Field-emission induced growth of nanowires

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Nanowires are grown from a cold-field-emission tip in the presence of a precursor, typically an organometallic or organic compound. Electron emission from the newly grown nanowire tip continues the growth and can give rise to nanowires that are tens of microns long. Single nanowires are obtained by limiting the field-emission current to values of typically 100 nA or less. Tungsten nanowires with diameters of less than 4 nm have been grown from $W(CO)_6$. Other nanowires grown include cobalt, iron, and carbon. Composite wires can be fabricated by continued growth with different precursors. Nanowires have been grown on etched wire tips, carbon nanotubes and scanning probe tips. Voltages applied to electrodes on an integrated circuit die can be used to attract a nanowire towards and contact a biased electrode. By such means, it is possible to connect the end of a pointed structure, such as a carbon nanotube, to an electrode. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1529084]

Nanowires and tubes have attracted research interest in recent years as their functional properties hold promise for incorporation into nanoscale devices and systems. In particular, carbon nanotubes have been used as field-emission sources,[1] scanning probe microscope tips,[2,3] and nanoscale electronic devices.[4–7] Although carbon nanotubes can be selectively grown by catalytic growth on prepatterned catalyst films[8–10] or other templates,[11] the nanotubes are often grown *ex situ*, harvested, and redeposited, micromanipulated, and connected as required for electrical characterization. These procedures are followed for other types of metallic and semiconductor nanowires grown by electrodeposition[12] and various schemes based on the vapor-liquid-solid (VLS) mechanism.[13–15]

The growth of metallic dendritic structures had previously been observed to result from electron emission from a cathode in the presence of metal carbonyls. The technique has been used for the production of field-ion emitters.[16] Similar dendritic structures were obtained by thermal and cold-field emission using $Cr(CO)_6$[17] and $Mo(CO)_6$.[18] It was proposed that the needles grow by metal ions supplied from a corona plasma that is sustained by the field-emitted electrons.

Here we report on the growth of single nanowires by cold-field emission in the ambient of a suitable precursor gas, typically an organometallic compound. Nanowire growth is initiated at a sharp tip where a sufficiently high electric field causes field emission to occur. The electrons dissociate precursor molecules ahead of the tip. Ionized molecular fragments attracted back towards the tip result in the self-sustained growth of a conductive nanowire, the tip front

of which forms the field emission source. Single-nanowire growth is achieved by controlled low-current emission. In contrast to *ex situ* growth techniques, the present technique allows the growth of a nanowire at a defined point that is simply a sharp tip. The point of initiation naturally provides a mechanically strong electrical anchor for the nanowire, while the other end of the nanowire can be contacted to another electrode by electrostatic attraction to complete a circuit where desired.

We carried out nanowire growth in the chamber of an environmental scanning electron microscope to facilitate immediate viewing during and after growth. The precursor gas is introduced into the chamber through a nozzle directed at the growth site around 1 mm away. In our setup, the nozzle also acts as an anode that is biased typically at a few hundred volts relative to the pointed tip. A feedback control to the high-voltage supply allows the field-emission system to operate in constant current mode which is important to achieve sustained single-nanowire growth. Prior to the admission of the precursor, relatively high voltages, at an anode–cathode spacing of typically 100 μm, are required to obtain a field-emission current of several tens of nA from a tip of around 50 nm radius. Upon admission of the gas, the voltage required to maintain the same current drops rapidly, after an initiation period, to typically 80–200 V as the result of the growth of a nanowire with much smaller tip radius. Figure 1 shows the rapid decrease in the anode voltage, initially at 3 kV, upon admission of the precursor gas into the chamber at a time indicated by point A. At point B, the current compliance of the control loop is reached, and the system subsequently operates in a constant-current mode. This period of decreasing voltage corresponds to the growth of a material cone at the point of field emission. The voltage profile then
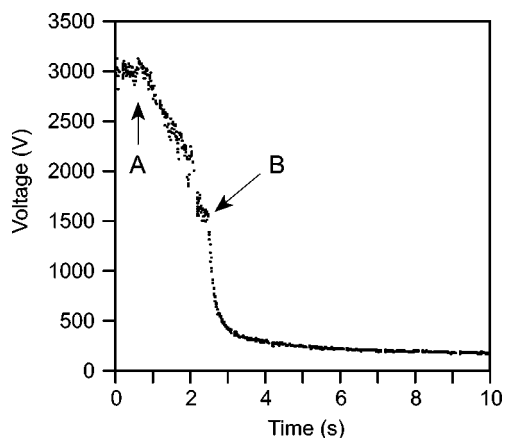
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FIG. 1. Anode voltage during nanowire growth. Precursor gas admitted at *A*. The transition at *B* is due to the control loop kicking in to operate in constant current mode.
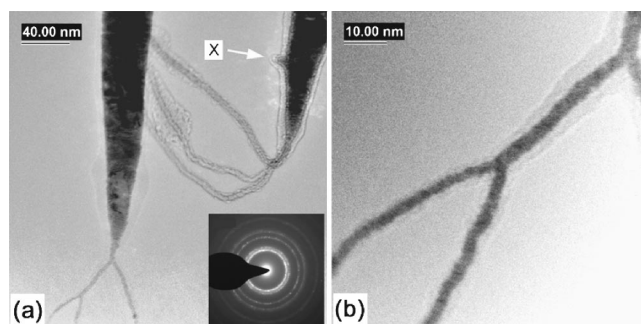

FIG. 2. (a) TEM (300 keV, Philips CM300) micrograph of two relatively thick tungsten tips grown at high current, followed by a reduction in the growth current to produce smaller nanowire branches. Point *X* shows the initiation of a new nanowire at the shank of the right-hand side tip. Inset shows the electron diffraction pattern near the tip of the shank confirming that the material is tungsten. (b) Higher magnification images of the smaller nanowires show that the tungsten core has a diameter of less than 4 nm towards the leading end. The amorphous carbonaceous coating which progressively thins out towards the growing tip.

flattens out in the steady-state nanowire growth regime.

Nanowire growth is easily carried out on naturally sharp tips such as electrochemically etched tungsten tips or atomic force microscope (AFM) tips, the latter providing an easy self-aligned route to fabricating fine, high-aspect ratio tips on a conventional scanning probe tip.[19] Using tungsten hexacarbonyl $[W(CO)_6]$ as the precursor, tungsten nanowires with core diameters as small as 3–4 nm and up to several microns in length can be grown. Low field-emission currents of around 100 nA are needed to maintain single-nanowire growth. Under similar growth conditions, iron nanowires grown from iron pentacarbonyl $[Fe(CO)_5]$ are comparable in diameter, typically less than 10–15 nm. On the other hand, cobalt nanowires grown from dicobalt octacarbonyl $[Co_2(CO)_8]$ and cobalt tricarbonyl nitrosyl $[Co(CO)_3NO]$ are around 30 nm in diameter, while carbon nanowires grown from acetylene are considerably thicker at around 250 nm. The diameter dependence on growth parameters and material is currently being studied.

Higher currents provide higher growth rates and thicker nanowires, but can give rise to random forking and the formation of multiple nanowires. Figure 2(a) shows a bright-field TEM image of the tips of a typical treelike tungsten structure. Point *X* on the micrograph shows the initiation of a new nanowire. Electron diffraction patterns confirm that the structure comprises tungsten polycrystals. Figure 2(b) shows that the leading edges of the tungsten nanowires are ~3–4 nm in diameter. A buildup of amorphous carbon can be observed along the length of the nanowires, becoming gradually thinner closer to the growing tip. The deposit most likely arises as a byproduct of the metal deposition process. The carbonyl group released from the precursor during the metal deposition reaction subsequently deposits along the length of the growing nanowire. The carbon deposit may serve the useful purpose of reducing the extent of oxidation of the metal nanowires upon exposure to atmosphere.

Material deposition had previously been observed on the tip in scanning-tunneling-microscopy (STM) assisted of materials.[20] Nanowire growth observed by Kent *et al.*[21] on a negatively biased STM tip was attributed to a field-induced reaction. With the present technique, material growth at the tip is not observed in the absence of field-emission. The pro-

posed growth mechanism is the dissociation and ionization of the precursor molecule by the narrow cone of electrons emerging from the field emitter: this is in contrast to growth arising from nonspecific electron emission results in massive dendritic structures.[22] As the threshold electron energies required to form W^+ and $W(CO)^{x+}$ ions from $W(CO)_6$ lie between 8 and 23 eV,[23] the peak ion distribution is at a short distance ahead of the tip as a result of the diverging electron beam and decrease in ionization cross-section at larger electron energies. Fragmentation of the molecule imparts a radial velocity component depending on the molecular species involved which means that the ionized fragments may not necessarily follow the electron trajectories back to the electron emission point on axis. Ions formed further away, and those with substantial radial velocities would impinge on the nanowire shaft causing it to thicken. A steady-state deposition profile is established whereby the electron-emission cone from the formed tip ionizing the molecules and the ensuing ion trajectories deposit a new tip surface that is identical to the underlying tip profile. Field-induced reactions at the tip may be responsible for further molecular dissociation at the growth front.

Positive ions attracted back towards the field emission tip are well known to be responsible for the sputtering of field emitters.[24] However, in the present case, the molecular flux involved is much higher, with gas pressure at the delivery nozzle estimated at 1 mbar, and the ionized species impinging on the cathode causes material buildup. At lower gas pressures, nanowire growth becomes erratic, which is believed to be due to a competing process of sputtering by high-energy ions. Composite nanowires can be grown by interrupting the growth and switching the precursor. In this manner, we have grown tungsten/cobalt/tungsten, tungsten/iron and other such systems.

We demonstrated the use of metallic nanowires to connect one end of a carbon nanotube (CNT). A sparse array of 70 nm diameter multiwalled CNTs was grown by plasma-enhanced chemical vapor deposition (PECVD) using a mixture of ammonia and acetylene and nickel catalyst on a silicon substrate. Field emission from a selected CNT in the presence of tungsten carbonyl was initiated by bringing an

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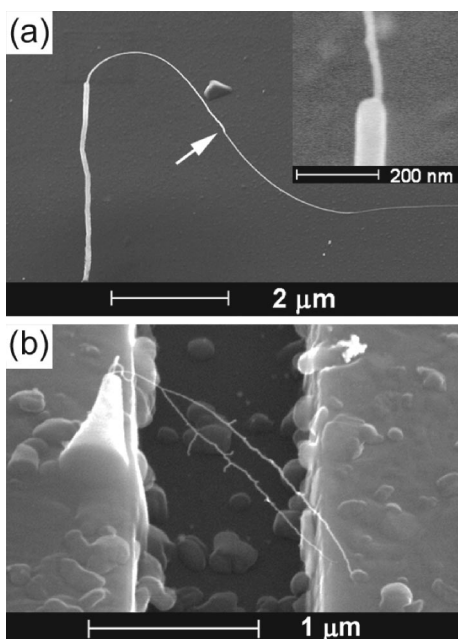
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FIG. 3. (a) Tungsten nanowire grown on carbon nanotube. The discontinuity indicated by the arrow is due to an interruption in the growth for an intermediate viewing of the nanowire which was bent, but still free-standing at this point. The final length of the nanowire allowed it to contact the silicon substrate after the removal of the anode bias. Inset: higher-magnification micrograph showing the attachment of the nanowire to the tip of the carbon nanotube. The estimated diameter of the nanowire is less than 15 nm upon initial viewing in the SEM, but appears thicker in the micrograph due to contamination buildup; (b) a forked pair of tungsten nanowires grown by field emission from cone-like structure deposited via electron beam deposition from tungsten carbonyl.

etched tungsten tip, acting as an anode, into close proximity to the CNT tip. Figure 3(a) shows a free-standing 3.5 μm length of tungsten nanowire of less than 15 nm diameter grown from the tip of the CNT. The growth was then continued to extend its length to 9 μm. Upon removal of the anode bias, the nanowire bent under its own weight to fall onto the substrate at the leading end.

The above technique could be used to connect nanostructures to electrodes on a silicon die with test electrodes connected externally via bond pads. As the requirement to initiate nanowire growth is a sharp point for field emission, a cone-like structure was first deposited on an electrode using electron-beam-induced deposition[25] using the focused SEM electron beam and tungsten carbonyl. The structure has a tip radius of around 30 nm which allowed the cone to field emit at a few hundred volts applied to a pointed anode placed above it. A free-standing tungsten nanowire was grown from the tip of the cone to a length of 1–2 μm. This nanowire can be deflected and bent by applying a voltage to an adjacent electrode and can be made to contact the electrode without fusing the nanowire if a sufficiently large current-limiting resistor is placed in series in the circuit [Fig. 3(b)]. Once contacted, the nanowire remains fixed to the electrode. A $I–V$ measurement (0–10 V) conducted on the deposited cone and series-connected nanowire shows near-ohmic be-

havior at room temperature. The measured resistance of 1 MΩ is attributed largely to the series resistance of the electron-beam induced deposited material. At much higher currents, the tungsten nanowires were observed to deform initially, and finally fused.

In summary, we have developed a technique for growing single nanowires by a self-field-emission process in the presence of an organometallic precursor. As the nanowire growth is initiated at a sharp point, the nanowires are well-anchored both electrically and mechanically to this point to form free-standing nanowires that can be used for scanning probe tips, and obviously for field-emission tips. Longer nanowires can be used for interconnection to the ends of nanostructures such as carbon nanotubes. We have also grown composite nanowires by switching precursors and continuing the growth. With the choice of suitable precursors to ensure compatibility between the diameters of the grown nanowires, it is possible to grow sub-20-nm nanowire systems such as an iron/tungsten segment on the end of a carbon nanotube. The deposition of composite magnetic nanowires would open up the possibilities of exploring spin electronics in such structures.

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