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Comment on “Paired Gap States in a Semiconducting Carbon Nanotube: Deep and Shallow Levels”

In a recent Letter [1], Lee *et al.* reported on paired, localized gap states in semiconducting carbon nanotubes. Pairs of gap states were found both near the band edges and in the middle of the gap. The authors explained their scanning tunneling microscopy (STM) experimental observations in terms of individual point defects, such as Stone-Wales (SW) and vacancy-adatom (VA) complexes. Here we point out that such an interpretation of the experiments is hardly consistent with the abundance and stability of such defects. We also suggest an alternative interpretation of the peaks, which we think is much more realistic and can explain all features reported in Ref. [1] in terms of a single type of defects.

The major problem with the interpretation of the experimental results given in Ref. [1] is the high formation energy of the SW and VA defects (5 eV or larger, the actual value depending on the tube diameter and chirality), which suggests that the equilibrium concentration of these defects is extremely low. In particular, the concentration of SW defects was estimated [2] to be one defect in a few tenths of a millimeter in the equilibrium state at typical growth temperature (~ 1500 K).

Similar concentrations can be expected for VA defects. Besides, it is not obvious that the barrier E_b for the recombination of VA defects is high enough for the defect to survive the heat treatment preceding the STM experiments. Indeed, even a value of 1 eV would give the lifetime of the defect at heat treatment temperature of 150°C of about 1 s. Thus there is no reason to believe such defects would exist following the heat treatment. Moreover, the highly reactive dangling bond of the C atom will likely be passivated by H atom, OH, or other chemical groups. Finally, the positions of the theoretical peaks (deep levels) clearly do not match the experimental STM spectra, which are almost symmetric with respect to the band edges.

We believe the double-peak structures likely originate from two close point defects such as hydrogen adatoms or vacancies or, in principle, any other point defects which, when isolated, result in a single peak near the middle of the gap of a sp^2 -bonded carbon system [3,4]. This effect can be expected for both single vacancies and adatoms, as a single hydrogen adatom chemisorbed on top of a sp^2 -hybridized carbon atom should change the hybridization of the atom from the sp^2 - to a sp^3 - type and thus effectively remove the atom from the π -electron network. Based on experimental data [5,6], one can conclude that

such defects must be stable at the temperatures used for heat treatment.

Hydrogen adatoms tend to cluster together and form close metastable pairs on graphite surfaces [7] due to long-range electronic interaction between the defects, similar to adatoms on metal surfaces [8]. Thus, one can expect that for two close defects the original state should split into two states. This can be understood within a simple theoretical picture illustrating the formation of the bonding and antibonding orbitals in a hydrogen molecule, albeit there is no direct overlap of electrons localized at H atoms, and the interaction is mediated by the nanotube electrons. Depending on the adatom-adatom separation, the positions of the peaks can be in the middle of the gap (deep levels), or close to the band edges (shallow levels). The splitting should be maximal for two adatoms on adjacent atoms and vanish at large separations between the adatoms. This picture is consistent with recent observations of paired gap states in semiconducting nanotubes subjected to hydrogen-plasma treatment, and confirmed by density functional theory calculations [9].

In summary, we think that Lee *et al.* carried out a remarkable experiment demonstrating the possibility of engineering the local electronic structure of carbon nanomaterials through point defects, but the authors misinterpreted their results.

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