

Counting Point Defects in Carbon Nanotube Electronic Circuits

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ABSTRACT

Carbon nanotubes are often imagined to be pristine, defect-free objects, but different types of synthesis and processing are known to result in materials of different qualities. We have developed a method for the quantitative characterization of nanotube defect densities which can readily be used to compare nanotubes from different batches or processes. The method relies on the enhanced chemical reactivity of defect sites as compared to the graphene lattice. By tailoring the potentials used in electrochemical deposition, we selectively seed the growth of metal particles at reactive defect sites without decorating the bulk of a carbon nanotube. Using this technique, nominally identical synthesis runs have produced defect densities varying from 1 defect per 100 nm down to 1 defect per 10,000 nm. Because the particles can be grown arbitrarily large, simple optical imaging can be used to generate wafer-scale statistics.

Keywords: Single-walled carbon nanotubes, defects, electrochemical deposition

1 INTRODUCTION AND MOTIVATION

Single-walled carbon nanotubes (CNTs) are molecular wires with highly robust chemical structure, and their quasi-one-dimensional electronic properties make them promising candidates for nanoelectronics applications [1]. However, the presence or absence of defects in CNTs can significantly change this promise, either for the better or the worse. For example, defects enable chemical functionalization schemes which further tailor electronic properties [2,3]. Efforts to understand CNT-based chemical sensors [4], hydrogen storage [5], and electronic transistors [6,7] have all implicated defects as components of these complex systems.

Despite the importance of defects, there has been little progress characterizing their density or distribution in CNT materials. On an individual basis, single CNTs have been investigated using high resolution scanning tunneling microscopy (STM) and spectroscopy (STS) [8-12], and indirectly probed by scanning gate microscopy (SGM) [6,13]. However, little is known about the density, distribution, and chemical nature of defects in CNTs. This situation is mainly due to the lack of fast and reliable

methods to locate defect sites, especially on a useful scale for comparing one batch with another.

Electrochemical deposition is a flexible and powerful solution to this problem. The enhanced chemical reactivity of CNT point defects allows various electrochemical processes to proceed at these sites without modifying the remainder of the CNT. Using the deposition of metals, for example, point defects can be made easily visible to optical or electron microscopes. Selective deposition has been previously demonstrated using the point defects and step edges of a highly oriented pyrolytic graphite (HOPG) crystal [14,15], which can be considered a model test system for CNTs. Furthermore, the metal deposition is completely reversible using proper oxidation potentials, so the technique is a nondestructive one as well. These properties make electrodeposition a promising technique for wafer-scale quantitative analysis of CNT electronic devices and for further research into the roles which defects play.

2 EXPERIMENTAL SETUP

Single-walled carbon nanotubes were produced by chemical vapor deposition (CVD) on a thermally oxidized silicon substrate, with a SiO₂ thickness of 200nm. Ti-Au electrodes defined by optical lithography connected the CNTs. The devices were tested and modified in a custom electrochemical cell, as depicted in Figure 1. The cell volume of about 3cm³ is sufficient to allow manipulation of probing needles to contact various parts of the CNT circuit. The needles themselves are polymer-coated to minimize leakage currents. The CNT circuit was configured as a working electrode, and platinum wires were used as counter and reference electrodes. The electrochemical deposition potentials were controlled by a customized potentiostat system.

In order to deposit nanoparticles selectively on only the CNT defects, a tri-potential pulse sequence was used [14,15]. First, an oxidizing pulse (A) prepares the CNT surface. A second, reducing pulse (B) strips oxygen atoms from carbonyls, ethers, hydroxyls, or any other oxygen-containing functionalities at defect sites. The height of pulse B can be adjusted so that metal deposition is seeded at these reactive sites while the CNT sp² lattice remains unaffected. Finally, a third potential (C) is used for further metal deposition at the seeded sites.

3 RESULTS AND DISCUSSION

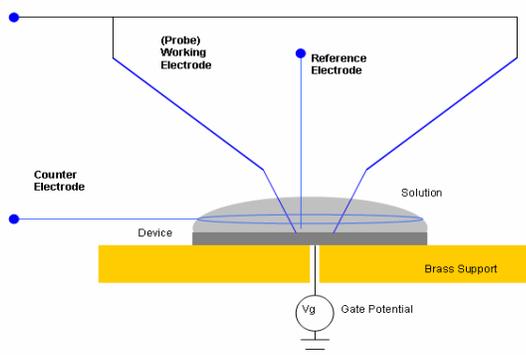


Fig.1 Schematic view of the electrochemical cell

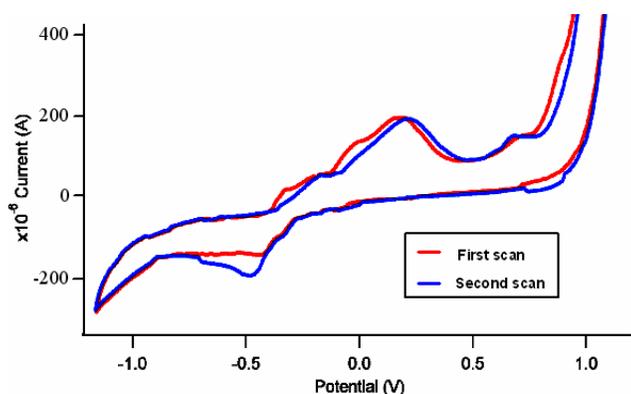


Fig.2 Cyclic voltammetry of HOPG surface

As one example of this technique, nickel dots were grown on CNT defect sites. For Ni deposition, the electrochemical solution was composed of 1mM NiSO₄ and 0.1M Na₂SO₄ at a pH of 5.0. To assess the appropriate electrochemical potentials, cyclic voltammograms were first obtained on clean graphite (HOPG) surfaces. As shown in Figure 2, the data exhibit a peak at -0.4 V corresponding to the deposition of Ni and oxidation peaks at +0.3 V and +0.7 V. With some iterative testing, an optimized pulse sequence was found to be A = (+0.8V, 5s), B = (-1.1V, 10ms), C = (-0.9V, 30-300s). The duration of the C pulse determines the size of the final nanoparticles, and can be tailored to make the particles 5nm, 50nm, or 500nm in diameter.

Successful deposition requires care in a number of experimental techniques. The oxidation pulse is essential for Ni attachment, probably because it prepares the defect sites into a reproducible chemical state with a low nucleation overpotential. Furthermore, the solutions must be purged with N₂ before each use in order to minimize dissolved O₂ in the cell. Finally, the sample must be thoroughly rinsed with ultrapure water following each deposition, or else salt precipitates foul the surface and complicate comparative imaging.

Figure 3 consists of atomic force microscopy (AFM) images of a single CNT device before and after various electrochemical modifications. The catalytic particle used to initiate the growth of the CNT is visible as a bright spot in the lower left-hand side of each image. The vertical stripe on the right-hand side of each image is the first of multiple electrodes connecting the CNT into a measurement circuit. The complete length of the CNT exceeds 20 μm, though only the initial 2.5 μm is visible in this image.

Following the tri-potential sequence described above, the chemically-reactive sites of this particular CNT can be readily identified by four new Ni nanoparticles (Fig. 3b) attached to the CNT wall. The average height of the four particles is 12.8 nm after a deposition time of 30 s. The average distance between the four particles is measured to be 310 nm.

In order to test the reliability and robustness of the electrochemical identification process, various experiments have been completed. Repeating the deposition process on the same CNT allows the particles to grow larger (Fig. 3c), but does not increase the number of particles attached. This observation is consistent with the premise that the deposition is selective, and that the chosen pulse sequence decorates point defects with a very high probability. After imaging, the removal of the deposited Ni can be accomplished using either a 90 s electrochemical oxidation or an acid wash (18% HCl for 10 minutes). In either case, the CNT is returned to its pristine state (Fig. 3d). Finally, a new deposition sequence can be initiated to grow Ni nanoparticles on the cleaned CNT. The new Ni particles deposit at identical positions and at the same rate as before. The one-to-one correspondence is excellent in all of the samples tested, through multiple cycles of deposition and removal. However, it is noteworthy that the acid treatment appears to also produce new reactive sites with a relatively low probability. Fig 3e demonstrates this effect, with an additional fifth Ni nanoparticle formed after repeated HCl washes.

The selectivity of the metal deposition is found to be very sensitive to the pulse profile. As in earlier studies with HOPG [14,15], the CNTs can be completely coated if the overpotential is too high and not decorated at all if the potential is too low. The oxidation of the carbon nanotube surface at +0.8 V is also a critical step. Presumably, this oxidation produces carbonyls, ethers, hydroxyls, or other oxygen-containing functionalities at the defects position, thereby increasing the affinity of metal adatoms at these sites. Experiments showed that all three pulses (A), (B), and (C) were necessary for the reproducible decoration of individual sites, with pulse (C) the most important for tuning the selectivity of the deposition.

To further confirm the hypothesis that the tri-potential sequence is selective to defect sites, we compared the process with an alternate approach previously studied. Using a gas phase reaction, selenium nanoparticles were

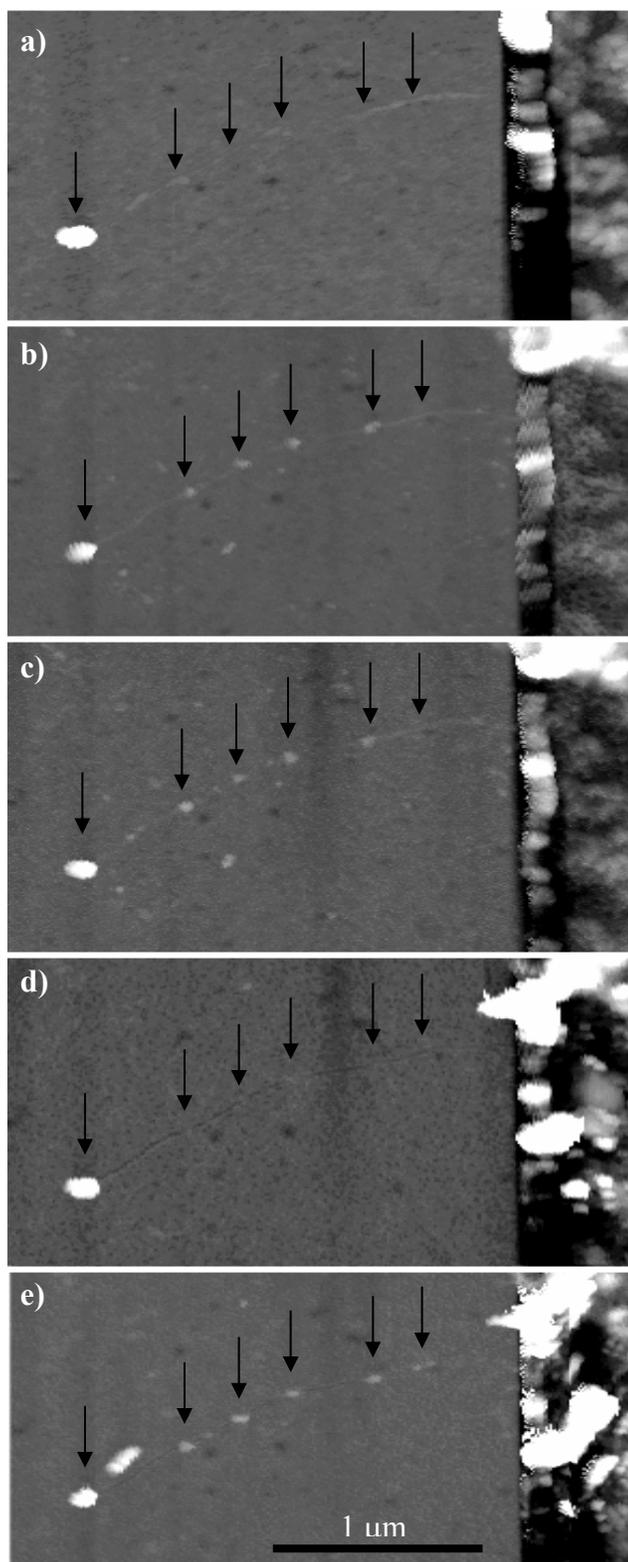


Fig.3 A carbon nanotube working electrode (a) before and (b, c) after selective deposition cycles. (d,e) Reversibility and reproducibility of the deposition. Vertical arrows guide the eye to identical positions in each image.

selectively precipitated onto CNTs from H_2Se [16]. We have reproduced this work and found a one-to-one correspondence on a given CNT between Se and Ni particle attachment sites. The electrochemical technique has the advantage that the deposition potential can be tailored to a wide variety of metals including Au, Ag, and Cu. Furthermore, the electrochemical technique can be re-verified in cases where a CNT appears to have zero defects because a slight increase in the deposition overpotential results in the uniform coating of the entire CNT.

The sample shown is representative of dozens of single- and multi-CNT devices tested from a single wafer. Over one hundred defect sites were readily found. The separation distance between consecutive defects was measured to have a mean value of 360 nm and a standard deviation of 330 nm. This mean is consistent with the reported phase coherence length for CNTs, which is estimated to be in the range of 150-750 nm [17-19]. The high value of the standard deviation of our measurements indicates the wide variability in defect spacing. In particular, curved CNT segments were observed to have higher defect densities than straight segments, possibly indicating that small fluctuations in the CVD environment can directly introduce these sites during growth.

Despite this variation, however, the simple mean is still likely to be a useful parameter for quantitative comparisons. In experiments which are still preliminary, we have reproduced the measurements on two additional wafers containing CNTs synthesized under different conditions. The mean density of defect sites varies considerably between the samples, ranging from a low value of 100 nm^{-1} to values exceeding 1000 nm^{-1} . Therefore, this method described may be quite useful for the quantitative comparison of CVD, arc discharge, and laser ablation synthesis methods. It may also identify differences in nominally identical CVD runs, as would be necessary for process and quality control of nanotube electronics.

A complexity and potential limitation of this electrochemical modification technique is the sensitivity of the CNTs to gating by the solution. Various researchers have reported CNT gating using electrolyte solutions [20], including a case combining electron transport measurements and resonant Raman spectroscopy [21]. Significant changes occur to the CNT's electronic transport properties and phonon spectra, and these changes are generally attributed to dopant shifts to the CNT Fermi level. In our experiment, the (A) oxidation pulse acts as a negative gate, generally increasing the conductivity of the CNT. The (C) deposition pulse, on the other hand, can potentially be rendered ineffective if it completely depletes the CNT of carriers. Experimentally, the most effective pulse heights and widths did not appear to be sensitive to this liquid gating effect. The problem may have been alleviated by the use of a global backside gate (the heavily doped Silicon substrate), which was maintained at ground potential throughout the deposition. Nevertheless, the

possible interference by liquid gating remains an issue which deserves further investigation.

4 SUMMARY

In conclusion, a simple and direct characterization technique is demonstrated for counting defects in large numbers of CNT electronic devices. A tri-potential deposition pulse sequence reversibly and reproducibly decorates defect sites with metal nanoparticles, as demonstrated here using Ni. The particles can be grown as large as necessary for a particular imaging technique, and can then be easily removed. The average spacing between defect sites was measured to be 360 nm, but it is likely that this number is highly sensitive to the particularities of the synthesis. Indeed, the method may be a very sensitive way to compare CNTs from one batch to another.

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