suggest that this behavior can be explained by the electroosmotic flow caused by the dc field.[24]

By manipulating this electroosmotic flow with the controlled ratio (E_{dc}/E_{ac}), a single MWCNT was deposited across a pair of electrodes.[26] Figure 4 schematically illustrates our strategy of using the composite field to selectively deposit a single MWCNT across a gap. As shown in Figure 4d, a periodic flow pattern, formed around the first MWCNT deposited, limits the access of additional MWCNTs.

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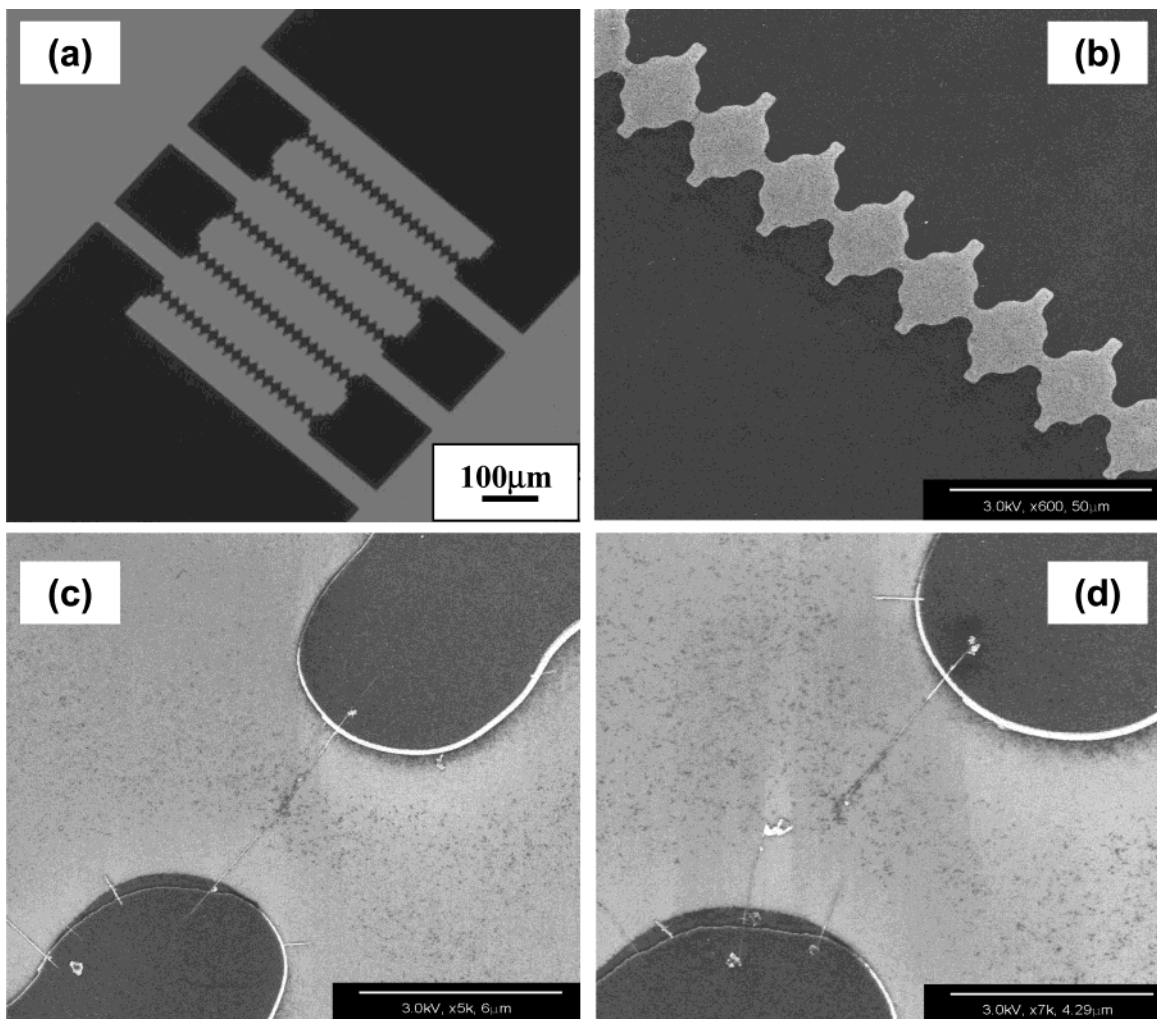(26) Chung, J.; Lee, J. *Sens. Actuators, A* **2003**, *104*, 229−235.

Figure 7. SEM images of MWCNT deposition on 100 gaps. Electrodes were fabricated with gold and the gap size was 6 μm. The composite electric field at 5 MHz was applied with $E_{dc}/E_{ac} = 0.348$. The strength of the applied electric field was 0.544 V_{rms}/μm. (a) Gap shape with six comb-shaped electrodes having 100 gaps. (b) Only one MWCNT was deposited across ~90% of the gaps. (c) A *success*: one MWCNT was deposited and spanned a gap. (d) A *failure*: the attracted MWCNT was shorter than the gap size. See also Table 1 showing the distribution of *successes* versus *failures* for a particular run.

Table 1. Typical Yield Table; Success (S) and Failure (F) on 100 Gaps (Yield = 89%)[a]

No	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
F/S																				
No	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40
F/S				F																
No	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
F/S							F			F										
No	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80
F/S		F											F		F					
No	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
F/S						F		F		F					F					

[a] A successful deposition means a single MWCNT deposition across a gap (Figure 7c) and a failure case means no connection between two electrodes with a MWCNT (Figure 7d). The number in the table indicates the labeled number of gaps in the array (Figure 7a).

The shape of electrodes is also essential to maintain a favorable distribution of the electric field, especially when MWCNTs need to be effectively attracted near the gap. To find the preferred electrode shape, the electric field was simulated; as previously shown, it was found that if the electrodes were too sharp, the electric field was concentrated at the tips and it was difficult to achieve strong directional deposition.[26] When the contour of the

electrode was more rounded, such as for the elliptical contour shown in Figure 5, a more favorable distribution was obtained. As shown in Figure 5, MWCNTs larger than the gap size are attracted along the ridge (line $a-a'$) by a dielectrophoretic force, but the overlapping portions are repelled at both a and a' (Figure 6). On the other hand, the dc field traps the attracted MWCNT near the gap and prevents further access of other MWCNTs.

100-Gap Array Studies. When the method of single gap deposition is extended to an array deposition, a particular value of the minimum spacing between neighboring pairs of gaps needs to be maintained to avoid a spillover of electric fields between them. In the current case, the spacing was fabricated to be two times larger than the electrode width.[27]

Two aluminum electrodes with 100 gaps were fabricated on a SiO_2 surface, Figure 7a. An approach similar to that for controlled deposition of a single MWCNT was used, but the optimum ratio of E_{dc}/E_{ac} differs for the 100-gap array versus the single gap because the electric field distribution for each differs. Figure 7b shows typical results of deposition whose yield rate was around 90% over the entire array in repeated trials (Table 1). The typical successful deposition result is shown in Figure 7c. Most failures in this presented case (~8%) were due to the deposition of MWCNTs shorter than the gap size (Figure 7d). Other failures (~2%) were due to large particles occupying the area between electrodes before a MWCNT was deposited. However, it needs to be emphasized that there was always at least one MWCNT present in a gap although, in some cases, the MWCNT was not sufficiently long to span the gap between the electrodes. Thus, the yield can be significantly improved with the use of higher-quality MWCNT samples with tighter length distributions. A 100-MWCNT array was, thus, fabricated by electric field-guided assembly using a combination of ac (5 MHz) and dc fields.

Conclusion

Discrete MWCNTs were deposited across 100 gaps by combining an ac and a dc electric field in a given ratio; the ac electric field (5 MHz) was used to attract MWCNTs, and the dc electric field was to trap a single MWCNT by electrostatic attraction. The yield of successful deposition was around 90% at repeated trials. The developed experimented method is scalable and can be extended to ultrahigh density (nanoscale) deposition. Though the spacing in the current array is 20 μm, it was determined on the basis of our using photolithography and can be substantially reduced with other nanoscale lithography methods such as electron beam lithography or nano-stamping/imprint methods.[13,28] Because the method is fast and highly parallel, we suggest it may become a method of choice for mass assembly of a variety of nanostructures and nanoscale devices, for a variety of applications.

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