US 20030190278A1

(19) **United States**

(12) **Patent Application Publication**

Wang et al.

(10) **Pub. No.: US 2003/0190278 A1**

(43) **Pub. Date: Oct. 9, 2003**

(54) **CONTROLLED DEPOSITION OF NANOTUBES**

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(21) Appl. No.: **10/410,629**

(22) Filed: **Apr. 8, 2003**

Related U.S. Application Data

(60) Provisional application No. 60/370,947, filed on Apr. 8, 2002.

Publication Classification

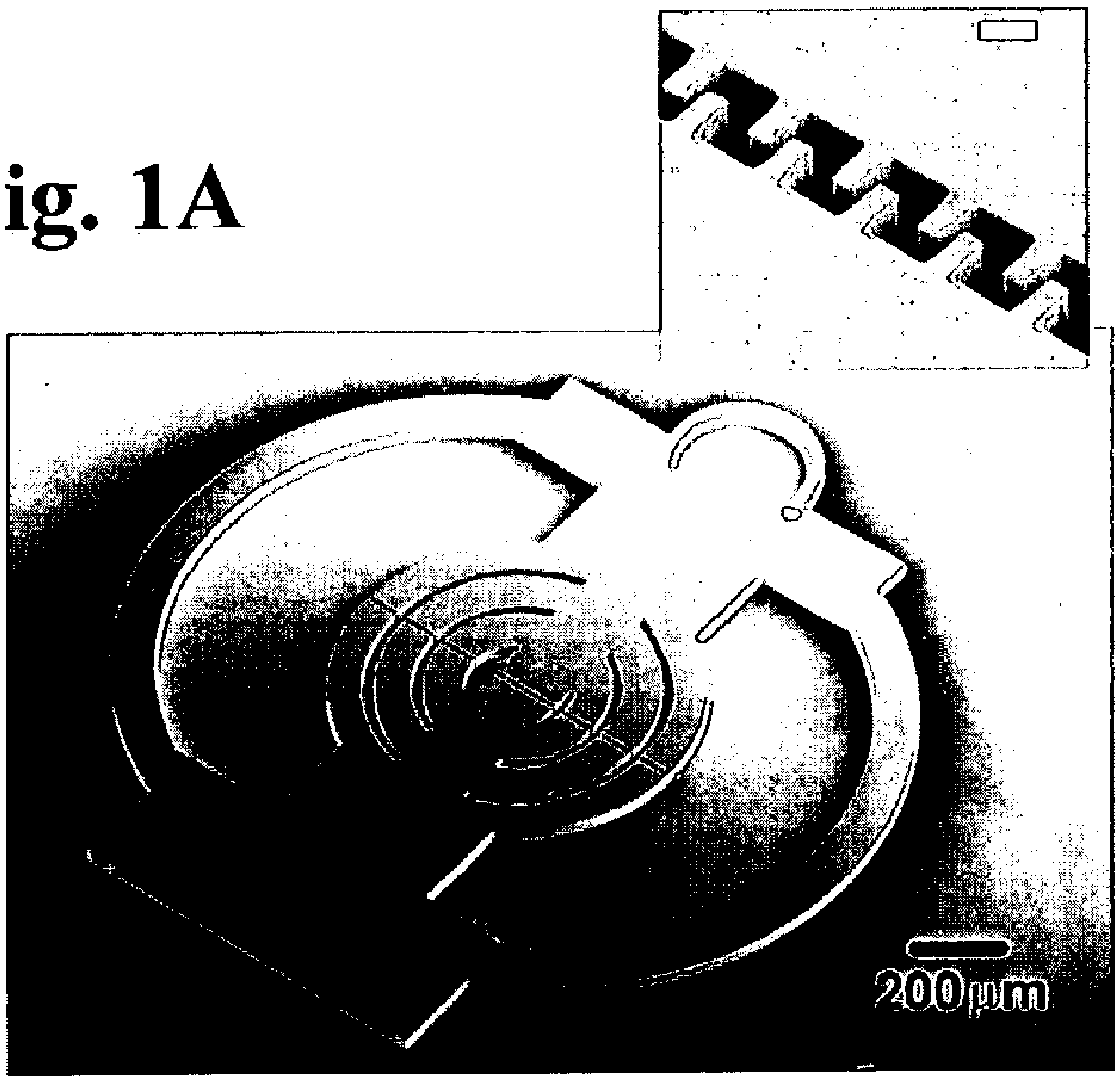
(51) **Int. Cl.**^{7} **D01F 9/12**

(52) **U.S. Cl.** **423/447.3**

(57) **ABSTRACT**

By a simple method single suspended carbon nanotubes (CNTs) are deposited at predetermined locations on a prepatterned device. A narrow trench is first formed on the device at the desired location for depositing a CNT. A fluid drying deposition process is then used to mount the CNT at the chosen location. A droplet of a solvent containing the CNTs in suspension is deposited at the desired location, and the solvent is allowed to evaporate. This leaves the CNT bridging the trench at the selected location. The effect is enhanced by applying an electric field. The method is also applicable to other nano-elongated objects such as nanowires and biomolecules.

Fig. 1A



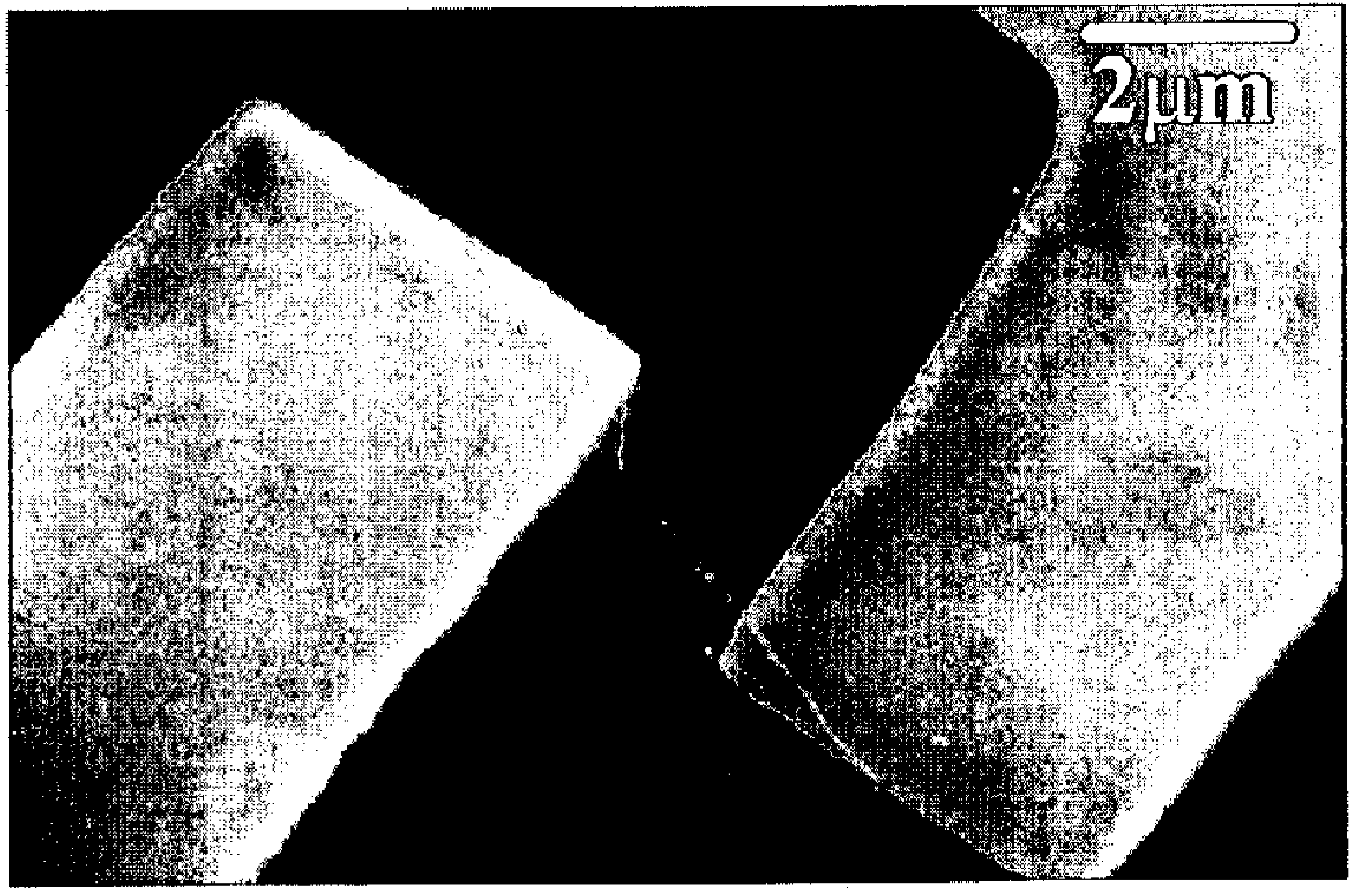


Fig. 1B

Fig. 2A

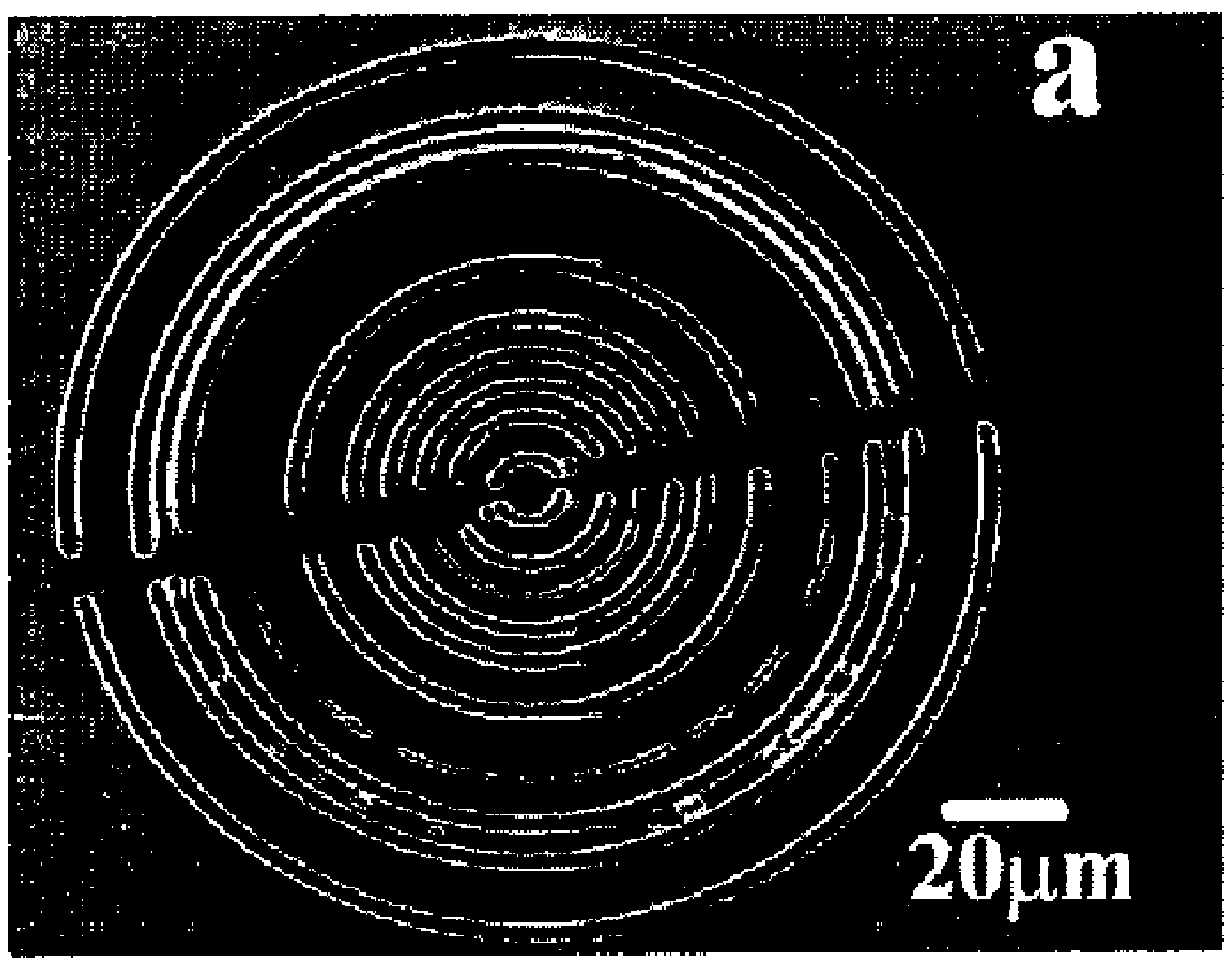
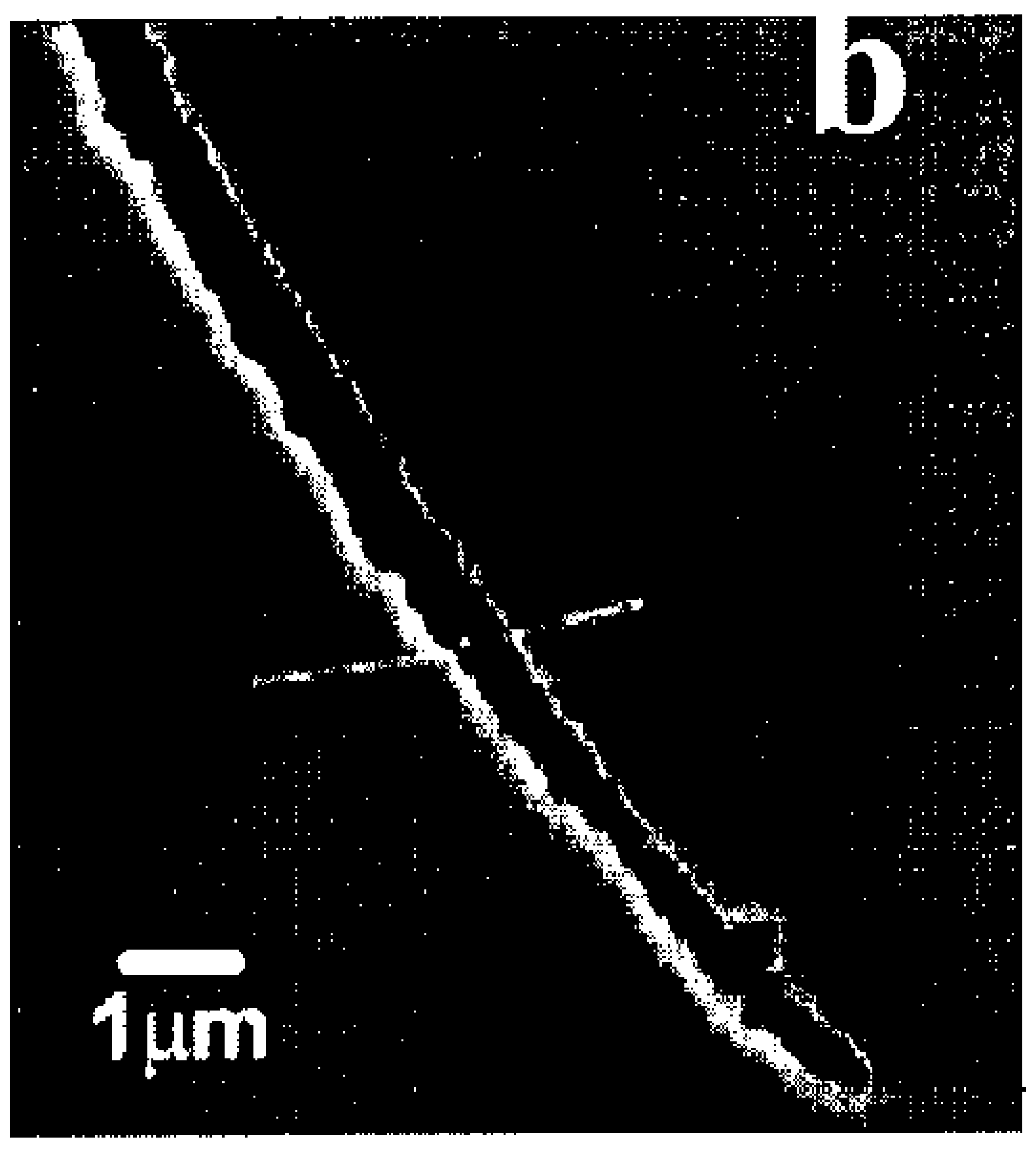


Fig. 2B



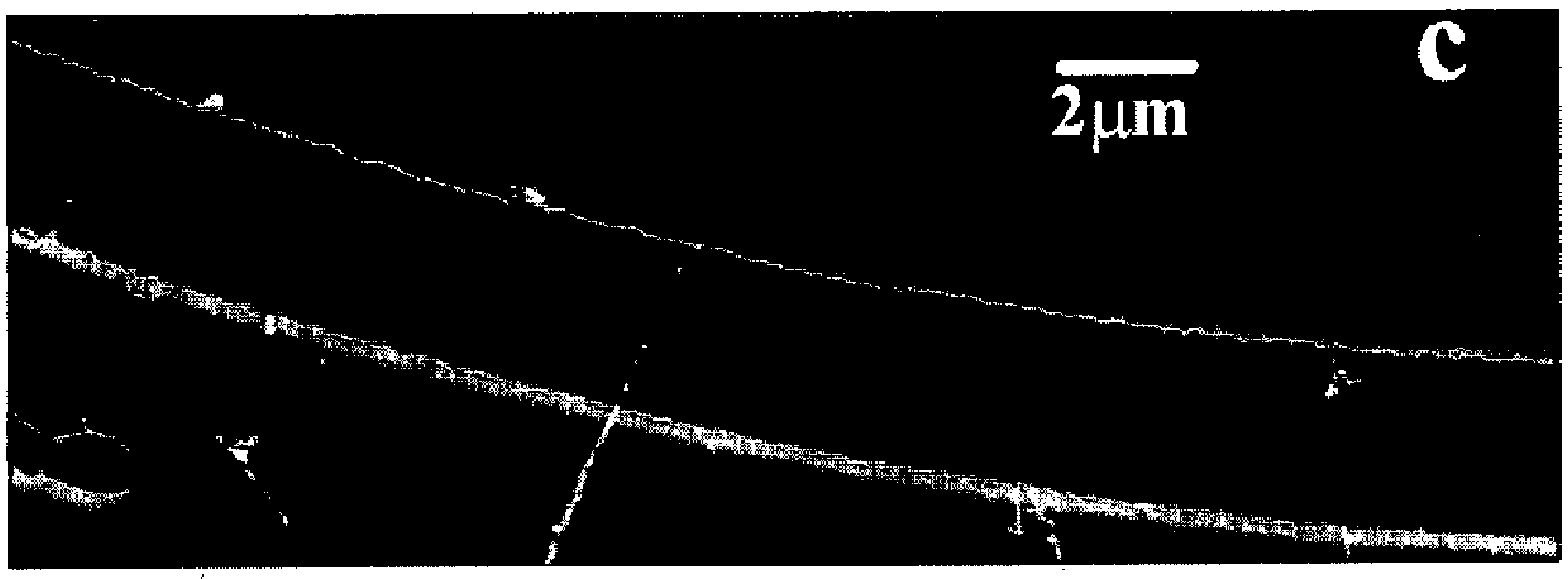
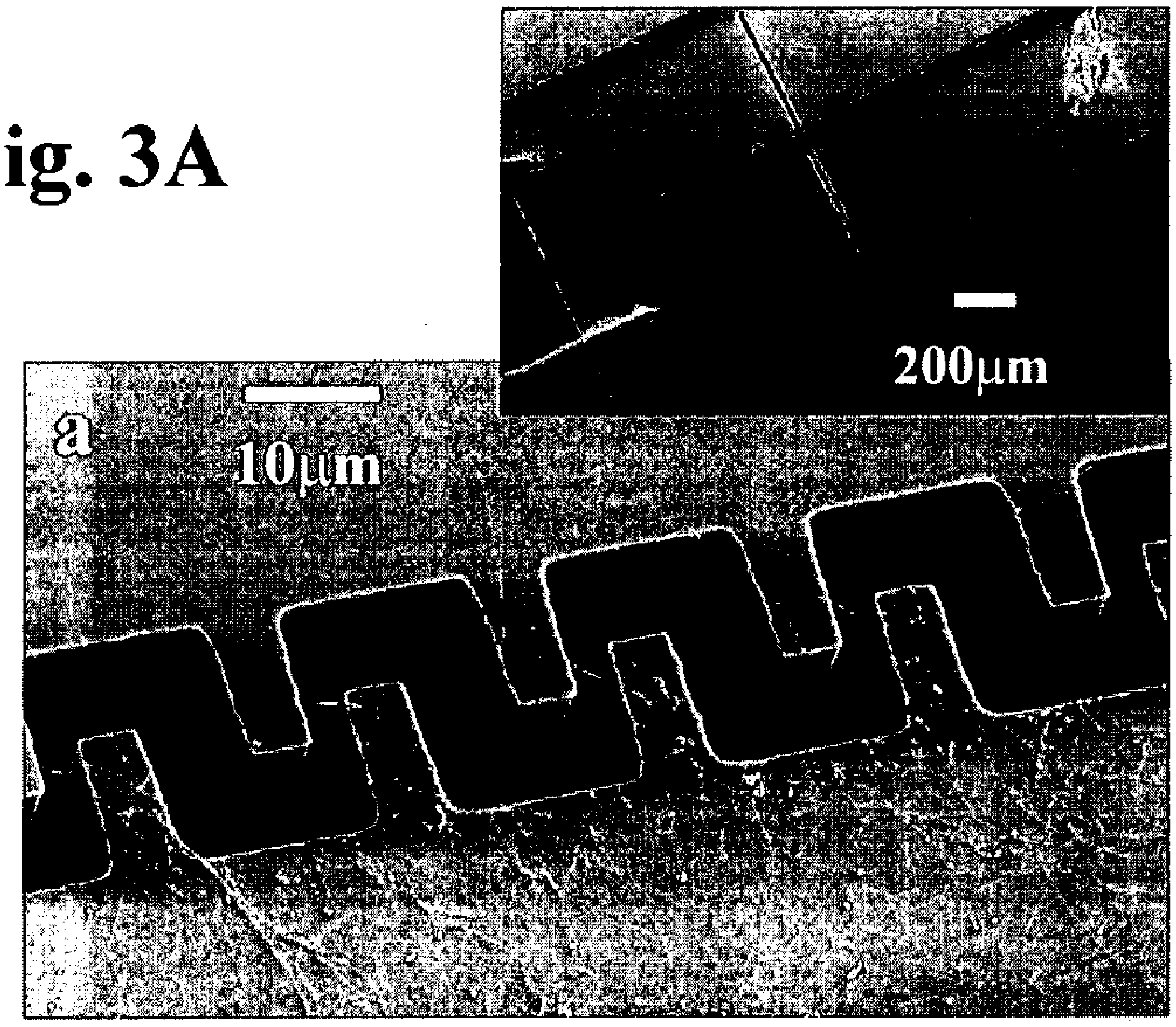


Fig. 2C

Fig. 3A



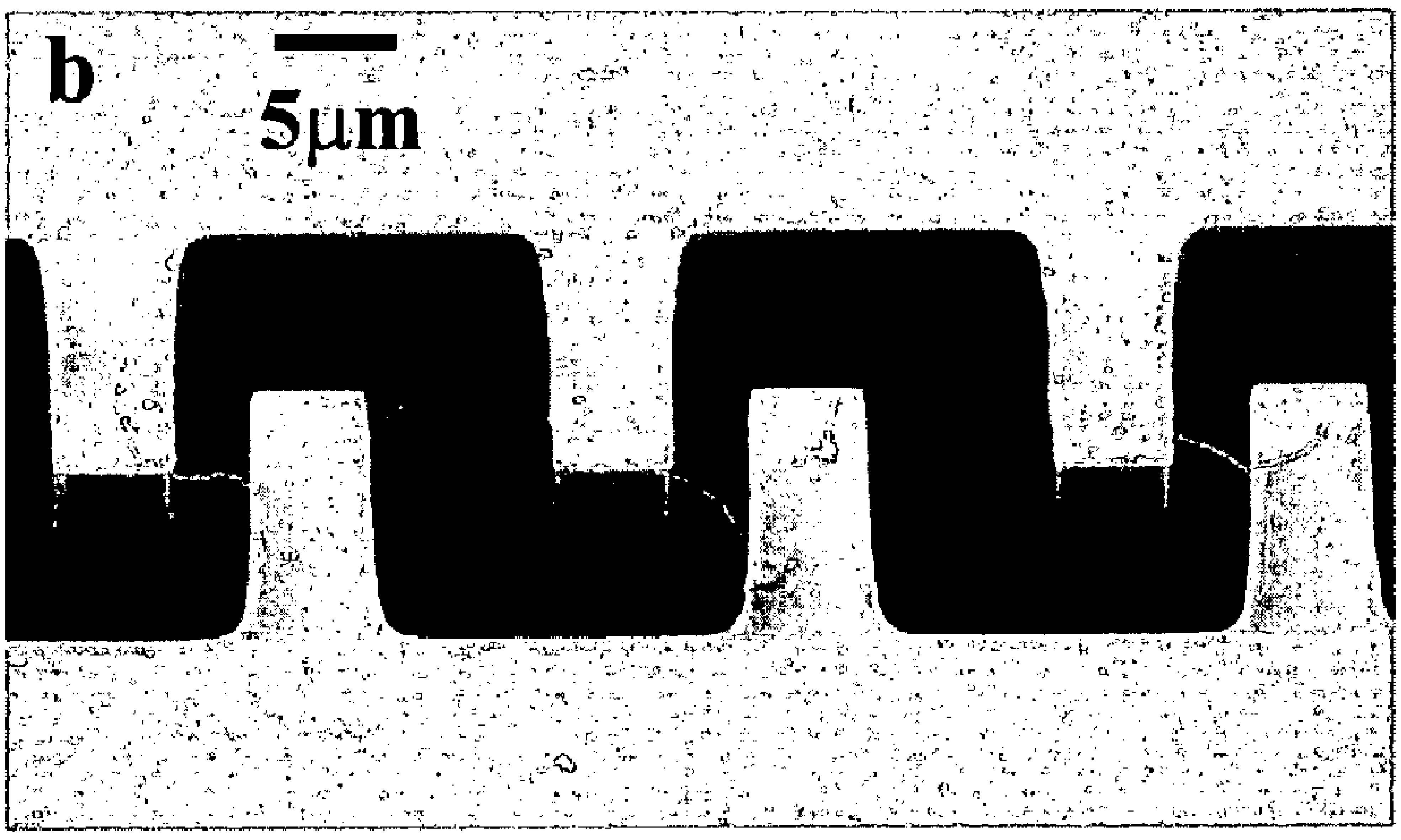


Fig. 3B

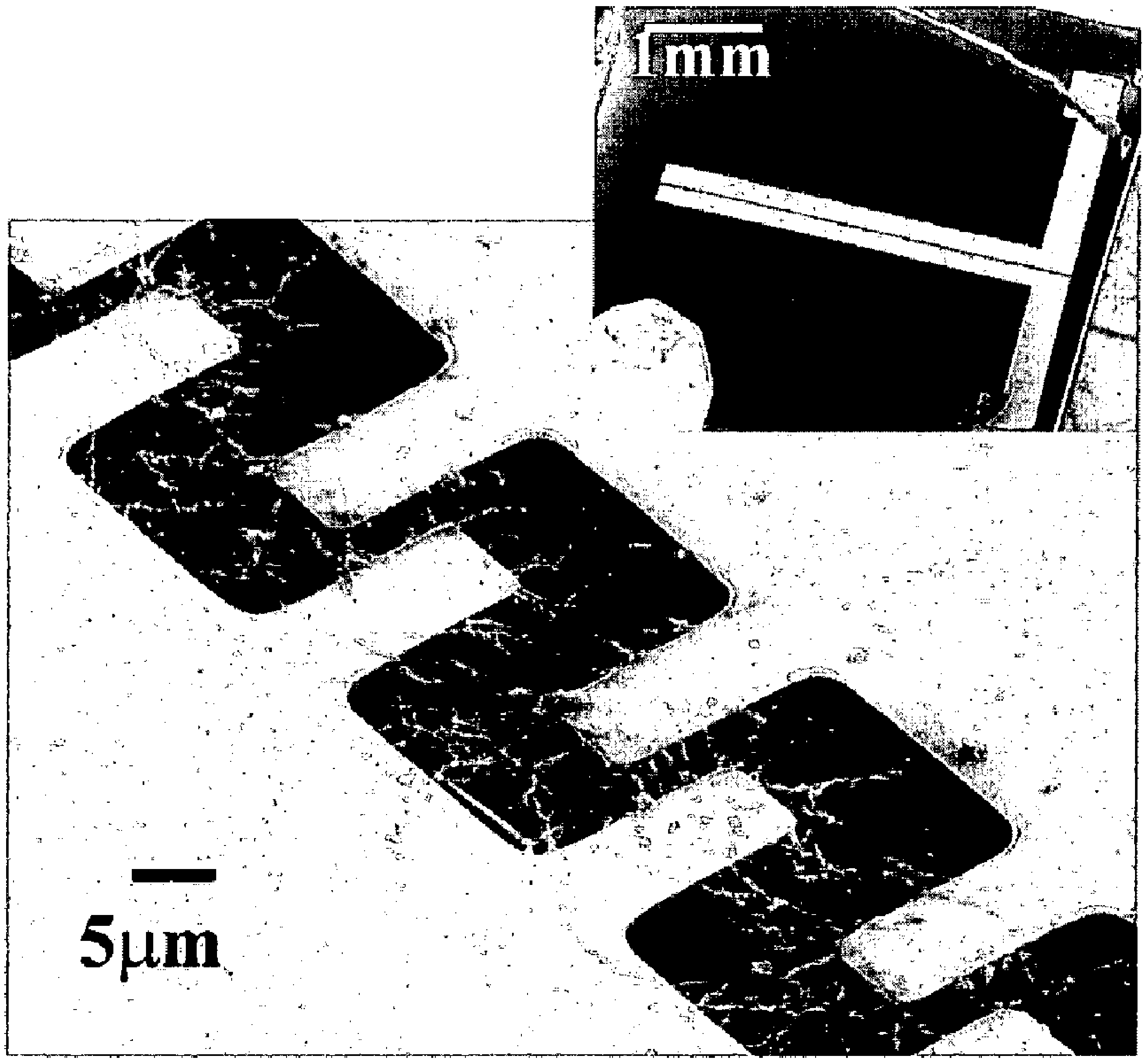


Fig. 4

CONTROLLED DEPOSITION OF NANOTUBES

RELATED APPLICATIONS

[0001] This application claims priority of Provisional Application Ser. No. 60/370,947 filed Apr. 8, 2002, which is herein incorporated by reference.

GOVERNMENT RIGHTS

[0002] The United States Government has rights in this invention pursuant to Contract No. DE-AC03-76SF00098 between the United States Department of Energy and the University of California.

BACKGROUND OF THE INVENTION

[0003] 1. Field of the Invention

[0004] The invention relates generally to nanotubes, and more particularly to device fabrication techniques involving the controlled placement of nanotubes in desired positions.

[0005] 2. Description of the Prior Art

[0006] Since the discovery of carbon nanotubes (CNT) in 1991, CNT has been a prominent building-block material for the next generation of nano-scale electronics. CNT-based devices include room temperature transistors, random access memory devices, p-n junctions and sensitive gas sensors. However, the device-fabrication technique is impeded by the use of the conventional "deposit and find" method, in which nanotubes are successively deposited and then located one at a time. This laborious method cannot meet the commercialization requirement of CNT-based electronics. An innovative method to assemble single nanotubes at predetermined locations is needed.

[0007] Prior efforts on controlling the CNT depositions mainly take either of two approaches—(1) synthesizing CNTs from patterned catalysts directly [e.g. Jing Kong, Hyongsok T. Soh, Alan M. Cassell, Calvin F. Quate and Hongjie Dai, Nature, 395, 878 (1998); Yuegang Zhang et al., Appl. Phys. Lett. 79, 3115 (2001)], or (2) depositing suspended CNTs using pretreated substrates [e.g. K. Yamamoto, S. Akita, and Y. Nakayama, Jpn. J. Appl. Phys. Part 2, 35, L917 (1996); K. Yamamoto, S. Akita, and Y. Nakayama, J. Phys. D, 31, L34 (1998); X. Q. Chen, T. Saito, H. Yamada and K. Matsushige, Appl. Phys. Lett. 78, 3714 (2001); Larry A. Nagahara, Islamshah Amlani, Justin Lewenstein, and Raymond K. Tsui, Appl. Phys. Lett. 80, 3826 (2002); Jie Liu, Michael J. Casavant, Michael Cox, D. A. Walters, P. Boul, Wei Lu, A. J. Rimberg, K. A. Smith, Daniel T. Colbert, and Richard E. Smalley, Chem. Phys. Lett. 303, 125 (1999); J. C. Lewenstein, T. P. Burgin, Aline Ribayrol, L. A. Nagahara, and R. K. Tsui, Nano. Lett. 2, 443 (2002)]. Neither approach has complete control of the locations, the orientations, and the quantity of the deposited nanotubes.

SUMMARY OF THE INVENTION

[0008] Accordingly it is an object of the invention to provide a method for controllably depositing nanotubes.

[0009] It is also an object of the invention to provide a method for nanotube device fabrication in which nanotubes are placed in desired locations.

[0010] The invention is a simple method to deposit single suspended carbon nanotubes (CNTs) at predetermined locations on a pre-patterned device. A narrow trench is first formed on the device at the desired location for depositing a CNT. A fluid drying deposition process is then used to mount the CNT at the chosen location. A droplet of a solvent containing the CNTs in suspension is deposited at the desired location, and the solvent is allowed to evaporate. This leaves the CNT bridging the trench at the selected location. The effect is enhanced by applying an electric field.

[0011] In an illustrative embodiment, a silicon Microelectromechanical Systems (MEMS) device pre-patterned with pairs of tooth-shaped contacts is used. With a single deposition, 50% of the contacts are connected by single nanotubes. By applying electric fields, the deposition rate is increased to 100%. Semiconducting nanotubes (the building-block of nanotube-based transistors) can be selectively deposited by a current-induced removal of the metallic nanotubes.

[0012] This simple method to deposit aligned single CNTs at predetermined locations can be implemented with only a Si MEMS device, a pair of tweezers, a pipette, and a power supply. The time scale of the process is minutes. A drop of suspended CNTs is deposited onto the pre-patterned device. When the solvent (acetone) dries, 50% of the contact pairs are connected by individual CNTs. With the application of an electric field, 100% connection rates are achieved. Semiconducting nanotubes can be selectively deposited by burning off the metallic nanotubes (by applying an electric current).

[0013] This technique provides a step towards the large-scale integration of CNT-based devices by providing the ability to controllably mount individual CNTs at desired locations. The technique can also be applied to non-carbon nanotubes and other nano-elongated objects. The invention also includes devices formed by connecting nanotubes between contact points on a substrate (e.g. a wafer or chip) using this technique.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] **FIG. 1A** shows a Scanning Electron Microscope (SEM) image of a silicon MEMS device for CNT depositions, with an inset showing the teeth pairs in the center of the device. **FIG. 1B** shows a straight CNT stretching across a pair of contacts.

[0015] **FIG. 2A** shows circular trenches in the center of the device. **FIGS. 2B, C** respectively show a single nanotube and three parallel nanotubes stretching across the trenches.

[0016] **FIGS. 3A, B** show depositions using electric fields.

[0017] **FIG. 4** illustrates trapping CNTs using gold electrodes.

DETAILED DESCRIPTION OF THE INVENTION

[0018] Multi-walled CNTs are synthesized using the pyrolysis method [C. N. R. Rao, R. Sen, B. C. Satishkumar, and J. Govindaraj, J. Chem. Soc., Chem. Commun. 15, 1525 (1998)]. They are suspended in acetone by sonication for 15 min. A 50 μm thick Si MEMS device shown in **FIG. 1A** is made from a silicon-on-insulator (SOI) wafer. The Si layer is etched all the way through using the Reactive Ion Etching

(RIE) method and the device is subsequently released from the substrate. The teeth pairs in the center of the device shown in the inset to **FIG. 1A** are the predetermined locations for CNT deposition.

[**0019**] The device is held in the air by a pair of tweezers and a nanotube droplet is deposited using a glass pipette. The droplet bulges out on both sides of the device. Within one or two minutes, the droplet dries and both surfaces of the teeth pairs are connected by individual CNTs. **FIG. 1B** shows a single carbon nanotube connecting a contact pair. The nanotube is suspended straight across without sagging. The area in the vicinity is clean. The ratio of the number of teeth pairs connected by one or a few nanotubes to the total number of pairs on the device is defined as the successful deposition rate. For this simple "fluid drying" deposition method, the successful deposition rate is 20% to 50%, where the rate variation originates from the shape difference of the contact pairs. Experiments with other patterns such as triangular pairs and pointed pairs found that the mismatched teeth pair of **FIG. 1A** inset was the optimal geometry with a successful deposition rate of 50%.

[**0020**] Alternative geometries can also be effective at trapping and aligning nanotubes. **FIG. 2A** shows a concentric-rings-geometry. For the same deposition method as above, nanotubes align perpendicularly across the trenches. **FIGS. 2B, C** respectively show a single and three parallel CNTs stretching across the trenches. Some short nanotubes land nearby the trenches in **FIG. 2C** since they are too short for the gap.

[**0021**] The mechanism attracting the suspended CNTs towards the teeth pairs is believed to be the strong capillary force generated by the narrow center trench. The width of the trench ranges from 2 μm at regions in between a teeth pair to more than 10 μm between pairs. Micron-sized gaps are narrow enough for capillary forces to become important. When a droplet is deposited, the trench sucks in the acetone from all directions. Since capillary pressure is inversely proportional to the size of an opening, the strongest force is located between a pair of teeth. The magnitude of the force is just strong enough to grab one CNT at a time with the inflowing acetone. The nanotube makes good contacts with Si when it lands and stays intact for the rest of the drying process. The wider regions of the trench create less capillary pressure and therefore do not attract nanotubes. As seen in **FIGS. 1B and 2B**, C, no nanotubes land on the inner walls of the trenches.

[**0022**] To confirm this capillary force model, the acetone drying process was observed for the device in **FIG. 1A** using a microscope. The two side open areas of the device dry first and acetone retreats to the center and the outer ring of the device. In the center, acetone dries away from the center trench, taking the unconnected nanotubes with it, and forms droplets in the upper and lower parts of the device. Nanotubes were later observed only at the upper and lower centers of the device and few elsewhere. During this time, the center trench has always been filled with acetone, and now it starts to dry. The capillary force must have been drawing any nearby acetone into the trench until the acetone runs out.

[**0023**] The nanotubes shown above are from a first deposition. When additional deposition is performed, more teeth pairs will be connected; however, the deposition rate never reaches 100%. The connected nanotubes from the first deposition disturb the local fluid pattern and therefore affect the consecutive depositions.

[**0024**] The design of the device is important for successful depositions. For example, to help better align the nanotubes, the rings in the center of the device in **FIG. 1A** match the circular symmetry of the whole device. The rings are separated to speed the acetone drying process. The trench cuts all the way across the device's center region, acting as an open channel for acetone to flow in and out. For trenches that are not etched all the way across, the deposition rate goes down to 10%.

[**0025**] Capillary forces trap only a fraction of the nanotubes in a droplet to the teeth pairs. To trap all nanotubes, electric fields are used. Although electric fields have been used to align suspended CNTs [Yuegang Zhang et al., Appl. Phys. Lett. 79, 3115 (2001); K. Yamamoto, S. Akita, and Y. Nakayama, Jpn. J. Appl. Phys. Part 2, 35, L917 (1996); K. Yamamoto, S. Akita, and Y. Nakayama, J. Phys. D, 31, L34 (1998); X. Q. Chen, T. Saito, H. Yamada and K. Matsushige, Appl. Phys. Lett. 78, 3714 (2001); Larry A. Nagahara, Islamshah Amlani, Justin Lewenstein, and Raymond K. Tsui, Appl. Phys. Lett. 80, 3826 (2002)], individual nanotubes were not isolated out from the aligned nanotube bundles to form functional devices.

[**0026**] In the present invention the chip is designed so that the electric field and the electric field gradient work together to trap and align all nanotubes in a droplet to form single-nanotube-based devices. The method of using a non-uniform electric field to move a polarized dielectric particle in a dielectric medium is called dielectrophoresis. Nanotubes (semiconducting and metallic) can be considered as point dipoles when polarize in electric fields [B. H. Fishbine, Full. Science & Tech. 4, 87 (1996)]. The electric field's force on a dipole moment P is $F=\nabla(P\cdot E)$. Since $P \propto E$ for dielectric particles with a linear response, $F \propto \nabla(E\cdot E)$.

[**0027**] A Si device for depositions using dielectrophoresis is shown in the inset to **FIG. 3A**. The structure consists of two Si islands separated by an array of teeth pairs. DC voltages are applied across the center trench. In a cylindrical coordinate system with the z-axis alone the trench direction, the electric field is inversely proportional to the azimuthal distance r as $E \propto 1/r$. The nanotubes can be treated as point dipoles that are always aligned with the electric field. The force $F \propto ?(E\cdot E)$ on a nanotube anywhere on the chip points towards the center trench. When the nanotube arrives at the trench, it strongly binds to the teeth pair contacts.

[**0028**] The nanotubes flying towards the center can be observed under a microscope. **FIG. 3A** shows the aligned nanotubes at a voltage of 6V. All teeth pairs are connected by one or a few CNTs. Excess nanotubes land on the anode side of the trench. A few nanotubes (less then 5%) are observed outside the center region. Using a higher voltage and a more dilute nanotube solution enables the deposit of single nanotubes only. In **FIG. 3**B, single nanotubes are aligned at 8V with no nanotubes observed anywhere else on the chip.

[**0029**] Without capillary force, would electric fields alone be effective in trapping nanotubes? To answer this question, "gold" teeth patterns on oxides (inset to **FIG. 4**) were studied. At 10V, all nanotubes in the droplet are trapped within the gap along the electric field line directions. No nanotubes are observed outside. This technique is called nanotube trapping. Since CNTs can be metallic or semiconducting, this technique traps both types of nanotube. However, only semiconducting CNTs are expected to be connected for the following reason.

[0030] The total resistance of the nanotube-gold device, which contains 200 teeth pair contacts, is 57 KΩ (measured). Assuming that each contact pair is connected by 20 nanotubes, and half of them are metallic, then the metallic nanotubes should determine the resistance of the device. The resistance of the device should be $R=R_m/(10\times200)=50\ \Omega$, where $R_m\approx100$ KΩ is the two-probe resistance of a metallic CNT [M. Ahlskog, R. Tarkiainen, L. Roschier, and P. Hakonen, Appl. Phys. Lett. 77, 4037 (2000)]. Thus R is 1000 times lower then the measured resistance of 57 KΩ. Could the device be connected only by semiconducting nanotubes? At 10V, the current through each metallic nanotube should be $I=(10V/50\ \Omega)/2000=100\ \mu A$. This current is high enough to burn up metallic nanotubes within one second [P. G. Collins, M. S. Arnold and P. Avouris, Science, 292, 706 (2001)]. Therefore, the logical explanation is that only semiconducting nanotubes are left connected.

[0031] In summary the invention is a method for controllably depositing CNTs. CNTs are produced by any available method and are suspended in a solvent. A trench is formed between two contact points on a device to which a CNT is to be attached. A droplet with suspended CNTs is applied between the contact points. The solvent is preferably acetone or another solvent that evaporates easily. The solvent in the droplet evaporates, leaving a CNT attached between the contact points. The trenches have micron-sized widths so that capillary forces act on the droplets. Greater attachment efficiency is obtained by creating an aligning electric field across the trench by applying a low voltage, typically about 5-10V, between the contact points.

[0032] In conclusion, the invention uses unique substrate geometries to trap and align single CNTs with nearly complete control. Aligned semiconducting nanotubes can be selectively deposited by burning off the metallic nanotubes. This technique provides an important step towards realistic applications of CNT-based-devices. The invention includes devices fabricated by this method, i.e. devices formed of a device substrate having one or more pairs of contact points (and any other circuitry or other device features) and a nanotube connected between each contact pair by this technique.

[0033] Although described with respect to carbon nanotubes, the invention also applies to nanotubes of other compositions. The invention can also apply to any other nano-elongated objects suspendable in a solvent, including nanowires and biomolecules (DNA, protein, etc.) The various nanomaterials may use different solvents that wet the substrate and react with the electric field differently.

[0034] Changes and modifications in the specifically described embodiments can be carried out without departing from the scope of the invention which is intended to be limited only by the scope of the appended claims.

1. A method for controllably depositing a nanotube between a pair of contact points, comprising:

forming a trench between the pair of contact points;

forming a suspension of nanotubes in an evaporatable solvent;

applying a droplet of the solvent with suspended nanotubes between the pair of contact points;

allowing the solvent to evaporate, leaving a nanotube connecting the pair of contact points.

2. The method of claim 1 wherein the trench has a micron-sized width.

3. The method of claim 2 further comprising applying an aligning electric field between the pair of contact points.

4. The method of claim 3 wherein the aligning electric field is applied by applying a voltage of about 5-10V between the pair of contact points.

5. The method of claim 1 further comprising applying an aligning electric field between the pair of contact points.

6. The method of claim 1 wherein the nanotubes are carbon nanotubes.

7. The method of claim 1 wherein the solvent is acetone.

8. The method of claim 1 wherein the trench has a width such that a substantial capillary force acts on the droplet.

9. The method of claim 1 further comprising removing metallic nanotubes and leaving semiconducting nanotubes.

10. The method of claim 9 wherein the metallic nanotubes are removed by passing an electric current therethrough to burn off the metallic nanotubes.

11. A device comprising:

a device substrate having one or more pairs of contact points thereon; and

a nanotube connected between each contact pair by the method of claim 1.

12. A device comprising:

a device substrate having one or more pairs of contact points thereon; and

a nanotube connected between each contact pair by the method of claim 3.

13. A device comprising:

a device substrate having one or more pairs of contact points thereon; and

a nanotube connected between each contact pair by the method of claim 9.

14. A method for controllably depositing a nano-elongated object between a pair of contact points, comprising:

forming a trench between the pair of contact points;

forming a suspension of nano-elongated objects in an evaporatable solvent;

applying a droplet of the solvent with suspended nano-elongated objects between the pair of contact points;

allowing the solvent to evaporate, leaving a nano-elongated object connecting the pair of contact points.

15. The method of claim 14 wherein the trench has a micron-sized width.

16. The method of claim 15 further comprising applying an aligning electric field between the pair of contact points.

17. The method of claim 14 further comprising applying an aligning electric field between the pair of contact points.

18. The method of claim 14 wherein the nano-elongated objects are selected from nanotubes, nanowires, and biomolecules.

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