Metal coating on suspended carbon nanotubes and its implication to metal–tube interaction

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Received 5 June 2000; in final form 29 September 2000

Abstract

Coating of various metals on suspended single-walled carbon nanotubes (SWNT) is carried out by electron-beam evaporation. Transmission electron microscopy studies reveal that Ti, Ni and Pd coatings on the suspended tubes are continuous and quasi-continuous, resulting in nanotube-supported metal nanowire structures. In strong contrast, Au, Al, and Fe coatings on the suspended SWNTs only form isolated discrete particles on the nanotubes. These results shed light into the nature of metal–tube interaction, an important topic to many fundamental and practical aspects of nanotubes. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Carbon nanotubes [1,2] are quasi one-dimensional systems ideal for studying the physics in molecular scale wires and exploring chemically derived nanostructures for future electronics [3–6]. Enabling low resistance ohmic contacts to nanotubes are critical to elucidating their intrinsic electrical properties and obtaining functional electronic devices with useful characteristics [5,6]. This requires an in depth understanding of the nature of metal–nanotube interaction. Such understanding is not at hand currently as systematic experimental and theoretical work to address this issue has been lacking.

We have found through a series of studies that low resistance metal–tube ohmic contacts can be consistently achieved with Ti, Nb and Ni metals [5–10]. The resistance of a Ti contacted metallic single-walled carbon nanotubes (SWNT) is as low as 12 kilo-ohms for several microns tube length [10], and is the lowest resistance measured with individual SWNTs among all reported results. Low resistance semiconducting samples are also obtained with Ti and Ni contacts and have led to high-transconductance nanotube field-effect transistors [9]. On the other hand, non-ohmic high resistance contacts are typically resulted with Au and Al in our sample fabrication approach [11]. These electron transport results suggest that the electrical characteristics of metal–tube systems is sensitive to the metal type, and motivate us to investigate the interactions between nanotubes and various metals.

Metal–nanotube interaction is also important in terms of forming nanowires on nanotube templates [12,13] or ‘substrates’ [14]. It could be a good approach to obtaining metallic or superconducting nanowires by continuously coating the sidewalls of nanotubes with metals. An excellent
example was given recently by Tinkham and coworkers [14] in obtaining superconducting nanowires by uniformly sputter-coating a SWNT bundle with Mo–Ge. Forming metal wires on a nanotube by deposition methods is essentially growing films on a quasi one-dimensional substrate. Similar to the growth of films on a two-dimensional surface [15], the metal–substrate (nanotube) interaction must play a central role in the process of metal wire formation.

This Letter presents results of various metal structures formed on suspended single-walled nanotubes by electron-beam deposition. Depending on the metal type, formations of continuous metal nanowires or decorations of isolated discrete particles are observed by transmission electron microscopy (TEM). These nanostructures lead to information about the interactions between nanotubes and various metals, therefore shedding light into the metal–tube contact issue. It is also found that pre-treating nanotubes with surfactant molecules improve the uniformity of metal deposition on nanotubes. Thus, as grown or pre-treated carbon nanotubes could be used as novel one-dimensional substrates for obtaining various metal nanowires.

2. Experimental

SWNTs were grown directly on gold micro-grids by chemical vapor deposition (CVD) of methane [16,17] using a fluid-phase catalyst precursor-material [18,19]. Preparation for the catalyst precursor-material involved dissolving a triblock copolymer, aluminum, iron and molybdenum chlorides in a mixed ethanol and butanol solution [18,19]. Gold micro-grids used for TEM were dipped into the precursor solution and immersed for a few seconds. The grid was then removed from the solution and then calcined at 400°C for ~12 hr in air. This led to a catalyst film coating on the gold grid-lines and extending into the enclosed holes. CVD growth was carried out with the catalyst coated gold grid in a tube furnace at 900°C under a 1000 ml/min methane flow for 15 min. SWNTs grown and suspended over the holes in the TEM grid were used for metal coating study. Coating of the nanotubes grown on the gold micro-grid was carried out by electron-beam deposition of various thickness of Ti, Ni, Pd, Au, Al, and Fe. Several samples were pre-treated by surfactant molecules. This was carried out by immersing the samples in a 0.1 mM Triton X-100 aqueous solution for 30 min followed by rinsing with pure water. Metal evaporation was monitored by a quartz oscillator to determine the rate and thickness of material deposited. The deposition rates were ~0.02, 0.2 and 0.2 nm/s for film thickness of 0.5, 5 and 15 nm, respectively. The metal coated nanotubes were examined by a Philips CM20 TEM operated at 200 kV.

3. Results and discussion

TEM of the as grown samples reveals the synthesis of individual SWNTs (diameter 1–4 nm) and small bundles of SWNTs. Many nanotubes are suspended over the holes of the gold-grid. The suspended nanotubes are nearly free of defects and amorphous carbon overcoating [17], and ideal for investigating the deposition of metal atoms on molecularly clean nanotube substrates.

The results of various metal coatings on as grown SWNTs for 15, 5 and 0.5 nm thickness are shown in Figs. 1–4. For 15 nm deposition, Ti forms continuous nanowires on suspended SWNTs (Fig. 1a). Ni and Pd also form uniform coating on SWNTs (Fig. 1b and c, respectively), but the wire structures are occasionally disconnected at certain locations (Fig. 1c) and are more so for Pd than Ni. The deposited Pd and Ni are in the form of fine particles connecting together on the nanotubes. On the other hand, Au, Al, and Fe deposited on the nanotubes form disconnected crystalline particles, leaving sections of the nanotubes free of metal coating (Fig. 1d–f, respectively). The Au particles decorating SWNTs are up to ~60 nm wide, larger than the deposited film thickness. This indicates that Au atoms deposited on the tubes have migrated and merged together to form large particles.

The striking difference in Ti and Au coatings can also be seen in scanning electron microscopy (SEM) data shown in Fig. 2. Ti coating clearly
leads to the formation of continuous and uniform nanowires on the nanotubes, whereas Au coating leads to disconnected large particles decorating nanotubes.

For 5 nm metal depositions, Ti coating on the nanotubes is also continuous and uniform (Fig. 3a). For Ni and Pd however, the discontinuity in the coating becomes apparent (Fig. 3b and c, respectively). Au, Al, and Fe still form discrete particles but with reduced sizes compared to the particles made by the 15 nm deposition. The Au and Al particles appear to be elongated along the axes of the nanotube (Fig. 3d–f), which differ from the particles formed under 15 nm depositions (Fig. 1d and e). The Fe particles are more or less spherical in shape (Fig. 3f).

As the metal deposition is further reduced to approximately 0.5 nm, we find that Ti coating on the sidewalls of nanotubes remains homogeneous but with fluctuations in the amount of metals deposited along the nanotube lengths (Fig. 4a). Coating of 0.5 nm of Au (Fig. 4b) and Fe (Fig. 4c) leads to the formation of particles with small sizes and low densities. Other features of the particles are similar to those formed by depositing 5 nm of metals.

It is well established by extensive research in thin film deposition on planar substrates that, the structure and morphology of the film is largely dictated by the interactions between the deposited
The various observed metal nanostructures formed on suspended SWNTs can lead to information about metal–tube interactions, since the nanotubes are used as quasi one-dimensional substrates. According to a classical nucleation theory [15], the condensation or sticking coefficient for atoms impinging on a substrate from the vapor phase is proportional to \( \exp(-E_b/K_B T) \), where \( E_b \) is the binding energy of an atom with the substrate. This is proportional to the rate that atoms can stabilize on the substrate and reach thermal equilibrium without being re-evaporated. The adatoms diffuse around on the substrate and join critical nucleation centers for cluster growth. The diffusion rate is proportional to \( \exp(-E_{\text{diff}}/K_B T) \), where \( E_{\text{diff}} \) is the diffusion activation energy. Empirically \( E_{\text{diff}} \approx E_b/4 \) [15], suggesting that weak binding allows fast surface diffusion. The density of nucleation centers strongly depends on the condensate–substrate interaction. Large condensate–substrate interaction leads to a higher nucleation density [15].

The Ti coating on nanotubes appear very uniform and continuous along the nanotube sidewalls. This points to high nucleation density, strong metal–substrate interaction and Ti–SWNT binding. On the contrary, the Au coating appears highly discontinuous with very low nucleation density. This suggests weak Au–SWNT interaction and a small binding energy. The weak interaction...
is correlated with a low activation barrier for diffusion, leading to rapid motion of Au atoms on the nanotube sidewalls. The low nucleation density and high diffusion rate cause metal atoms or even small clusters to merge into isolated large particles [20]. A quantitative measure of the binding energies between various metal atoms and SWNTs has not been carried out at the present time. Nevertheless, based on the observed sticking behavior of metals on the nanotubes and the resulting metal nanostructures, we tentatively suggest that $E_b(\text{Ti}) > E_b(\text{Ni}) > E_b(\text{Pd}) > E_b(\text{Fe}) > E_b(\text{Al}) > E_b(\text{Au})$.

It is known that in three-dimensional bulk materials, different metals exhibit different interactions with carbon. In general, the ability for transition metals to bond with carbon atoms increases with the number of unfilled d-orbitals. Metals such as Al, Au, and Pd have no d-vacancies and negligible affinity for carbon. Metals with few d-vacancies such as Ni, Fe, and Co exhibit finite solubility for carbon in certain temperature ranges. 3d and 4d metals with many d-vacancies such as Ti and Nb can form strong chemical bonds with carbon and thus highly stable carbide compounds. For two-dimensional systems, experimental and theoretical investigations of the interactions between metals and the basal plane of graphite have been carried out previously. Although controversy exists, it is generally believed that the interactions between deposited metals and a graphite basal plane are weak [20–28]. This includes Ti [21], Ni [22,23] and certainly the rest of metals [20,24–28] concerned by the current work. The interactions are suggested to be through van der Waals forces and do not involve chemical bond formations between the metal and carbon atoms in the graphite basal plane. This should be due to the high chemical inertness of the ordered sp² carbon network of a graphene sheet. Several studies have also been carried out to investigate the interactions between metals and $C_{60}$ (zero-dimension) [29–31]. In has been shown that certain metals interact much more strongly with $C_{60}$ than graphite including Ti [29] and Ni [31]. Deposition of Ti on $C_{60}$ can lead to the formation of Ti–C carbide bonds revealed by photoelectron spectroscopy using X-rays from a synchrotron source [29].

Interactions between metals and quasi one-dimensional SWNTs could be significantly different than those between metal and carbon in two- and zero-dimension. A nanotube differs from a graphene sheet in their drastically different electronic structures and that the cylindrical sidewall of a nanotube is curved and in a non-planar sp² bonding configuration. A nanotube differs from $C_{60}$ in dimensionality, radius and that $C_{60}$ contains pentagons in its structure, whereas the sidewall of a nanotube contains exclusively hexagons. $C_{60}$ should therefore be more reactive with metals than a nanotube.

A detailed theoretical account for the interactions between various metals and nanotubes is currently lacking and called for. Nevertheless, a recent theoretical study by Menon and co-workers [32] sheds some light into this important issue. The authors used a tight binding molecular dynamics and ab-initio method to calculate bonding configurations of Ni with the sidewall atoms on a SWNT, and compared the results with Ni bonding on a graphene sheet. Covalent bonding characteristics of Ni (on certain sites) with carbon atoms on the nanotube was identified from the calculations. The interaction was found to be stronger than ionic-like Ni bonding with a graphene sheet. The strong Ni–SWNT interaction was attributed to curvature-induced rehybridization of carbon sp² orbitals with the Ni d-orbital [32]. This result could be consistent with our experimental observation that Ni exhibits significant condensation/sticking coefficient on SWNTs, and the deposition leads to quasi-continuous Ni nanowires. Therefore, the Ni–SWNT interaction could have certain covalent bonding characteristics, and is consistent with the electrical transport result that low resistance ohmic contacts are obtainable in Ni contacted SWNTs.

Ti atoms deposited on nanotubes exhibit the highest condensation/sticking coefficient among Ni and other metals. The Ti–SWNT interaction should be stronger than that for Ni–SWNT and could involve covalent bonding. This can be attributed to the high affinity of Ti for carbide formation and the curvature induced rehybridization effect. The intimate Ti–SWNT interaction is consistent with our result that low resistance ohmic
electrical contacts to individual SWNTs can be reliably made by depositing Ti electrodes onto nanotubes. It is interesting to note that Ti has been the favorite metal for making ohmic contacts to doped diamonds. In this case, as deposited Ti forms carbide bonds with the very surface of diamond, and ohmic contacts are obtained by thermal annealing that leads to a layer of carbide at the Ti–diamond interface [33].

Our coating results suggest that the interactions between Au and Al with SWNTs are very weak and presumably van der Waals in nature. The low condensation coefficient and diffusion barrier is evident for Au from the deposited metal structures. This is also consistent with our electrical measurement result that Au and Al contacted SWNTs tend to be high in resistance and often exhibit non-ohmic behavior and with non-linear current-voltage characteristics.

The quasi-continuous coating of Pd on SWNTs points to a high condensation/sticking coefficient for Pd on nanotubes, which could be related to the similarity between Pd and Ni in the periodic table. The observed weak Fe–SWNT interaction is somewhat surprising as Fe shares certain common chemical characteristics as Ni in terms of carbon solubility or carbide formation. The difference in Fe and Ni depositions on SWNTs is not understood at the present time.

It is important to note that metal coating on nanotubes could be influenced by various deposition conditions including temperature. We believe that heat generated in metal evaporations may be responsible for the shape changes of Au and Al crystallites (Fig. 1d and e, and 3d and e), due to facilitated diffusions and re-arrangements of metal atoms or small clusters at high temperatures. Also, it is necessary to employ clean SWNTs for the investigation of metal–tube interactions. If extensive amorphous carbon overcoating exists on the sidewall of nanotubes, the outcome of metal deposition could be drastically different from clean tubes. It is known from previous work that metal coating on amorphous carbon can from continuous films, as opposed to large clusters on the basal plane of graphite [34]. We have found that a thin layer of Triton X-100 surfactant molecules pre-absorbed on SWNTs allow for nearly uniform and continuous Au coating (Fig. 5), in strong contrast with the isolated Au particles formed on clean nanotubes. This also suggests that rational pretreatment of nanotubes could enable quasi-one-dimensional nanotube substrates with tunable surface properties for the formation of various interesting nanostructures.

Finally, we note that metal–substrate interactions strongly depend on the type of substrate [15,35]. It is well known that Ti, Ni, Cr and Al adhere well on SiO₂ and glass substrate. The interactions are strong in these cases and are believed to involve metal–oxygen bonds formed at the interface during metal deposition [35]. The strong interactions between Ti and Ni with oxide substrates and carbon nanotubes must have different mechanisms due to different chemical nature of the metal–substrate interfaces. For Al, the interaction with oxide substrates appears much stronger than with carbon nanotubes.

4. Conclusion

We have carried out depositions of various transition metals on carbon nanotubes to gain an understanding of metal–tube interactions. Depending on the metal type, continuous metal (Ti,Ni,Pd) nanowires or isolated particles (Au,Al,Fe) are formed on nanotube substrates. Ti, Ni interact strongly with the sidewall of nanotubes, and the interactions are likely to be related to
partial covalent bonding between the metals and carbon atoms. Au and Al interact weakly with SWNTs through van der Waals forces. These results shed light into electrical coupling between nanotubes and metal contacts, an issue important to fundamental electrical properties of nanotubes and their applications as high performance devices. Clean or pre-treated carbon nanotubes can be used as novel one-dimensional substrates for obtaining various nanowires.

Acknowledgements

This work was supported by NSF, SRC/Motorola, a David and Lucille Packard Fellowship, a Terman Fellowship, ABB Group, Laboratory for Advance Materials (LAM) at Stanford, the Camile Henry-Dreyfus Foundation and the American Chemical Society.

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