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Towards Nanotube Fountain Pen

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Abstract- A nanotube fountain pen (NFP) is designed for the fabrication of three-dimensional (3D) complex nanostructures by adding a reservoir to the injector for electromigration-based deposition (EMBD). This enhanced EMBD technique is prototyped using a metal-filled carbon nanotude (m@CNT) as an pen-tip injector and a network of m@CNTs as a reservoir for continuous mass feeding. The deposition is based on nanofluidic mass flow from the pen-tip nanotube and the continuous mass feeding is implemented by inter-nanotube mass transport of the encapsulated metals. Experimental investigations have been performed using copper-filled CNTs using nanorobotic manipulation inside a transmission electron microscope. The threshold energy for mass delivery and the sizes of nanotube openings are co-related and the size-dependence of the fabricated nanostructures to the nanotubes is revealed. Furthermore, layer-by-layer prototyping processes are developed, and metallic nanostructures with larger dimensions are deposited using a single nanotube. As a general-purposed nanofabrication process for complex metallic nanostructures, nanotube fountain pen will be a key tool to scale up EMBD-based nanostructures.

Index Terms—nanotube fountain pen, electromigration-based deposition, nanorobotic manipulation, nanostructure

I. Introduction

Electromigration-based deposition (EMBD) is an emerging additive nanolithography technique based on the mass transport of metallic materials from a nanoinjector against a surface (Fig. 1(a)). Recent development has shown some unique applications such as attogram-scale mass transport [1, 2], nanorobotic spot welding [3], nanofluidic junctions [4] and networks [5], and spherical nanostructure formation [6]. EMBD can be realized under a low bias (typically several volts). Compared with other additive nanolithography technologies such as electron-beam-induced deposition (EBID) [7] and focused ion-beam chemical vapor deposition (FIB-CVD) [8], this is much more energy-effective because no high-voltage electron/ion beams (typically several to several tens of kV) are needed for the deposition. Carbon nanotubes (CNTs) have been used as the injectors due to their superior thermal stability, mechanical strength, and electrical conductivity. The feature size of the deposits from the EMBD is mainly determined by the diameter of the nanotube injectors (diameter: 0.4 ~ 100 nm), which is comparable to the available electron/ion beam diameters, but no needs of the expensive focusing and correction lens. The servo mechanism for writing can be a scanning probe microscope (SPM) stage, which is similar to that of dip-pen nanolithography (DPN) [9], but EMBD is particularly designed for obtaining pure metallic nanostructures, which is unattainable from DPN. This is also superior to EBID with which pure metallic structures are hardly available due to incompletely dissolved precursors and the contamination inside a vacuum chamber.

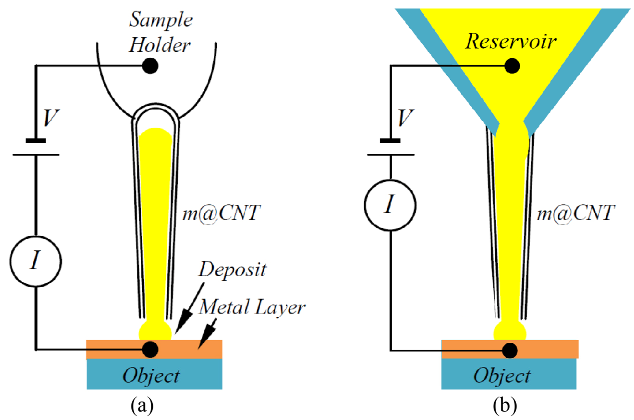

Fig. 1 (a) Schematic of electromigration-based deposition (EMBD). A metal-filled CNT (m@CNT) is used as an injector for deposition. By applying a bias, the encapsulated metal can be flowed out for deposition. (b) Enhanced version of an EMBD setup: nanotube fountain pen (NFP). A reservoir is installed behind the nanotube injector for continuous mass feeding.

However, the limited mass encapsulated inside a CNT requires a frequent change of them for depositing complex structures. This will obviously become a bottle-neck for leading EMBD towards applications. The objective of this effort is to make a breakthrough on continuous mass feeding to the injector by using a reservoir (Fig. 1).

II. Continuous Mass Feeding

We have experimentally investigated the feasibility of NFP using a scanning tunneling microscope (STM) built inside a transmission electron microscope (TEM) holder, FM2000E STM-TEM holder (Nanofactory Instruments AB). Copper-filled CNT networks are used as a reservoir. We have observed that the copper inside the neighbor CNTs to the CNT injector can be sucked into the injector (Fig. 2) if they attached to each other. It has been estimated from the

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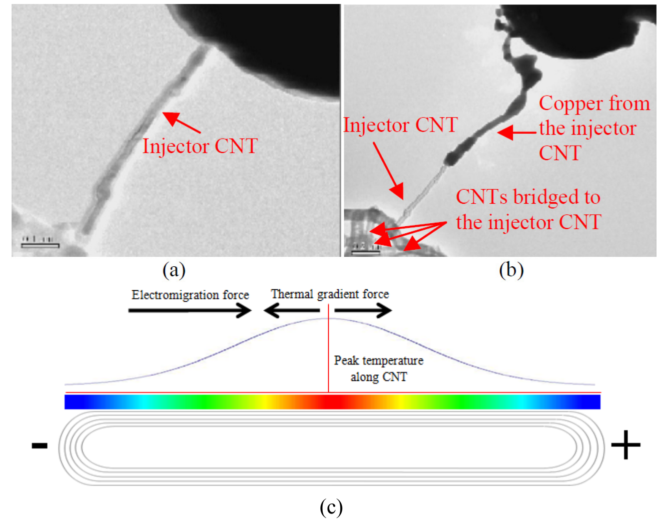

Fig. 2 Large structure fabricated by delivering the copper from neighbor CNTs. The initial mass inside the nanotube injector is 1.9 fg (a), while the deposited mass shown in (b) is 29.0 fg (about 15 times more than the original mass). (c) The force distribution along the CNT.

apparent geometry and the density of the copper that the initial mass inside the nanotube injector is 1.9 fg (Fig. 2(a)), while the deposited mass shown in Fig. 2(b) is 29.0 fg. It is obvious that the extra mass (the mass in the deposit is about 15 times more than the original mass) is from the sources outside of the CNT injector.

To understand the mechanism of the mass transport, several hypotheses have been taken in previous works [3, 10, 11]. Among them, the electromigration effect and the thermal gradient effect are the main factors to induce the copper melting and flowing. The thermal gradient force comes from the momentum transfer from phonons of CNTs to the encapsulated molecules or atoms. Because the temperature along the CNT is caused by resistive heating, the current versus time relation can reveals the thermal situation along the CNT. From the continuous feeding experiment we have observed that the current is of a steady value at about 91.1 μA during the mass feeding period. Although we cannot determine the gradient force on individual atoms, it can be concluded that the temperature profile of CNT is stable during the feeding process, as well as the thermal gradient distribution.

The electromigration force is induced by the net charge of the migrating atoms and the scattering of the current-carrying electrons by the atoms [12, 13], and can be expressed as:

$$F_{EM}=e\rho J\,(Z_d+Z_w) \quad (1)$$

where e is the electron charge, ρ is the resistivity of the CNT, which is counted as $0.9\times10^{-5}\ \Omega\cdot\mathrm{m}$ [10], J is the current density, and Z_d (=+1) [13] and Z_w (=-11) [12] are the valence equivalents of the direct and wind force, respectively. In this attempt, the current density is calculated by the average current value 91.1 μA dividing the cross section area 1781 nm^2, as $5.116\times10^{10}\mathrm{A/m^2}$. Then, the electromigration force is calculated to be 0.74 pN per atom. This value is substantially close to a previous investigation (1 pN [10]).

Since there is competition between these two forces during the mass transportation [11], we have to distinguish them by their characteristics. It is known that the peak temperature along a CNT occurs at the middle of it [14], and the direction of thermal gradient force is pointing from the central peak to colder ends (Fig. 2(c)). Then, if the thermal gradient force is the main driven force, the inner copper would flow out to both ends of the CNT. In contrast, what has been observed is that the inner mass continuously delivered in one direction from the cathode to the anode, which is coincident to the direction of electromigration force but opposite to the current flow. Moreover, the observation obviously reveals that the single direction of the driven force, without any obstacle from the thermal gradient force (Fig. 2(c)). As a result, the electromigration effect is the main possible mechanism for the flow. As shown in a previous investigation [4], electromigration can also induce mass transport between nanotubes, which made it possible to feed mass from neighbor tubes to the injector.

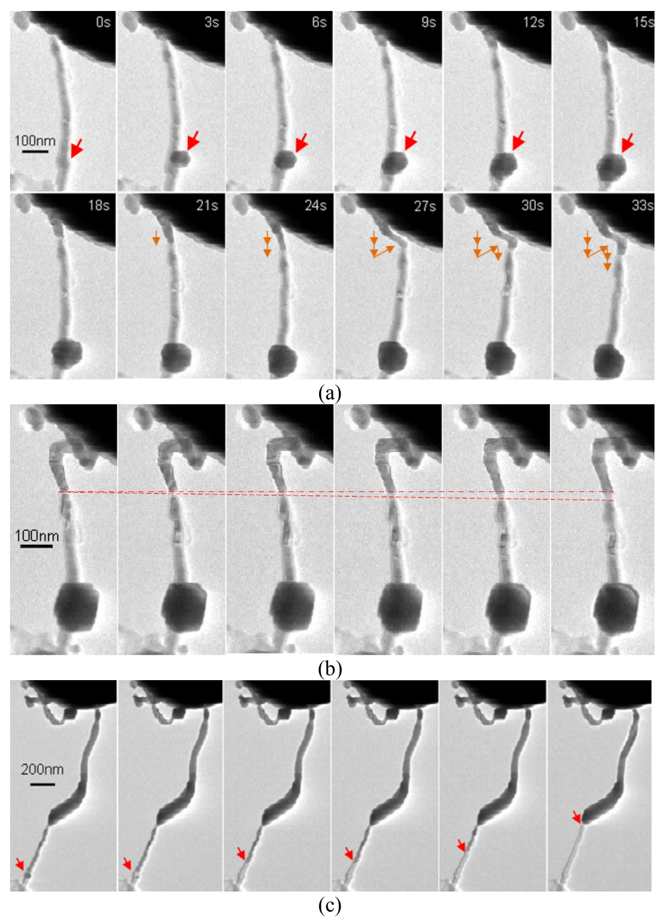

Fig. 3 (a) As t = 0-18 s, Cu is accumulating to a spot, which serves as a reservoir. As t = 18 -24 s, the injector is pulled back from the surface. As t = 24 – 27 s, the injector is moved towards the surface and shifted to the right. As t= 27 – 33 s, the injector is withdrawn again. Then, a zigzag "N" path is formed. (b) Continuous writing generated a kink. (c) The last stroke is "written". The reservoir becomes smaller and smaller (as indicated by the arrow), and finally the tube is drained off.

III. 3D NANOSTRUCTURE PROTOTYPING USING NFP

NFP has been used to "write" a variety of nanostructures (Fig. 3) by manually positioning the injector. This is of particular interest for such applications as arc welding and assembly, nanoelectrodes direct writing, and nanoscale metallurgy, where relatively large amount of mass are needed in the process.

By applying the continuous mass feeding on Cu@CNTs with different diameters (from 26.9 nm to 69.9 nm), we figured out that the smallest available width of deposited copper nanowire is similar to the diameter of CNT (Fig. 4(a)), hence, it is possible to construct a nanostructure with component in different sizes that generated by CNTs with different diameters (Fig. 4(a), inset).

We then tested the continuous feeding performance of CNTs differ in diameter. By increasing the voltage from 0 V in a step of 0.1 V, when it reached the range between 1.2 V to 2.5 V, the accumulation of the mass from outside reservoir began, and then the continuous feeding started. During the process, the current is stable until the nanotube is drained off, and the external bias is also unchanged during the mass accumulation and the delivery. This phenomenon suggests that a power threshold P ($P=IV$) must be exceeded for the accumulation and flow of external mass (Table I).

TABLE I

Comparison of power threshold of CNTs with different sizes

D (nm)	I (μA)	V (V)	P (μW)
26.9	44.3	1.2	53.2
37.5	91.1	1.5	136.7
47.2	193.8	2.0	387.6
56.0	205.5	2.3	472.7
69.9	331.5	2.5	828.8

Moreover, a comparison among them indicated that P is roughly proportional to the diameter of the CNT, D (Fig. 4(b)). The linear fitting relation, $P = 18.211D - 489.24$, suggests that an increased diameter of CNT leads to a linearly increased P. We attributed this to the gradual melting of the mass inside the injector and reservoir. To different volume of the inner copper, the melting power can be diverse. The simulation is undergoing for fully understanding this mechanism. We modeled the CNT injector and network combined NFP system as an entire Cu@CNT (Fig. 4(c)). With a bias (2V) added on the two ends of the CNTs, the current as well as thermal distributions of them can be plotted. From these plots, we found that the temperature profile along the small diameter CNT is apparently higher than the larger one, which is because the current density is much more intensified that makes the CNT with smaller diameters easier to reach a higher temperature to melt the inner material. Additionally, the intensified current would generate greater electromigration force to migrate the atom. However, to the CNT with a large size, higher power will be needed.

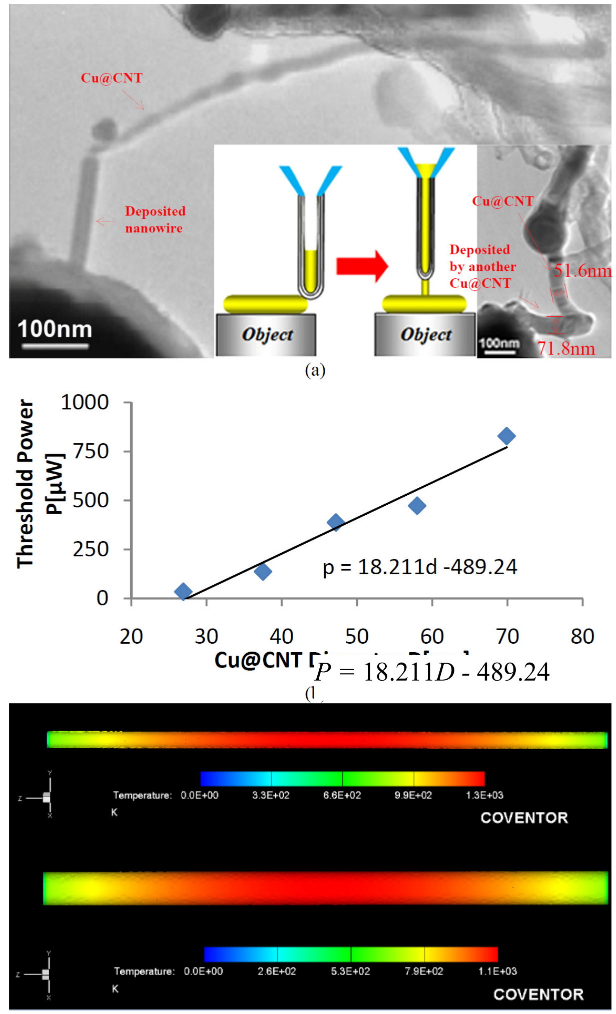

Fig. 4 (a) The similar size between nanotube and the deposited nanowire. The inset shows a demonstration of using different sized CNTs to generate the nanostructure. (b) Correlation of the Cu@CNT diameter D and the threshold power P. (c) The simulation of the thermal distribution along Cu@CNTs with different sizes. The diameters of the top one is 30 nm and the bottom one is 70nm. Both of them are stressed with a bias of 2V. It is obvious that the nanotube with a smaller diameter has a higher thermal profile than the one with a large diameter.

Due to the complexity in using the nanotubes with different diameter for fabrication, we have also investigated to use a single nanotube to fabricate the nanostructure with the components in different sizes. As the molten copper will continuously deposit onto the object surface and bring out the thermal energy, the former deposit will not cool down instantaneously but remain in melting state. Therefore, it makes it possible to control the width of deposit by modulate the position of injector during the layer-by-layer delivery process. As shown in the representative demonstration (Fig. 5(a), left), the injector moved back and forth in a small range, and tried to deposit the mass in the same height as much as possible. Then, those deposits would melt together and formed a component that is much larger than the original size of copper core inside the CNT (Fig. 3(c) and Fig. 5(a), right). To demonstrate the potential of this approach, we wrote a letter "**V**" on the object. By using a single CNT, a copper nanowire with similar size to the tube was initially

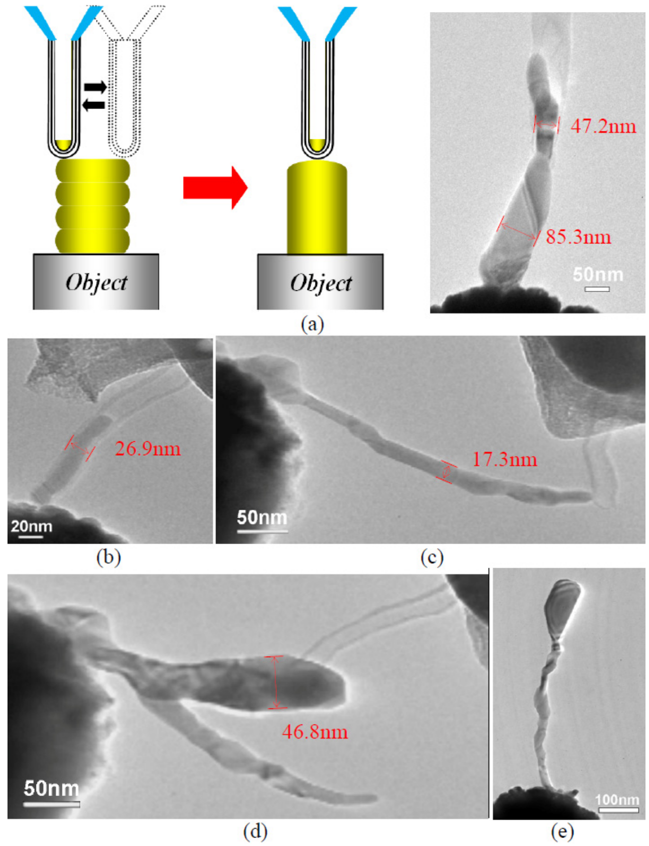

Fig. 5 (a) Prototyping by adjusting the position of injector layer-by-layer. The original diameter of nanotube is about 47.2 nm; however, the diameter of deposited nanowire is 85.3nm, which is much larger than the size of nanotube. (b) The injector nanotube has the diameter of 26.9 nm. (c) The deposited nanowire has a diameter of 17.3nm. (d) The second deposited nanowire has a diameter of 46.8nm. (e) A nanoscale golf club.

generated (Fig. 5(b) and (c)), and then, by manually modulating the injector when the mass flowing out, a nanowire with a larger size can be generated (Fig. 5(d)). The powerful technique of NFP here has the potential to provide feasible method to depict 3D novel feature in nanoscale, such as those letters mentioned in former paragraph and some interesting structures, as a nanoscale golf club (Fig. 5(e)).

IV. Conclusions

In summary, we have designed a nanotube fountain pen as an enhanced EMBD system for the fabrication of 3D complex nanostructures. This technique has been investigated using a copper-filled CNT as the injector and a network of such CNTs as a reservoir for continuous mass feeding. The deposition is based on nanofluidic mass flow from the pen-tip nanotube and the continuous mass feeding is implemented by inter-nanotube mass transport of the encapsulated metals. Experimental investigations have shown that the copper inside the neighbor CNTs to the CNT injector can be sucked into the injector. The relationship between the threshold energy of mass delivery and the size of nanotubes has been revealed and nanostructures have been fabricated by using nanotubes with different sizes. Furthermore, by changing the injector positions during the delivery process, metallic nanostructures with larger dimensions are prototyped using a single nanotube. As a general-purposed nanofabrication process for complex metallic nanostructures, the nanotube fountain pen is more energy and cost effective than EBID and FIB-CVD. Metallic nanostructures are more readily available from it than DPN.

Reference

[1] K. Svensson, H. Olin, and E. Olsson, "Nanopipettes for metal transport," *Physical Review Letters,* vol. 93, no. 14, art. no. 145901, Oct. 2004.

[2] P. M. F. J. Costa, D. Golberg, M. Mitome, S. Hampel, A. Leonhardt, B. Buchner, and Y. Bando, "Stepwise current-driven release of attogram quantities of copper iodide encapsulated in carbon nanotubes," *Nano Letters,* vol. 8, no. 10, pp. 3120-3125, Oct. 2008.

[3] L. X. Dong, X. Y. Tao, L. Zhang, X. B. Zhang, and B. J. Nelson, "Nanorobotic spot welding: Controlled metal deposition with attogram precision from copper-filled carbon nanotubes," *Nano Letters,* vol. 7, no. 1, pp. 58-63, Jan. 2007.

[4] L. X. Dong, X. Y. Tao, M. Hamdi, L. Zhang, X. B. Zhang, A. Ferreira, and B. J. Nelson, "Nanotube fluidic junctions: Inter-nanotube attogram mass transport through walls," *Nano Letters,* vol. 9, no. 1, pp. 210-214, Jan. 2009.

[5] L. X. Dong, X. Y. Tao, L. Zhang, X. B. Zhang, and B. J. Nelson, "Plumbing the depths of the nanometer scale: Attogram mass transport via nanochannels," *IEEE Nanotechnology Magazine,* vol. 4, no. 1, pp. 13-22, Mar. 2010.

[6] Z. Fan, X. Y. Tao, X. D. Cui, X. D. Fan, and L. X. Dong, "Spheres on pillars: Nanobubbling based on attogram mass delivery from metal-filled nanotubes," in *Proc. of the 10th IEEEConf. on Nanotechnology (IEEE-NANO2010)*, Seoul, Korea, Aug. 17-20, 2010.

[7] H. W. P. Koops, J. Kretz, M. Rudolph, and M. Weber, "Constructive 3-dimensional lithography with electron-beam-induced deposition for quantum effect devices," *Journal of Vacuum Science & Technology B,* vol. 11, no. 6, pp. 2386-2389, Nov.-Dec. 1993.

[8] S. Matsui, T. Kaito, J. Fujita, M. Komuro, K. Kanda, and Y. Haruyama, "Three-dimensional nanostructure fabrication by focused-ion-beam chemical vapor deposition," *Journal of Vacuum Science & Technology B,* vol. 18, no. 6, pp. 3181-3184, 2000.

[9] R. D. Piner, J. Zhu, F. Xu, S. H. Hong, and C. A. Mirkin, ""Dip-pen" nanolithography," *Science,* vol. 283, no. 5402, pp. 661-663, Jan. 1999.

[10] K. Svensson, Y. Jompol, H. Olin, and E. Olsson, "Compact design of a transmission electron microscope-scanning tunneling microscope holder with three-dimensional coarse motion," *Review of Scientific Instruments,* vol. 74, no. 11, pp. 4945-4947, 2003.

[11] J. O. Zhao, J. Q. Huang, F. Wei, and J. Zhu, "Mass transportation mechanism in electric-biased carbon nanotubes," *Nano Letters,* vol. 10, no. 11, pp. 4309-4315, 2010.

[12] J. P. Dekker and A. Lodder, "Calculated electromigration wind force in face-centered-cubic and body-centered-cubic metals," *Journal of Applied Physics,* vol. 84, no. 4, pp. 1958-1962, 1998.

[13] J. P. Dekker, A. Lodder, and J. van Ek, "Theory for the electromigration wind force in dilute alloys," *Physical Review B,* vol. 56, no. 19, pp. 12167-12177, Nov. 1997.

[14] P. G. Collins, M. Hersam, M. Arnold, R. Martel, and P. Avouris, "Current saturation and electrical breakdown in multiwalled carbon nanotubes," *Physical Review Letters,* vol. 86, no. 14, pp. 3128-3131, Apr. 2001.