Effect of Ozone Oxidation on Single-Walled Carbon Nanotubes

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J. Phys. Chem. B 2006, 110, 7113 - 7118
Introduction

- Nanotubes - nonspecific sensors of various gases
- Variation in the electrical property makes them sensitive
- Three mechanisms for the resistance change
  - Charge transfer doping to the nanotube
  - Modification of the potential barrier between CNTs and metal electrode
  - Direct change in the conduction channel
- Determining the relevant mechanism can be difficult because of a number of mechanisms that are possible.
Experiments - mechanism is not doping but a change in the work function of the metal electrode along with a modification in the metal electrode- nanotube Schottky barrier

Theoretical works - charge transfer from chemisorbed oxygen to nanotube

Oxygen-nanotube interactions are of great interest because it is the first step in most of the functionalization of nanotubes

Ozone - Potential form of oxygen

Dissociation of ozone by 254-nm UV light can generate highly reactive singlet oxygen atoms and molecules

Ozone oxidation offers the possibility of controllably oxidizing the nanotubes that have been integrated into functional devices at room temperature without affecting the device thermal budget
- Effect of UV generated ozone on the physical and electronic structure of single walled carbon nanotube

- Upon exposure to oxygen resistance increases

- Resistance change is irreversible

- For the comprehensive understanding of the effects of ozone on carbon nanotubes used different techniques such as Raman Spectroscopy, X-ray Photoelectron Spectroscopy and Ultraviolet Photoelectron Spectroscopy

  Raman Spectroscopy $\rightarrow$ Correlates change in resistivity to the defect density

  Photoelectron Spectroscopy $\rightarrow$ Correlates defects to the presence of various chemical species present

**What causes the metal - nanotube - metal device to undergo a change in its electrical property?**
Experimental procedure

1. Nanotubes grown by CVD → Electrical property measurement
2. Laser ablation grown CNTs → XPS and UPS study

CVD grown nanotube device with metal contacts

SEM Image of a CVD grown nanotube mat Device with metal contacts

Optical image of a completed CVD device with schematic circuit diagram for four probe transport measurements
Raman spectrum of a CVD grown mat of CNTS

SEM image of a mat of laser-ablation-grown nanotubes used for Raman and photoelectron spectroscopic measurements.
Transport data for an individual single walled nanotube during ozone oxidation.

- Small decrease in resistance after the UV was switched off - readesorption of photodesorbed oxygen.

- As the ends of the nanotube has been buried under the metal electrode it doesn't form a part of the conduction channel and hence any change in nanotube electrical property is due to the modification of the side wall.

- Permanent change in the nanotube mat device resistance can be attributed to the modification in the conducting path of the SWNTs either by doping or defect creation or by modification of the schottky barrier.
Changes in the two-probe resistance are due to modifications to the entire device, including contacts.

Changes in the four-probe resistance are due only to the changes in the nanotube mat.

The similarity between the two-probe and four-probe resistance changes indicates that ozone primarily affects the conduction in the nanotube mat and not at the nanotube-metal contact.

Two-probe (a) and four-probe (b) resistances of a CVD grown nanotube mat during ozone exposure.
(a) Raman spectra of a mat of CVD-grown nanotubes from, during ozone oxidation. During ozone exposure, the intensity of all nanotube bands decreases. At 7 min, the intensity of the RBM is abruptly extinguished, accompanied by a change in G-band line shape, indicating that the nanotubes resonant with the 2.41 eV photon energy have been removed. (b) Ratio of the area of the D-band to that of the G-band.
XPS spectra of the nanotube mat before and after a 1-h exposure to ozone generated by a high-intensity UV lamp in air. After ozone exposure, there is a large increase in the intensity of the ether and carbonyl core levels and a decrease in the intensity of the $\pi - \pi^*$ shakeup peak.
The intensity of the conjugated π bonds is decreased after ozone exposure, leading to a decreased density of states near the Fermi level.

The increased work function is apparent from the shift in the high binding-energy cutoff.

Inset: expanded view near the Fermi level highlighting the disruption of the π states.

**UPS valence-band structure of the nanotube mat, before (solid line) and after (dashed line) ozone exposure.**
Conductivity → States at the Fermi level and valence-band

- After exposure of ozone there was a reduction in the density of electronic states (DOS) near the Fermi level as in previous figure - due to the disruption of the π conjugation.

- There was a 1 eV shift in the high binding energy cutoff towards lower binding energy.

\[ \Phi = h\nu - E_{cutoff} \]

- 1 eV increase in the work function - reduction in the π conjugation / increase in the surface dipole due to oxygen-containing functional groups.

- Effect of ozone on nanotubes include the creation of additional chemical Groups not yet addressed by theory.
Conclusion

- Raman spectroscopy and transport measurements have been used to study the ozone oxidation of carbon nanotubes.
- The electrical resistance of the nanotubes increases upon exposure to ozone and is irreversible.
- Comparison between nanotube mats and individual nanotubes indicates that the resistance change is due to the side wall oxidation and the disruption of the conduction network on individual nanotube level.
- It's not caused by the end-cap oxidation, destruction of the intertube contacts, or photodesorption induced changes in the metal-nanotube Schottky barrier.
- Various spectroscopic techniques confirmed that ozone oxidizes the nanotube and causes a significant disruption of the conjugated π bonding on the nanotube sidewall which causes a 1eV increase in the work function of the oxidized nanotubes, accompanied by a loss of electronic states near the Fermi level.
Thank You