High-resolution nanofabrication using a highly focused electron beam

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High-resolution nanofabrication using a highly focused electron beam

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A highly focused electron beam can be used to shape nanodevices. We demonstrate electron beam etching of nanoholes through multiwalled carbon nanotubes (MWNTs) and niobium nanowires. Nanoholes, as small as ~2.5 nm in diameter, can be reproducibly fabricated. This technique can also be used to fabricate constrictions and larger nanoholes in MWNTs. We argue that with some improvement, this technique might be used to pattern suspended graphene by the removal of targeted single atoms. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2957590]

I. INTRODUCTION

The ultimate goal of nanotechnology is to make structures and devices with atomic precision. One method for fabricating atomic structures, such as quantum corrals, is based on a scanning tunneling microscope.[1,2] This approach is very powerful but is not typically used to fabricate electronic devices. Here we propose a different approach, one which might in the future be developed into a technique for fabrication of electronic devices with atomic precision. This approach is the electron-beam expulsion of single atoms (EBESA) from nanoscale objects (such as carbon nanotubes, graphene layers, and metallic nanowires). The most interesting target for EBESA would be graphene, which is a stable monoatomic layer of carbon atoms. It was recently shown that it is possible to produce atomically thin graphene, i.e., isolated graphite layers.[3] Graphene is an ideal choice for single atom manipulation due to its exotic Dirac electronic spectrum. In particular, this spectrum explains the dependence of the metallicity of carbon nanotubes on their crystal orientation.[4] In graphene, the electronic properties of the Dirac electrons are extremely sensitive to boundary conditions on the atomic scale.[5] By controlling the geometry, one expects that various transistors and switches can be fabricated from graphene if it is properly shaped.[6] Tunable nonlinear devices, such as a signal multiplier, might be fabricated from a graphene nanoribbon with perfect edges.[7] Atomically perfect ribbons may find further applications in spintronics[8,9] and in quantum information processing.[10] Although graphene is naturally a zero-gap semiconductor, the inducement of an energy gap has already been demonstrated for epitaxially grown graphene on a SiC substrate.[11] This indicates that atomic manipulation of samples on a suitable substrate, such as SiC, could lead to semiconductor devices. The ability to introduce atomic defects[12] into a graphene layer is also of fundamental interest for connecting electron transport measurements with relativistic Dirac scattering.[13] A schematic representation of EBESA, as applied to graphene, is shown in Fig. 1. Here, the circles represent the atoms of graphene. They form the well-known honeycomb lattice. The electronic beam (red) is focused on individual single atoms and is expelling the targeted atoms thereby forming cuts in the graphene layer with atomic precision. In the example of Fig. 1, a schematic tripod device is being fabricated, with three graphene strips coming together at a single hexagon (black). The actual geometry of a working device might be different from this example.

We show a high resolution (although not yet atomic resolution) nanofabrication with the help of a high energy, highly focused electron beam. This method was not directly applied to graphene as fabricating transmission electron microscope (TEM) compatible suspended graphene samples is an arduous, although not impossible, task.[14] Instead, we applied this method to multiwalled carbon nanotubes (MWNTs), which are composed of a number of rolled-up graphene layers. We demonstrate etching of nanoholes (with diameters as small as ~2.5 nm; see Fig. 2) in carbon nanotubes. We also fabricated larger nanoholes, as large as 11 nm in a 26 nm diameter nanotube, and constrictions in a nanotube (see Fig. 3). In addition, we etched nanoholes with diameters as small as ~2.5 nm in niobium nanowires (see Fig. 4). This work is a continuation of our previous effort to lo-

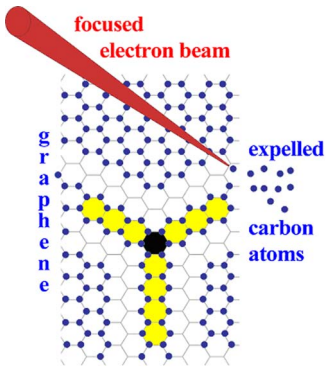

FIG. 1. (Color online) Schematic drawing illustrating the idea of atomic scale nanofabrication with EBESA. The process is illustrated with a graphene layer, which is a monolayer of carbon atoms in a hexagonal lattice. The electron beam, focused into a spot of a size smaller than the distance between the atoms, is used to expel unwanted atoms from the graphene layer. By this approach, nanofabrication with atomic resolution might be achieved. The drawing illustrates a hypothetical tripod electronic device (yellow and black). The exact shape of the device can be tailored to the desired function of the device.

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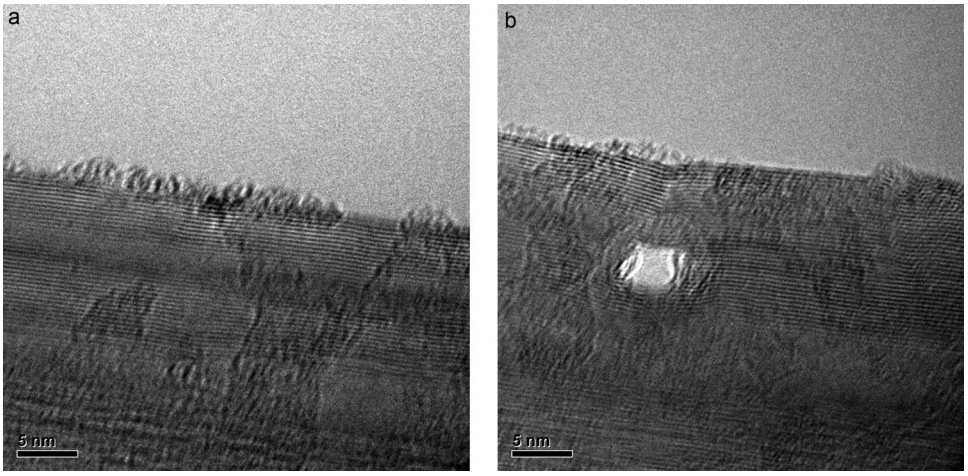

FIG. 2. Electron beam modification of a freely suspended MWNT. (a) Freely suspended arc discharge MWNT (scale of bar=5 nm). (b) Freely suspended arc discharge MWNT with an e-beam drilled 2.5 nm diameter nanohole. The majority of the nanotube is unchanged (scale of bar=5 nm). Modification was in a hot stage at 500 °C.

cally modify nanowires with an electron beam.[15] We describe the details of the fabrication and consider possible applications of this method.

The level of precision in removal of material with a TEM beam required for EBESA has not yet been achieved. Previously, pores, wires, constrictions, and other structures have been fabricated with a TEM using a similar method. Direct etching of resists by a focused electron beam has been explored.[16,17] Nanopores in silicon nitride and silicon oxide membranes have been fabricated.[18,19] Constrictions in niobium have also been made.[15] Gold nanogaps have also been fabricated.[20] Wires, constrictions, loops, and other structures were recently reported.[21,22] Nanoholes in carbon and various other materials have also been reported.[23] Exposure of carbon nanotubes to uniform electron beams have been extensively investigated and effects such as bonding,[24] etching,[25–27] and amorphization[28] have been seen. Focused electron beams have been used to cut bundles of SWNTs.[29] A focused electron beam was also used to etch a single wall of a MWNT[30] and to create dislocations in SWNTs.[31] Cuts have been etched in boron nitride nanotubes as well.[32]

II. EXPERIMENT

We etched nanoholes in both MWNTs deposited directly on TEM compatible (i.e., transparent to the electron beam) membranes and MWNTs suspended across slits. We used low stress silicon nitride membranes (SPI Supplies, Inc.) which were 100×100 μm^2 and 100 nm thick. The silicon frame supporting the membrane was 3×3 mm^2 and 200 μm thick to fit into a standard TEM holder or a hot stage. Using potassium hydroxide (KOH) etching, we also fabricated our own 50 nm thick membranes in a 5×8 mm^2 and 400 microns thick silicon frame. We built a custom TEM holder to accommodate our membranes. Arc discharge MWNTs (Alfa Aesar) were deposited by crushing the soot powder containing the MWNTs between two pieces of polydimethylsiloxane (PDMS) (Sylgard 184, Dow Corning), thus dispersing the nanotubes. Touching and removing the nanotube covered PDMS to the membrane or slit transferred nanotubes to the sample.[33] This ensured that the nanotubes were only on one side of the membrane facing away from the TEM beam when the sample was inserted into the TEM. Because the silicon nitride is electron transparent, the nanotube is visible (see Fig. 5). The main disadvantage of placing the nanotube directly on the silicon nitride is the loss of detail from the amorphous silicon nitride obscuring the nanotube.

Suspending nanotubes across an open slit in a substrate improves the resolution of the TEM images (see Fig. 2 or 3). 200 nm–1 μm wide slits were formed by making cuts with

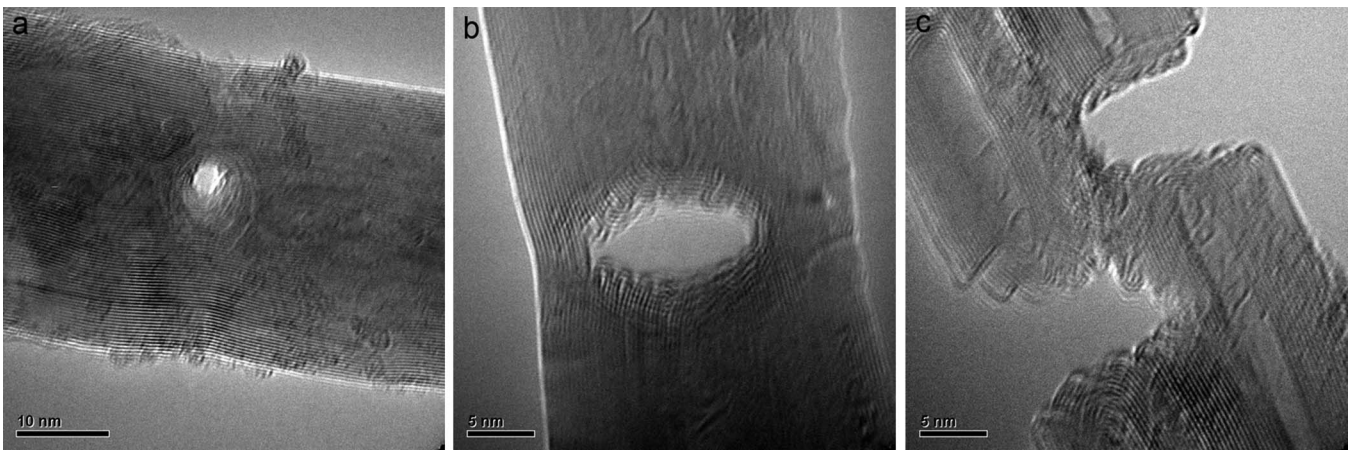

FIG. 3. Various modifications of MWNTs with a focused electron beam. (a) A "small" (~2.5 nm diameter) nanohole in a MWNT (scale of bar=10 nm), (b) a "large" ~11 nm across elliptical nanohole in a 26 nm diameter MWNT (scale of bar=5 nm), and (c) a constriction in a MWNT fabricated by etching in from both sides (scale of bar=5 nm). Modification was in a hot stage at 500 °C.

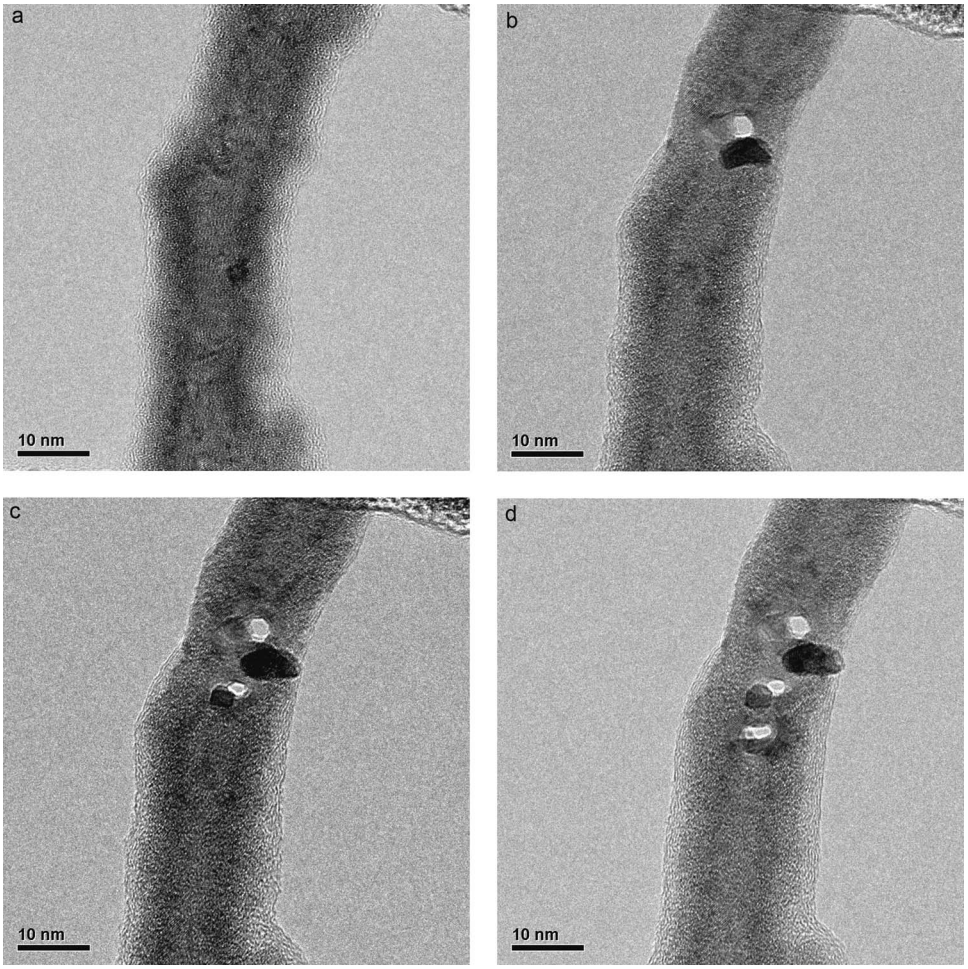

FIG. 4. Drilling multiple holes in a niobium nanowire with a 200 keV electron beam. The width of the wire is about 20 nm. (a) Initial unmodified niobium wire (scale of bar=10 nm). (b) Single nanohole drilled with a focused electron beam (scale of bar =10 nm). (c) Two nanoholes drilled with a focused electron beam (scale of bar=10 nm). (d) Three nanoholes drilled with focused electron beam (scale of bar=10 nm). The sizes of the holes are 3, 2, and 2 nm, respectively. The distances between the holes are 6 and 9 nm. Grains of the material typically form near the holes drilled and are visible as darker spots. Modification was at room temperature.

a focused ion beam (FIB) machine starting on the membrane and ending on the silicon support chip. The increased thickness of the silicon support provided more rigidity than slits cut directly in the membrane but limited the length of slits to ~ 3 μm.

We also etched nanoholes in metallic nanowires (see Fig. 4). The fabrication of metallic nanowires was done by molecular templating which has been previously described.[34] We fabricated several 100–200 nm$\times$10 μm long slits directly on a 500 nm thick silicon nitride membrane (SPI supplies) by FIB milling. Subsequently, fluorinated single walled carbon nanotubes (FSWNTs) were deposited on the slits by dipping the chips in a nanotube solution. FSWNTs (Carbon Nanotechnologies Inc.) used for molecular templating were suspended in isopropanol. The nanotubes were deposited on the samples by dipping the samples into the isopropanol/FSWNT suspension followed by a dip in clean isopropanol and then blown dry with a nitrogen gun. Metal was deposited on top of the nanotube by dc sputter deposition process to form a wire.[34]

The TEM used was a JEOL 2010F, which uses a field emission gun operating at 200 kV. The TEM compatible sample with the nanotubes or nanowires was loaded into the TEM. For heating the sample, a Gatan hot stage was used. Standard alignment procedures were followed to obtain an image. Images were captured at low magnification with low beam intensity. A charge coupled device (CCD) camera captured the image using a Gatan Micrograph software. For etching, high magnification ($800000\times$-$1.5\times10^6\times$) was used. The beam is focused to a caustic spot which is used for etching. Low intensity illumination around the caustic spot is used for visual feedback. However, at room temperature, the beam is intense enough to cause amorphization of the nanotube (as is known to happen for high enough beam intensities).[28] Heating the MWNTs to 500 °C in a hot stage minimized this amorphization effect.[30] Overfocusing the microscope causes a distorted magnification effect, making it easier to get direct visual feedback of the etching process. Etching is confirmed by the observation of the appearance of black edged rings since overfocused objects have a black diffraction edge (when underfocused they have a white diffraction edge).[35] In this case, the edges of the hole as they are being formed are what we are seeing. Small holes are formed by keeping the beam in one spot. Larger holes, slits, and constrictions are formed by sweeping the beam manually with the beam shift (see Fig. 3). Etching is viewed on the green phosphor screen (intensity of caustic spot is too high to view in the CCD). Typically, spot size 1 and alpha 3 were used but milling was also observed with different spot sizes and alphas. Finding optimum conditions for etching requires some on the fly adjustment of focus and beam intensity, but the etching effect itself is quite reproducible in all materials.

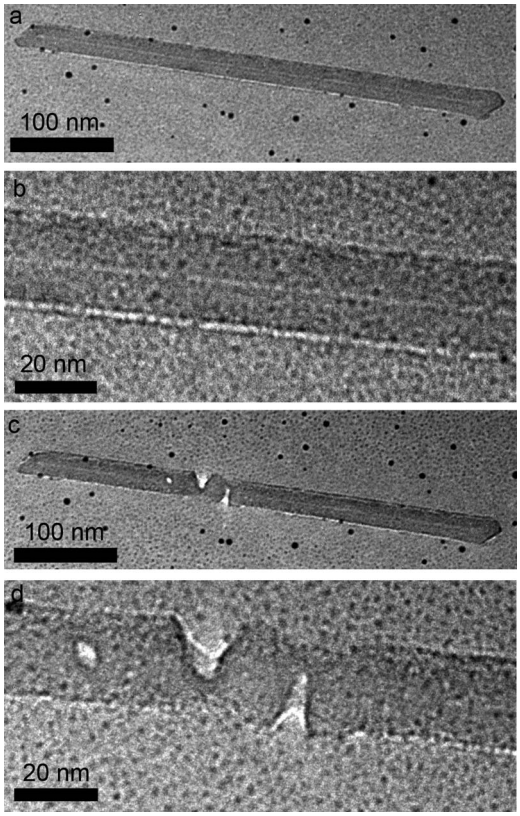

FIG. 5. Electron beam modification of a MWNT on a silicon nitride membrane. (a) TEM micrograph of an unmodified nanotube placed on the surface of a 50 nm low-stress silicon nitride membrane (scale of bar=100 nm). The gray colored background corresponds to the amorphous SiN membrane. The image is underfocused (creating white diffraction lines at the edges) to contrast the nanotube against the amorphous layer. The black spots are from the deposition process. (b) Close-up TEM micrograph of the unmodified tube in a scale of bar=20 nm. (c) TEM micrograph of the nanotube after modification with the electron beam of the TEM (scale of bar=100 nm). (d) Close-up TEM micrograph of the modified nanotube with a nanohole (on the left, $\sim 2.5 \times 4$ nm^2) and two nanoconstrictions. In the nanoconstrictions, the silicon nitride can still be seen (scale of bar=20 nm). Modification was at room temperature.

III. DISCUSSION

We etched nanoholes in both carbon nanotubes and niobium nanowires. For metals[35] and nanotubes,[27] beam heating should be negligible and the dominant modification effect should be knock-on (displacement of the atoms by collision with the electrons). The maximum energy transferred when a relativistic electron strikes an atom follows the formula

$$T_{\max} = \frac{2E(E + 2m_e c^2)}{Mc^2},$$

where $T_{\max}$ is the maximum energy transferred to the atom struck by the electron, E is the energy of the electron, m_e is the mass of the electron, c is the speed of light, and M is the mass of the atom struck.[36] Assuming 200 keV for the energy of the electrons (since the 2010F has a 200 kV acceleration voltage) we can calculate the maximum transferred energy for C where $T_{\max}=43.7$ eV and for Nb where $T_{\max}=5.64$ eV. The displacement energy of materials (the energy needed to displace an atom) is typically between 5 and 50 eV and depends on the type of chemical bond of the material.

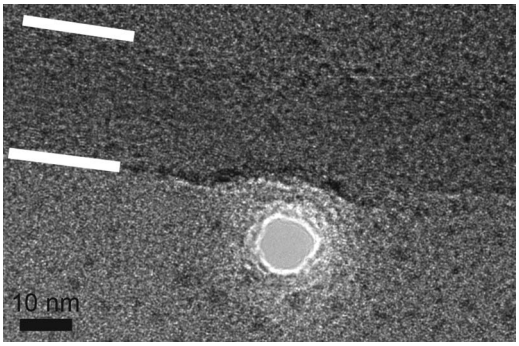

FIG. 6. A TEM micrograph of a nanopore etched in a SiN membrane with a 200 keV focused electron beam (scale of bar=10 nm). The white lines indicate the location of the MWNT. The hole is purposefully positioned near a MWNT. This sample design might be useful for experiments where molecules or nanoparticles are translocated through the pore and detected or characterized with the nanotubes. This sample design might be useful for DNA/nanopore sequencing.

For C (MWNT) $E_d=15-20$ eV[36] and for Nb $E_d=24$ eV.[35] If the energy transferred exceeds the displacement energy, the material will be expelled. The energy needed to displace a carbon atom is exceeded so the carbon atoms are quickly expelled and a nanohole is cleanly etched through the carbon nanotube. For Nb, the energy imparted is not enough to expel the atom from a bulk sample. However, the energy required for sputtering (knocking an atom from the edge of a surface) is typically about 50% or less of the displacement energy.[35] Furthermore, other effects such as radiation induced diffusion or impurity enhanced displacement which this simple model does not take into account may also enhance the etching.[36] The less energetic expulsion of atoms from the niobium nanowire may be the source of the grains we observed near the nanoholes. The nanoholes etched in niobium were still comparable in size to those obtained in carbon nanotubes (see Fig. 4).

MWNTs and metallic nanowires have interesting and potentially useful transport properties. Local modification of a MWNT or nanowire might extend the usefulness of these properties. The constriction shown in Fig. 3 could be expected to impede electron flow and have significantly different transport properties from an unmodified nanotube. Two constrictions in series could possibly be used to make a single electron transistor, perhaps even one operating at room temperature. The nanoholes might be used as nanoscale magnetometers. On a side note, modification of the silicon nitride membrane near the MWNT is also possible. Such a sample design might be applicable to DNA/nanopore sequencing. It has been shown that a DNA molecule can be made to translocate through a nanopore lengthwise with each base pair going through the nanopore one by one.[37–41] It has been suggested that a nanopore articulated with nanotube electrodes might be able to detect differences between these base pairs and thus sequence DNA. By modifying the silicon nitride membrane near the nanotube, a nanopore articulated with a SWNT or a modified MWNT could be fabricated (see Fig. 6). The nanotube near the nanopore might even be modified to be a room temperature single electron transistor.[15,42,43]

This approach might allow an unprecedented amount of information about the molecule translocating the nanopore to be detected.[41,44]

In the above section we demonstrated that the electron beam can be used to etch extremely small nanoholes, as small as 2.5 nm in diameter. The next goal would be to achieve true EBESA, i.e., removal of single atoms. Here we argue that with existing technology this goal should be possible to realize. We choose graphene as our example. One requirement is that the layer on which EBESA is to be performed should be extremely thin, i.e., a monolayer or just a few atomic layers. Otherwise, scattering of electrons will not allow the beam to focus on a small enough area. TEM compatible graphene samples with a graphene monolayer suspended on TEM grids have been produced.[14] Graphene samples with a graphene monolayer suspended across a trench have also been produced.[45] EBESA requires a beam of electrons focused onto a spot comparable or smaller than the distance between the atoms in an atomic layer. The beam of electrons in existing TEMs can be focused on such a small size. Spot sizes as small as 0.75 Å have been demonstrated.[46] This is two times smaller than the smallest distance between atoms in graphene, which is 1.4 Å. Furthermore, it is known for single wall carbon nanotubes that the threshold energy, i.e., the energy the electrons require to knock out a carbon atom from the nanotube, is 80–140 keV.[28] The threshold energy for graphene can be expected to be similar. Modern TEMs (such as the 2010F we used) routinely operate at 200 kV so this energy requirement is easily satisfied. While it seems feasible to fabricate devices with atomic resolution using this method, there are still several technological difficulties to overcome. Keeping the modification localized to a single atom area and imaging a single atom dislocation in a TEM are the most obvious examples.

IV. CONCLUSION

In conclusion, we have demonstrated that a highly focused electron beam can be used to fabricate nanoholes and nanoconstrictions in MWNTs and niobium nanowires. We have discussed some potential applications of this fabrication method, such as articulating a nanopore with nanotube electrodes for DNA/nanopore sequencing experiments. We have also suggested that this fabrication method might in the future be extended down to the atomic scale, i.e., EBESA.

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