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Shaping the Nanostructures from Electromigration-based Deposition

Zheng Fan, *Student Member, IEEE*, Xinyong Tao, Xudong Cui, *Member, IEEE,* Xudong Fan, Xiaobin Zhang, and Lixin Dong, *Senior Member, IEEE*

***Abstract*—Electromigration-based deposition (EMBD) is proposed for the fabrication of three-dimensional (3D) metallic nanostructures. The process is based on nanofluidic mass delivery at the attogram scale from metal-filled carbon nanotubes (m@CNTs) using nanorobotic manipulation inside a transmission electron microscope. By attaching a conductive probe to the sidewall of the CNT, it has been shown that mass flow can be achieved regardless the conductivity of the object surface. Experiments have also shown the influence of heat sinks on the geometries of the deposits from EMBD. By modulating the relative position between the deposit and the heat sinks, it becomes possible to reshape the deposits. As a general-purposed nanofabrication process, EMBD will enable a variety of applications such as nanorobotic arc welding and assembly, nanoelectrodes direct writing, and nanoscale metallurgy.**

I. Introduction

Additive nanolithography technologies such as electron-beam-induced deposition (EBID) [1-3] and focused-ion-beam chemical vapor deposition (FIB-CVD) [4-6] are of growing interest for the fabrication of three-dimensional (3D) nanostructures such as atomic force microscope (AFM) cantilever tips [7], helices [4], and grippers [6], and the interconnection of nanostructures [8]. Electromigration-based deposition (EMBD) is an emerging technique in this category, with which the deposition of materials to a surface is caused by the movement of the ions on the opposite direction of current in a conductor due to the momentum transfer between conducting electrons and diffusing metal atoms. Previous development has shown some unique applications such as attogram-scale mass transport [9-11], nanorobotic spot welding [12], archival memories [13], nanofluidic junctions [14], nano-evaporators [15], and spherical nanostructure formation [16]. Comparing with EBID and FIB-CVD, EMBD is more cost effective because the process is not based on the high-energy beams, the deposition rate of EMBD is higher and pure metal structures are more readily achievable because no gas introduction systems are necessary, and potentially parallel deposition is easier to be implemented using multiple injectors. However, conventional setup for EMBD required the object surface to be conductive so that an electrical circuit can be formed (Fig. 1(a)). Deposition against a non-metallic object surface was not available. Furthermore, the post modification of the geometries of deposits is limited by the thermal distribution in the loop, because typically the metal layer has a larger thermal capacitance than the nanochannels and the deposits, which made it impossible to reheat and reshape the as-deposited nanostructures. Against an object surface with excellent thermal conductivity, the shapes and sizes are determined instantly by the metallic materials flowing out from a carbon nanotube (CNT). Reheating or reshaping is unattainable because the minimum thermal energy exists at the deposition site between the nanotube tip and the probe, which formed a heat sink. Hence, the feeding rate of the metal from the nanotube and the positioning of the nanotube tip are the main factors to be considered in determining the geometries of the deposition. On the other hand, if the object surface is thermal and

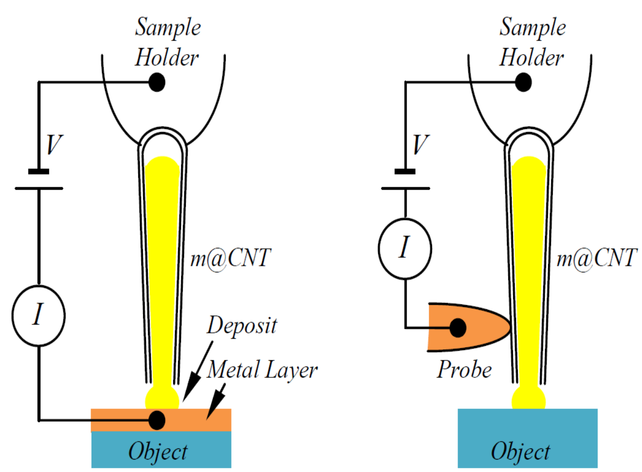

Fig. 1. Schematic of electromigration-based deposition (EMBD). The metal filled CNT (m@CNT) is used as an injector for deposition. By applying a bias, the encapsulated metal can be flowed out for deposition. (a) A metal layer on the object surface is necessary to form the electric circuit for EMBD. (b) By using a probe attaching to the side wall of the m@CNT, the surface of the object can be either conductive or insulating.

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Z. Fan and L. X. Dong are with the Department of Electrical and Computer Engineering, Michigan State University, East Lansing, MI 48824-1226, USA (phone: 517-353-3918; fax: 517-353-1980; e-mail: ldong@egr.msu.edu).
X. Y. Tao is with the College of Chemical Engineering and Materials Science, Zhejiang University of Technology, Hangzhou 310014, China.
X. D. Cui is with the Department of Material Science & Technology, Research Center of Laser Fusion, China Academy of Engineering Physics, Mianyang, Sichuan 621900, China.
X. D. Fan is with the Center of Advance Microscopy, Michigan State University, East Lansing, MI 48824-1226, USA.
X. B. Zhang is with the Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China.

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electrical resistive, e.g., another nanotube as used in the experiment, reheating and reshaping will be possible, which provides a post-process method for such applications as the fabrication of spherical nanostructures, removing welded nanostructures, and free-shape prototyping.

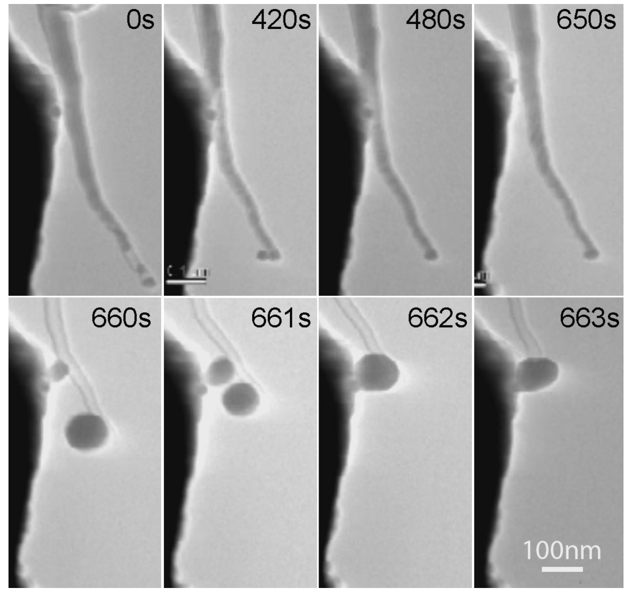
II. Towards the Deposition to a Non-conductive Surface

To apply EMBD against a non-conductive surface, the surface must be excluded from the electrical circuit. This can be implemented by taking the architecture as shown in Fig. 1 (b). The difference from the conventional one (Fig. 1(a)) is that the electromigration will only occur in the section between sample holder and the probe rather than the entire tube. Thermal energy generated in the in the section between sample holder and the probe will be transported to the tip part of the nanotube so that the encapsulated materials in this section between the probe and the object surface will be passively pushed out by those between the probe and the sample holder.

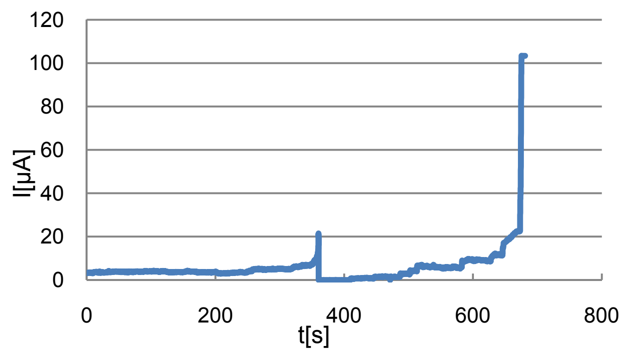
Our experiments were performed in a transmission electron microscope (TEM, JEOL 2200FS) with a field emission gun. The samples we used were Cu-filled CNTs. The Cu-filled CNTs are synthesized using an alkali-doped Cu catalyst by a thermal CVD method [17], and their outer diameters are in a range of 40-80 nm. The single crystalline Cu nanoneedles are encapsulated in graphite walls approximately 4 to 6 nm thick at the tips of CNTs.

A scanning tunneling microscope (STM) built in a TEM holder, FM2000E STM-TEM holder (Nanofactory Instruments AB), is adopted for the experiments. The probe can be positioned in a millimeter-scale workspace with sub-nanometer resolution with the STM unit actuated by a three-degree-of-freedom piezotube, making it possible to selectively contact to a specific CNT. Physical contact can be made between the probe and the sidewall of a nanotube. Applying a voltage between the probe and the sample holder establishes an electrical circuit through a CNT and injects thermal energy into the system via Joule heating. By increasing the applied voltage, the local temperature can be increased past the melting point of the copper encapsulated in a tube. Then, the encapsulated materials can be delivered from the carbon shells.

Experimental results are shown in Fig. 2. Fig. 2 (a) is a series of TEM images showing the EMBD using the configuration as shown in Fig. 1(b). The dark area on the left of the figures is the probe tip of the manipulator. The initial mass inside the CNT is estimated to be 6.0 fg at 0 s. At 663 s, 4.7 fg (78.3%) has been deposited while the rest mass evaporated and/or diffused onto the surface of the probe. It can be seen that at 0 s, there was an empty section close to the tip of the CNT, which was filled up at 420 s; showing that the flow started inside the CNT. The extra sphere at the CNT tip was a result of that. The fact that the transport direction was pointing to the CNT tip confirmed that the electromigration is responsible for this flow. Then, at 480 s, the volume of the sphere at the CNT tip decreased as a result



(a)



(b)

Fig. 2. (a) TEM images recorded the EMBD using the configuration shown in Fig. 1(b). The initial mass inside the CNT is estimated to be 6.0 fg at 0 s. At 663 s, 4.7 fg (78.3%) has deposited while the rest mass evaporated and/or diffused onto the surface of the probe. (b) The current-time curve recorded during the whole process.

of evaporation. There was no obvious change occurred till the moment of 650 s. At 660 s, within 3 seconds, the CNT was drained off and a large sphere formed on the CNT tip. Because the distance between the deposit and the probe is small and the contact between the probe and the CNT was not firm, the CNT slid back and the deposit dropped onto the probe. Fig. 2(b) is the current-time curve recorded during the whole process. The peak at 360 s represents that the contact resistance between the probe and the CNT improved, which was caused by relative slipping of the probe and the CNT. Before and after that moment, no obvious changes of the current have been observed. During the same period, no remarkable mass flow has occurred according to the video. When the flow started at 660 s, an abrupt inflation of the current has been monitored, in the meantime, the CNT was drained off and a large spherical deposit (diameter: 98 nm) appeared at the CNT tip.

III. SHAPING THE DEPOSITS

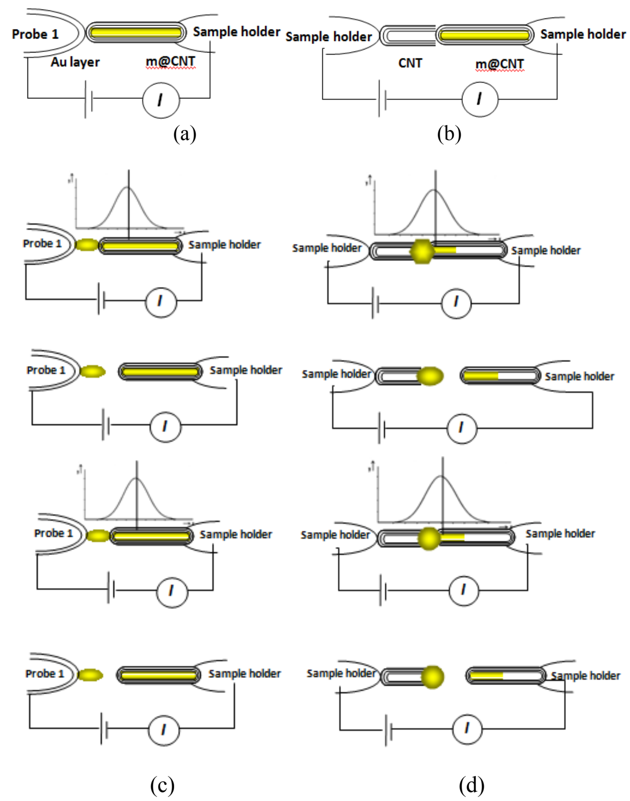


Fig. 3. Influence of thermal energy distribution on the geometries of the deposits from EMBD. (a, b) The experimental setup for the EMBD against an electrical and thermal conductive surface (an Au-coated W-tip) (a) and a resistive surface (an empty CNT) (b). (c, d) The processes for the EMBD against the conductive surface (c) and the resistive surface (d).

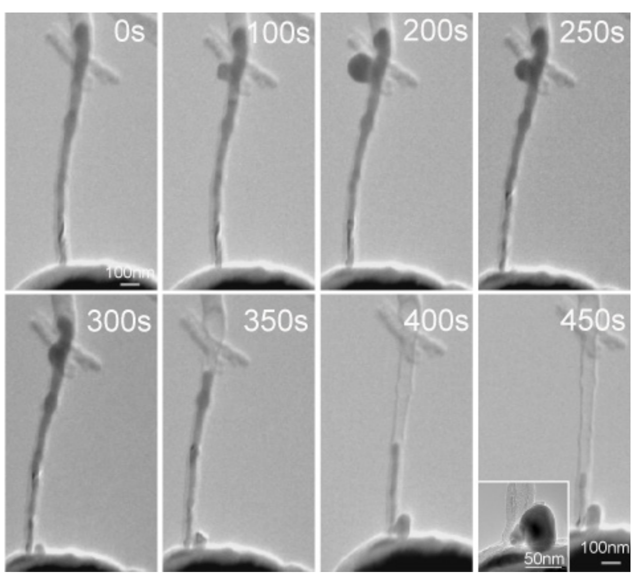


Fig. 4. TEM images (frames of a video) of EMBD against an electrical and thermal conductive surface. The shape of the deposit is fixed instantly. Reshaping was unachievable due to the heat sink located between the nanotube tip and the probe tip.

In order to understand the factors that determine the geometries of the deposits from EMBD, experiments were performed with two setups: (1) the Cu-filled CNT is positioned against an excellent electrical and thermal conductor and (2) the Cu-filled CNT is positioned against a resistive surface. Here we use a tungsten probe (diameter: 10 μm, length: 1 mm, tip radius: 100 nm) coated with a thin gold film (21-nm thick) for (1) and an empty CNT for (2). The setups for (1) and (2) are shown schematically in Fig. 3(a) and (b), and the processes are shown in Fig. 3(c) and (d). Qualitative distributions of the thermal energy are attached to some panels in Fig. 3(c) and (d) by referring the CNT and metallic electrode system [18]. As illustrated in Fig. 3(a) and (c), when the Cu-filled CNT contacts to the probe, due to the larger thermal energy capacitance of the probe than the CNT, the heat sinks locate at the interface between the CNT and the probe/the sample holder, where the temperature is the lowest. Reattaching the Cu-filled CNT to the deposit once the deposition is finished, the shape of the deposit will not be able to be changed. In the second case, by replacing the probe with an empty CNT, the deposit location will have a higher temperature when the Cu-filled CNT reattaches to the empty CNT. Then, the deposit will be reheated and the shape can be changed.

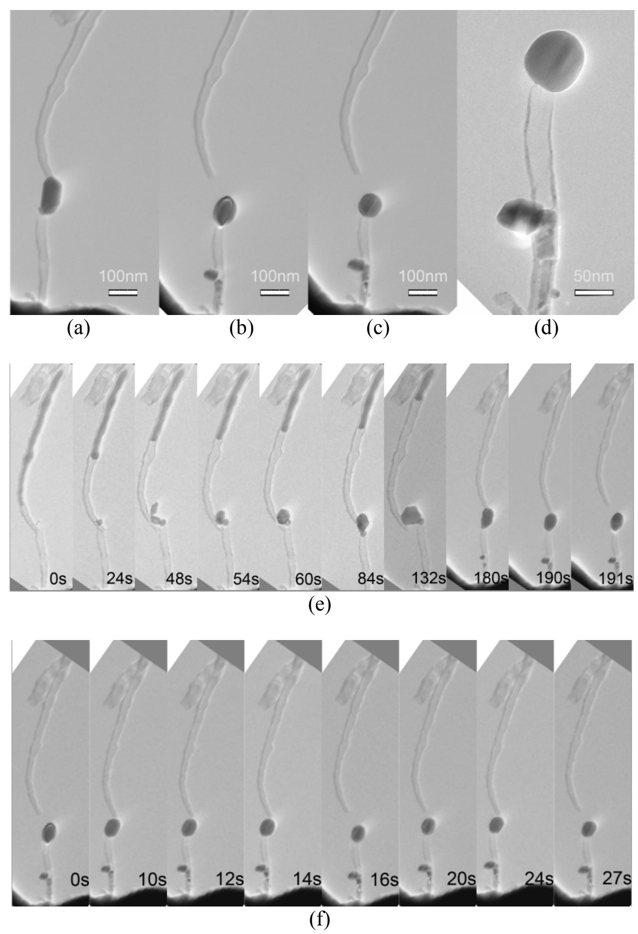


Fig. 5. Shaping and reshaping the deposits from EMBD. An intermediate step (a) and the oval shape obtained after the CNT injector departing from the object CNT (b). (c) The final shape after reshaping. (d) An enlarged image of (c). (e, f) Video frames recording the time sequence of the processes of shaping and reshaping.

A. Instant Shaping of the Deposits

This experiment is designed to justify that it is impossible to reshape the deposit from EMBD in the case of Fig. 3(a). Selected video frames of the EMBD processes in an experiment are shown in Fig. 4(a). By increasing the bias from 0 V at a step of 0.1 V, the inner copper core flowed out to the tip of CNT when it reached 2.0 V. The shape of the deposit was formed instantly due to the excellent thermal conductivity of the probe that cools down the deposit in a short time. Reheating of the cooled-down deposit was unable to be achieved because the volume of the probe (tip radius: 121 nm, root radius: 5 μm) is larger than that of the copper deposit. The probe serves as a heat sink with essentially infinite capacity comparing with the copper deposit.

B. Reshaping the Deposits

The same EMBD procedure has been applied to an empty CNT. The process was recorded by TEM images and real-time videos. Fig. 5 shows an intermediate step (a) and the oval shape obtained after the CNT injector departing from the object CNT (b). Fig. 5(c) is the final shape after reshaping and (d) is an enlarged image of (c). Fig. 5 (e) and (f) are video frames recording the time sequence of the processes of shaping and reshaping. In the experiment shown in Fig. 5(e), the EMBD process started at 2.1 V, and had continued for about 191 s. The mass flow rate was found to be 3.3 nm/s according to the length change of the inner copper core. The copper deposit first appeared as polyhedral (182 s) then changed into an oval. The oval was then reshaped into a sphere (Fig. 5(f)) by repeatedly attaching the CNT injector to it. As having shown in the first panel of Fig. 3(d), the contact point is close to the hottest spot. Therefore, the deposited metal could be changed.

The experiments imply that by arranging the position of heat injection away from heat sinks, it is possible to reheat and reshape a deposit. In an EMBD system, when this is not attainable, the factors influencing the instant shaping must be considered.

IV. Conclusions

In summary, we have experimentally investigated key techniques for extending the capability of EMBD including the deposition against a non-conductive surface and the shape control of the as-deposited nanostructures. By attaching a conductive probe to the sidewall of the CNT, it has been shown that the mass flow can be achieved regardless the conductivity of the object surface. Experiments have shown the influence of heat sinks on the geometries of the deposits from EMBD. By modulating the relative position between the deposit and the heat sinks using two CNTs, it has been possible to reshape the deposits. In an EMBD system, when this is not attainable, the factors influencing the instant shaping such as mass flow rate and feeding speed must be considered. As a general-purposed nanofabrication process, EMBD will enable a variety of applications such as nanorobotic arc welding and assembly, nanoelectrodes direct writing, and nanoscale metallurgy.

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