

Formation of metal nanowires on suspended single-walled carbon nanotubes

Y. Zhang and Hongjie Dai^{a)}

Department of Chemistry, Stanford University, Stanford, California 94305

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Suspended single-wall carbon nanotubes are used as substrates for deposition of various metals by evaporation. Deposition of many types of metals normally forms discrete particles on nanotubes due to a weak interaction between the metals and nanotubes. However, continuous nanowires of virtually any metal are obtained by using titanium, a metal with strong interaction with carbon, as a buffer layer on nanotubes. The metal nanowires can be ≤ 10 nm wide with continuous length up to tens of microns. © 2000 American Institute of Physics. [S0003-6951(00)05545-5]

Carbon nanotubes are ideal templates for obtaining a variety of nanowire materials.^{1,2} The unique structures of nanotubes provide confined platforms for physical processes and chemical reactions. Successful examples include the conversion of nanotubes into carbide or nitride nanorods,^{3,4} and the filling of carbon nanotubes with metal or its compound materials.⁵⁻⁹ However, those methods are not suitable for the formation of nanowires of most elemental metals. A new approach has been reported to fabricate Mo-Ge superconducting nanowires using sputter deposition on a carbon nanotube substrate.¹⁰ In principle, nanowires of any metal can be obtained in a similar way by simply depositing metal onto nanotubes if the formation of a homogenous coating on carbon nanotubes is possible. This is true only for a limited number of metals including titanium that have strong interactions with nanotubes, as shown in a previous study.¹¹ Many types of metals do not form continuous structures on a nanotube surface because of weak metal-carbon interaction. In this letter, we show that by using titanium as a buffer layer, the homogeneity of subsequent coating of various metals on the nanotubes are greatly improved. Continuous nanowires of virtually any metal are obtained by evaporating the metal on titanium-coated nanotubes. These metal nanowires, with widths ≤ 10 nm and lengths up to tens of microns, are difficult to fabricate by lithographic methods and should be useful in basic studies of metallic or superconducting nanomaterials.

Suspended single-wall carbon nanotubes (SWNTs) used in this work were grown directly on gold microgrids by chemical vapor deposition (CVD) of methane¹²⁻¹⁶ using a liquid phase catalyst precursor material. The catalyst precursor material was prepared by dissolving AlCl_3 , a triblock copolymer, iron, and molybdenum chlorides in a mixed ethanol and butanol solution, as described previously.^{15,16} Gold microgrids used for transmission electron microscopy (TEM) were dipped in the catalyst solution for a few seconds. After calcinations at 500 °C for ~ 12 h in air, a layer of catalysts was formed to partially cover the holes of the microgrids.¹¹ CVD growth was carried out in a 1 in. tube furnace at 900 °C under a 1000 mL/min methane flow for 15 min. Individual

and bundled SWNTs grown and suspended over the holes in the TEM grid were used for metal coating experiments. Metal deposition was carried out in an electron-beam evaporator. The gold microgrids were placed on a sample stage at room temperature, although some irradiation heating of the sample might have occurred during deposition. A quartz crystal oscillator was used to monitor the film thickness. The metal deposition rate was controlled at ~ 0.2 nm/s. The coated nanotube samples were characterized in a Phillips CM20 TEM operating at 200 kV.

TEM micrographs in Fig. 1 show the structures of Au, Pd, Fe, Al, and Pb coatings on as-grown SWNTs. The thickness of deposited metals was measured to be 5 nm. The metals all formed noncontinuous discrete particles on nanotubes, although the spacing between Pd particles is small compared to the other metals. Formation of disconnected particles is attributed to the weak interactions between SWNTs and the metals that lead to low nucleation rate and high surface diffusion rate of absorbed metal atoms.^{11,17} Clearly, continuous nanowires cannot be formed by directly coating the metals on nanotubes under typical metal deposi-

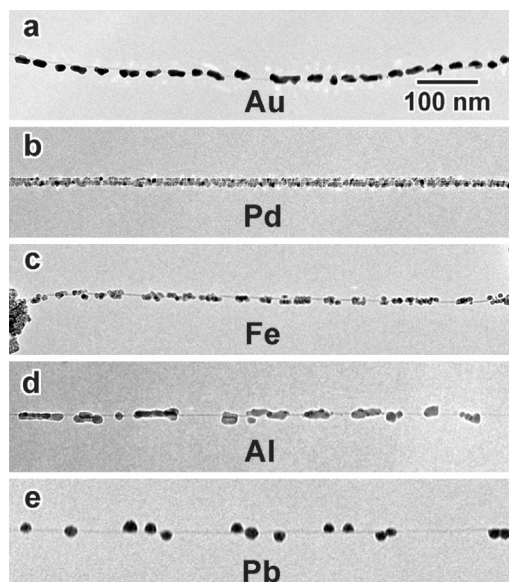


FIG. 1. TEM images of: (a) Au, (b) Pd, (c) Fe, (d) Al, and (e) Pb coating on carbon nanotubes with a nominal thickness of 5 nm.

^{a)}Author to whom correspondence should be addressed; electronic mail: hdai@chem.stanford.edu

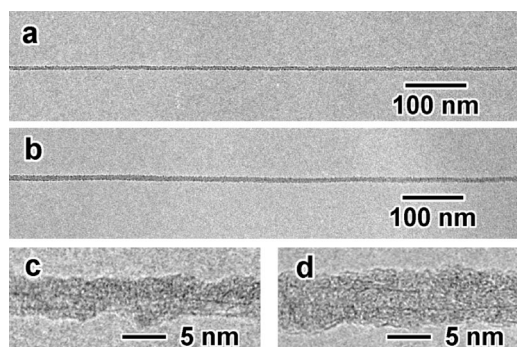


FIG. 2. TEM images of Ti coating on carbon nanotubes with a nominal thickness of 1 nm (a) and 2 nm (b). (c) and (d) are high-resolution TEM images from (a) and (b), respectively.

tion conditions. In strong contrast, evaporation of Ti leads to the formation of a continuous and uniform coating on nanotubes even at a nominal thickness of 1 nm (Fig. 2). This is attributed to strong interaction between Ti and SWNTs, high nucleation, and a low diffusion rate of Ti atoms on nanotubes.¹¹

With 1 nm Ti buffer layer on the SWNTs, subsequent deposition of other metals lead to nearly continuous and uniform metal coatings (Fig. 3). The 5 nm Pd and Fe coatings are found to form perfectly continuous nanowires on the Ti buffered SWNTs. Al coating is also continuous with certain variations in thickness along the nanotubes [Fig. 3(d)]. The Au and Pb coatings are nearly continuous, with small gaps (~ 1 – 2 nm) existing between metal particles at certain positions along the nanotubes. As the thickness of the Ti buffer layers are increased to 2 nm, continuous nanowires of Au, Pd, Fe, Al, and Pb are formed on the Ti buffered nanotubes (Fig. 4). Evidently, the continuity and homogeneity of all of the metal coatings on the 2 nm Ti modified SWNTs are dramatically improved over on the as-grown clean nanotubes. The various metal nanowires formed on the SWNTs buffered by 2 nm Ti are polycrystalline with widths measured from TEM data to be ≤ 10 nm for 5 nm metal depositions. The lengths of the nanowires are determined by the lengths of the SWNTs and are typically from several μm to $100 \mu\text{m}$. The Pb nanowires show appreciable variation in thickness with bead-like structures along the wires. This phenomenon could be due to the low melting temperature (327.5°C) of Pb and irradiation heating from the evaporation source during the deposition.

Earlier¹¹ and current work have found that many types of metals (e.g., Au, Al, Pd, and Fe) interact weakly with the sidewalls of carbon nanotubes, and the nature of the interaction is presumably Van der Waals. The binding energies of these metal atoms and carbon atoms on a nanotube are low, accompanied by low energy barriers for diffusion of metal atoms on the nanotube substrates. The weak interaction and high diffusion rates lead to few nucleation sites for metal crystal growth and large particle formations on nanotubes. Titanium is a $3d$ metal with many d vacancies and has a strong tendency to form carbide with a heat of formation of -54 kcal/mole.¹⁸ Furthermore, the curvatures of nanotubes¹⁹ may make SWNTs more reactive toward Ti. These may have led to covalent bonding characteristics of the Ti-SWNT system, as the d orbitals of Ti hybridize with the p orbitals of

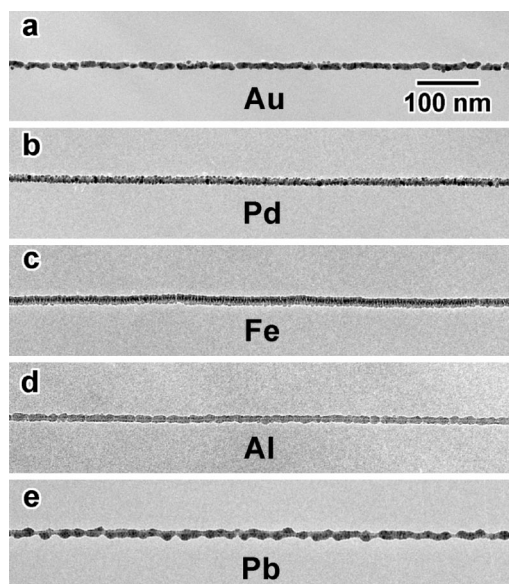


FIG. 3. TEM images of 5 nm (a) Au, (b) Pd, (c) Fe, (d) Al, and (e) Pb coating on carbon nanotubes with a 1 nm thick Ti buffer layer.

the carbon atoms on the nanotubes. The high Ti-SWNT binding energy, high condensation/sticking coefficient, nucleation rate, and diffusion barriers should be responsible for Ti forming continuous and uniform wires on SWNT substrates. Examined by high-resolution TEM [Figs. 2(c) and 2(d)], the Ti layers appear amorphous and may correspond to TiO_2 since the thin coatings have been exposed to air prior to TEM imaging. Also, the Ti coating has a roughness on the order of ~ 1 nm.

After a buffer layer (or adhesion layer) of Ti is formed on nanotubes, other metal atoms can stick to the substrates easily since metal-metal bonds can be formed and are stronger than simple Van der Waals interactions between metals and nanotubes. This effect is apparent in the case of Fe coating. Fe is a $3d$ metal with a few d vacancies; it should have stronger interaction with Ti than Au does because Au has no d vacancy and is chemically inert. This is consistent with the

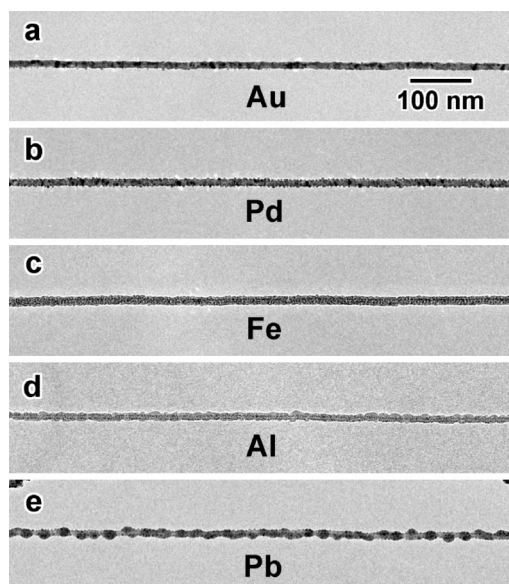


FIG. 4. TEM images of 5 nm (a) Au, (b) Pd, (c) Fe, (d) Al, and (e) Pb coating on carbon nanotubes with a 2 nm thick Ti buffer layer.

experiment results; Fe coating on a 1 nm Ti buffer layer forms very continuous nanowires, while Au does not.

Ti buffering for metal nanowire formation reported here bears some similarity to the widely known and used metal film deposition on certain substrates (SiO₂, glass, etc.) containing a buffer/adhesion layer (Ti, Cr). In the latter systems, the buffer metal (e.g., Ti, Al) interacts strongly with the substrate (e.g., SiO₂) presumably via metal–oxygen bonds.²⁰ Subsequent deposition of various metals on the buffered substrate leads to metal films that adhere strongly to the substrate. The current work identifies Ti as a buffering metal for carbon nanotubes and the likely interaction mechanism is through Ti–C bonds. Other early 3d metals including Nb, V, Sc, and Ta could also interact strongly with the sidewalls of nanotubes²¹ and are being investigated at the present time.

Our simple approach readily obtains ≤ 10 nm wide metal nanowires with controllable lengths up to tens or hundreds of microns. These nanowires are a challenge to be fabricated by lithography methods. The nanowires are composites of SWNTs in the core and Ti and a second metal on the outside. It will be interesting to investigate the properties of these wires (metallicity, superconductivity, and magnetoresistance) and explore their usage.

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