Lecture 14. Properties of Carbon Nanotubes: Metals or Semiconductors

The purpose of the lecture: to familiarize students with properties of carbon nanotubes as metals or semiconductors.

Expected results: students getting information about properties of carbon nanotubes as metals or semiconductors.

CNTs are formed by the folding of a hexagonal graphene sheet consisting of unit cells. Each cell contains two identical carbon atoms having two identical zero-energy electron states: one in which the electron resides on atom A, the other in which the electron resides on atom B. The three electrons of each carbon atom are bonded with neighboring atoms, resulting in one free p electron for each atom, which can be found in an inverted-cone density of state, above or below the sheets' plain. The lattice structure of grapheme, made out of two interpenetrating triangular lattices a1 and a2, are the lattice unit vectors, while d1, d2, and d3 are the nearest-neighbor vectors.

Electrons can dislocate from one atom to another within a cell. In addition, the electrons travel through the graphene sheet as if they carry no mass, as fast as just one hundredth that of the speed of light.

Thus, the different patterns of graphene folding caused differential changes in b1 and b2 values that may be responsible for their differential electronic properties. Armchair CNTs exhibit metallic properties, while the zigzag and chiral CNTs can be semiconductors (containing a bang gap between HOMO and LUMO) if n _ m is a multiple of 3; otherwise they are metallic. Band gaps of 0.4 to > 1 eV have been reported for SWNTs. Recently Matsuda et al. (2010), using an improved technology, showed the presence of minor (<0.2 eV) gap energy in many of the zigzag and chiral CNTs that were previously classified as metallic CNTs with zero gap. The energy gap was inversely related to the CNTs' diameter.

Thus, as the diameter decreases, the electrons in the HOMO require relatively great energy to overcome the Fermi barrier.

Why do CNTs, depending upon their geometry, exhibit metallic or semiconductor properties?

The following possibilities may answer this question:

1. The geometric differences allow CNTs to have certain unique intrinsic properties, such as a s-p hybridizing effect and/or curvature stress that is inversely related to their diameter and has been shown to induce semiconductor-metal-semiconductor phase transitions in primary metallic SWCNTs.

2. CNTs possess various types of structural defects that modulate their electronic properties. There has been sufficient evidence showing that vacancy defects may be an important factor in altering the CNTs' geometry and electronic properties.

Zeng et al. (2011) have shown that a variety of mono-vacancy, di-vacancy, tetra-vacancy, and hexa-vacancy defects differentially altered the electronic properties of semimetallic (12,0) CNTs, possibly due to the presence of mid-gap states originating from the defect, thereby enhancing conduction. The pristine (12,0) SWNT, due to a curvature effect, has a small band gap of about 0.07 eV with two DOSs in HOMO and LUMO bands. The defects of increasing severity (mono-to hexavacancy) did not cause a proportional increase in the conduction, but they cause different types of mid-gap DOSs. This suggests that the nanotube conductance is not a monotonic function of the defect size.

3. The electronic properties of CNTs, in addition to the vacancy defects, are also modulated by the adsorption of foreign materials (doping) such as catalyst impurities, hydrogen molecules, or polymers. The effects of hydrogen adsorption on CNTs are of current interest because of the tube's ability to store hydrogen. A number of studies have reported alterations in electronic properties of CNTs in response to hydrogen adsorption. Chen et al. (2012) have reported effects of partial hydrogenation and vacancy defects on the electronic properties of metallic CNTs. They

showed that the hydrogenation, depending upon the adsorption site, transitioned metallic CNTs in semiconductor CNTs lacking magnetic properties (some pristine metallic CNTs exhibited magnetic properties). The energy band structure of H-adsorbed metallic CNTs exhibits a spin-polarized flat band near the Fermi level.

These observations, taken together, suggest that vacancy defects and/or doping may allow tuning of CNTs' electronic and mechanical properties for developing nanomachines for different purposes. Conversely, defects and doping may cause unique adverse effects not recognized at present.