Effect of Ozone Oxidation on Single-Walled Carbon Nanotubes

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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 he 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 → **Correlates change in resistivity to the defect density**

Photoelectron Spectroscopy → **Correlates defects to the presence Of various chemical species present**

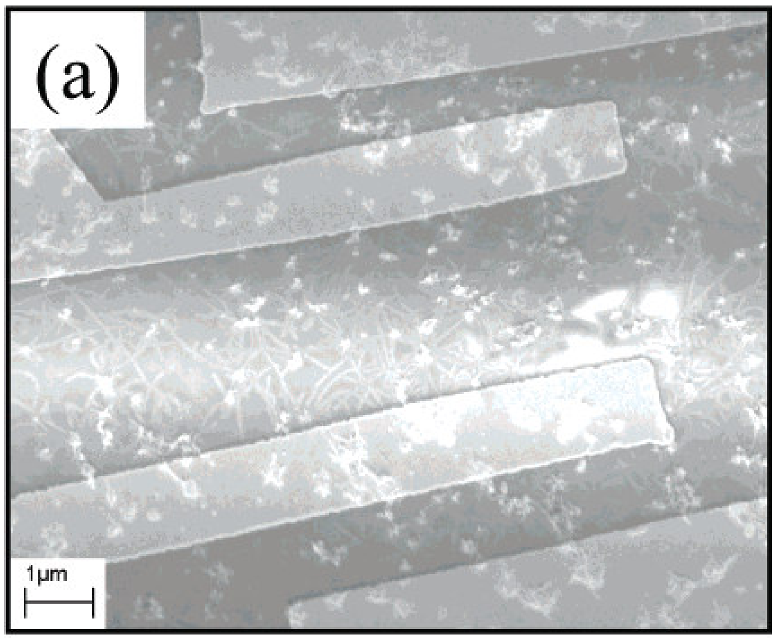
What causes the metal - nanotube - metal device to undergo a change in its electrical property?

Experimental procedure

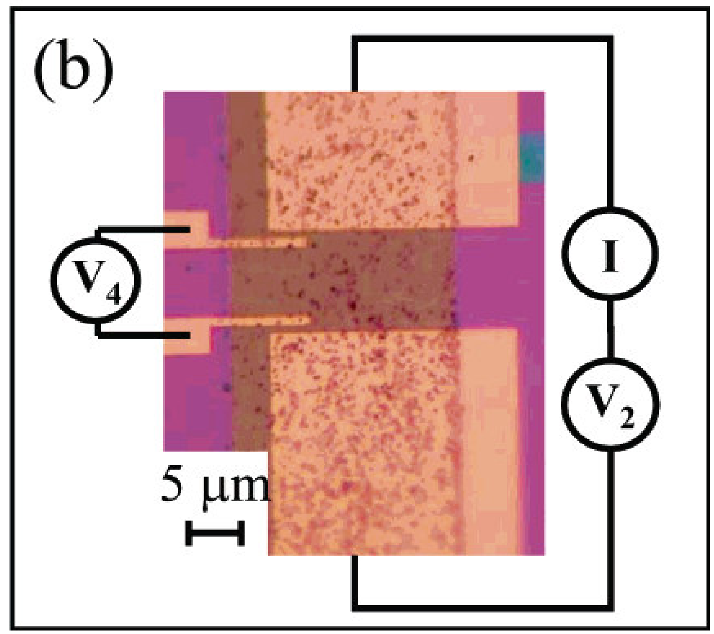
1. Nanotubes grown by CVD → Electrical property measurement

2. laser ablation grown CNTs → XPS and UPS study

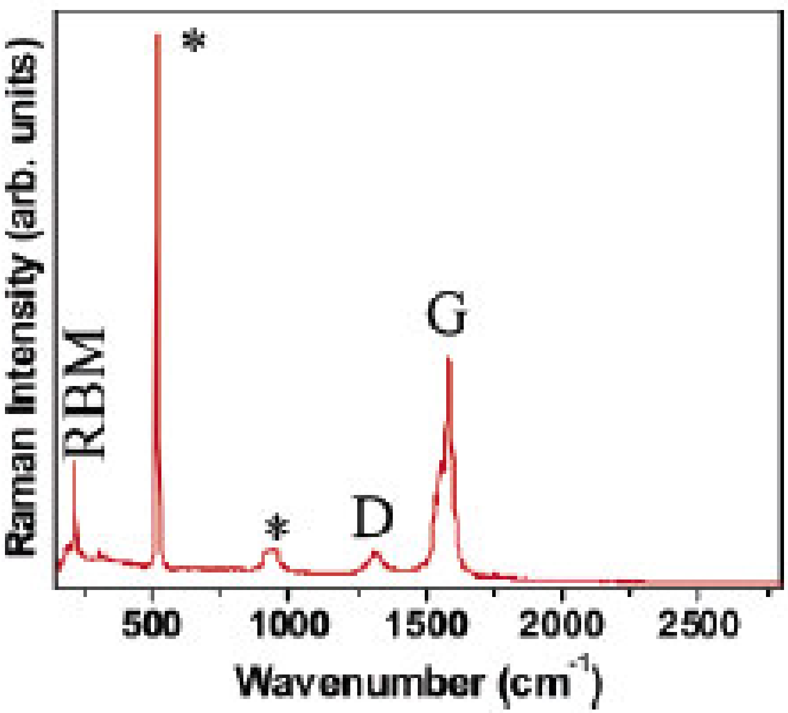
CVD grown nanotube device with metal contacts



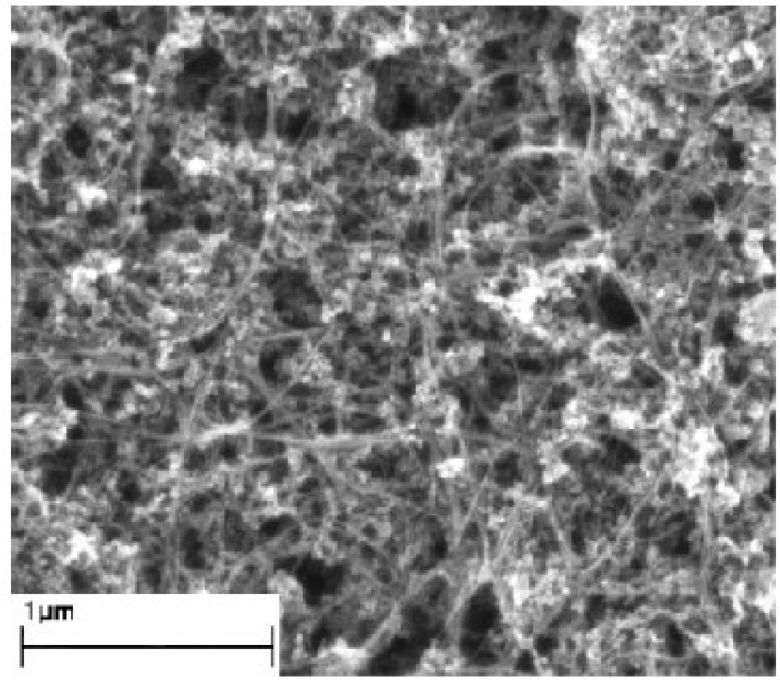
SEM Image of a CVD grown nanotube mat
Device with metal contacts



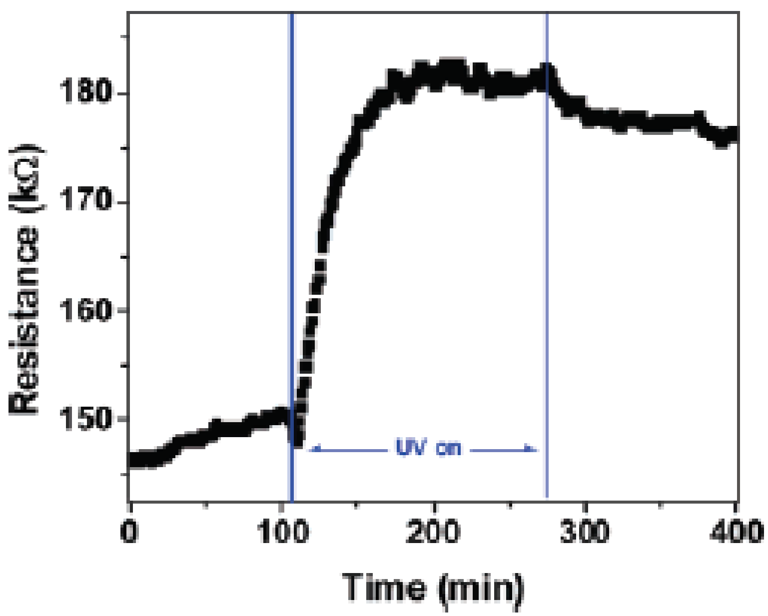
Optical image of a completed CVD device
with schematic circuit diagram for four probe
transport measurements



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.

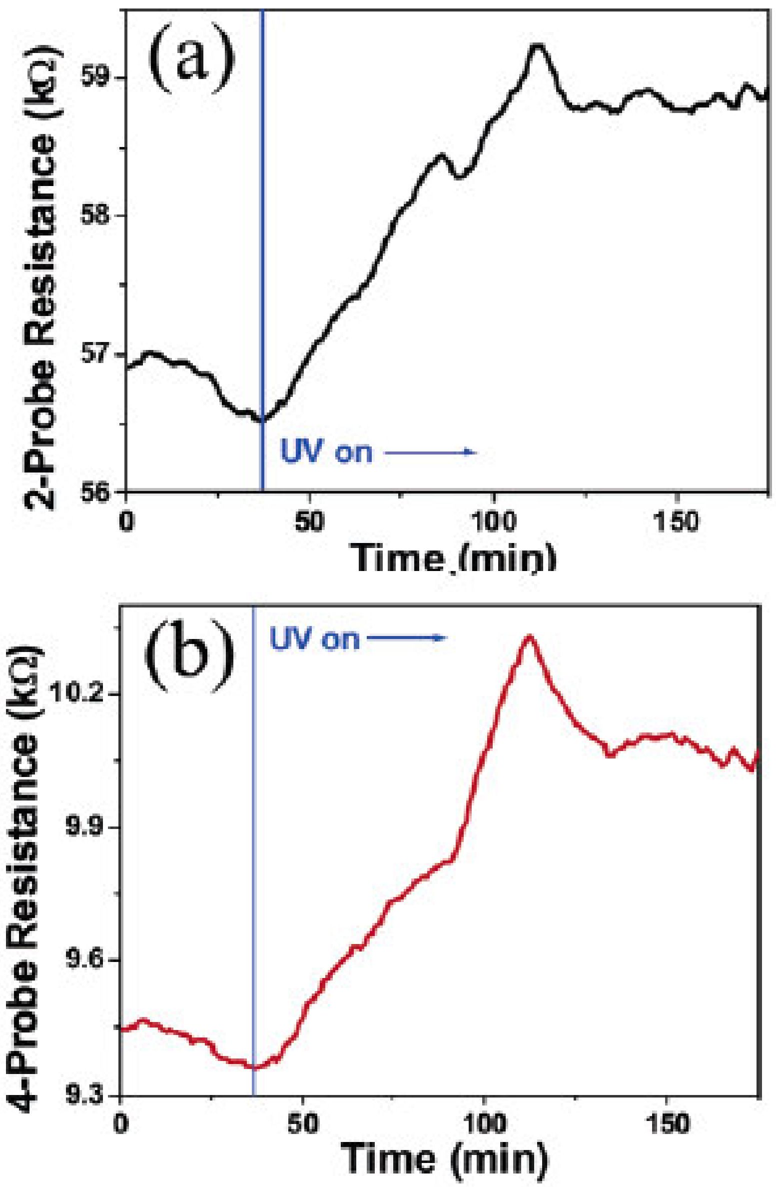


Transport data for an individual single walled nanotube During ozone oxidation

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

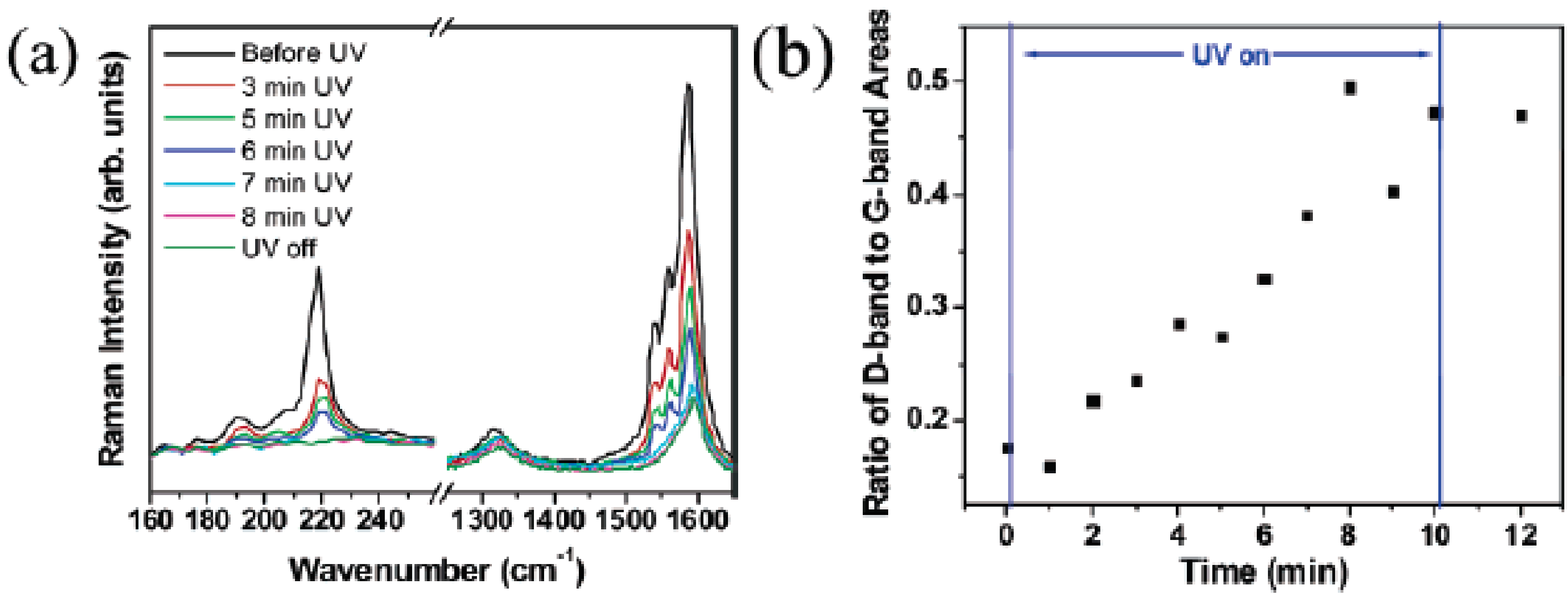
- As the ends of the nanotube has been buried under the metal electrode it doesn't form a part of the conduction channel and hence any change in nanotube electrical property is due to the modification of the side wall.

- 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.

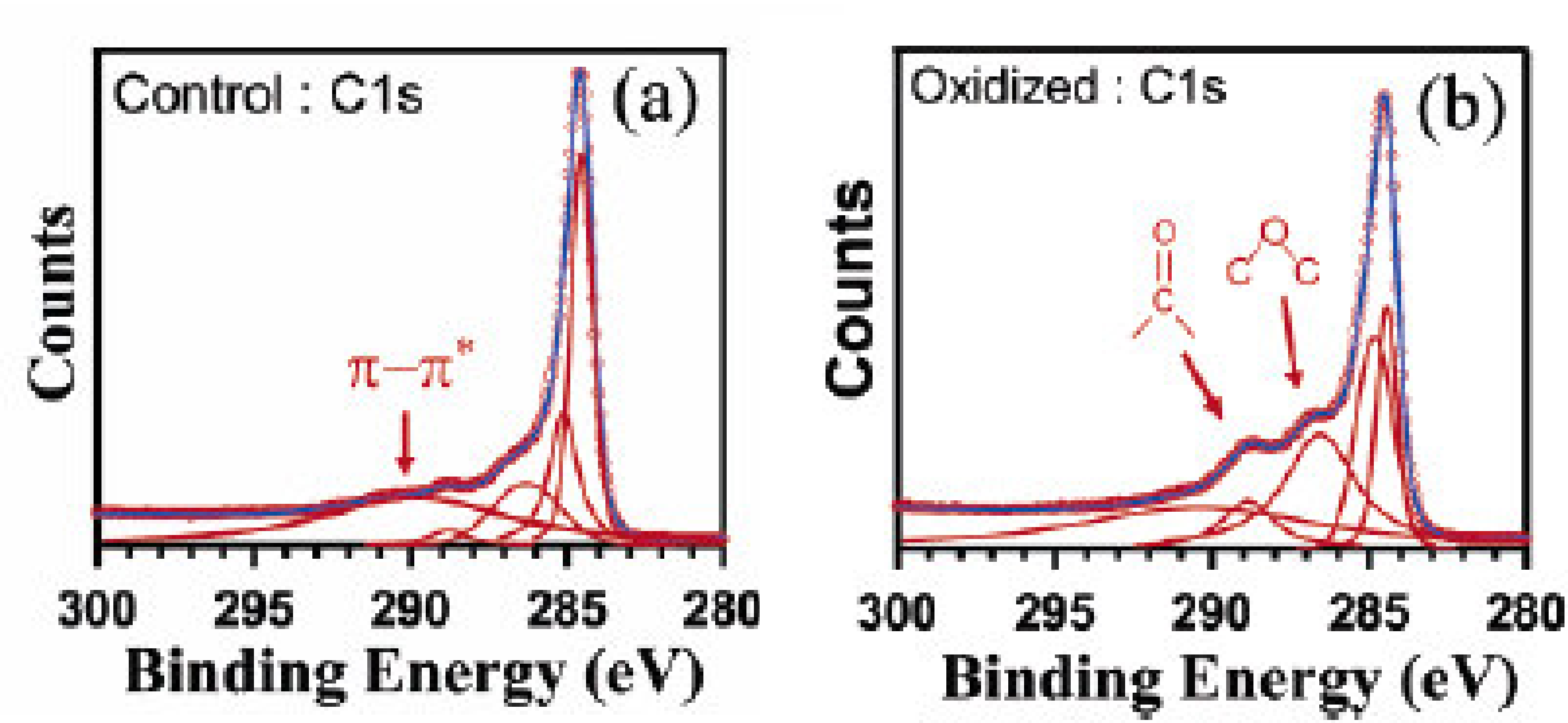


Two-probe (a) and four-probe (b) resistances of a CVD grown nanotube mat during ozone exposure.

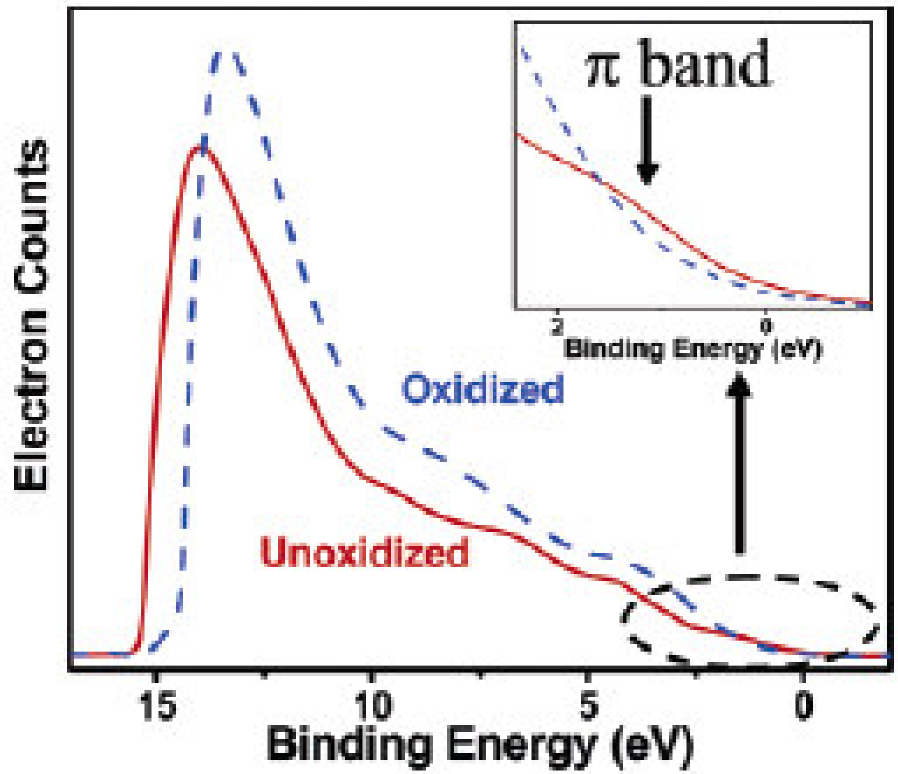
- Changes in the two-probe resistance are due to modifications to the entire device, including contacts.
- Changes in the four-probe resistance are due only to the changes in the nanotube mat.
- The similarity between the two-probe and four-probe resistance changes indicates that ozone primarily affects the conduction in the nanotube mat and not at the nanotube-metal contact.



(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 π - π* shakeup peak.



UPS valence-band structure of the nanotube mat , before (solid line) and after (dashed line) ozone exposure.

- 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

Conductivity ⟶ **States at the Fermi level and valance-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
- Its 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