Doping and Phonon Renormalization in Carbon Nanotubes

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SUPPLEMENTARY MATERIAL

Experimental methods

Single wall carbon nanotubes were deposited on a heavily doped, oxidized Si substrate by a methane-derived CVD process with a Fe/Mo catalyst [1]. The gate oxide thickness was 100nm and the substrate was used as the gate. Patterns for the source and drain electrodes were written on the substrates after the deposition of the carbon nanotubes using e-beam lithography. The contacts were made of 30 nm of Pd with a 0.7 nm Ti adhesion layer. The Raman spectra were obtained using the spectrograph stage of a 0.5m triple monochromator to disperse the Raman scattered light with a liquid nitrogen cooled Si CCD detector. Calibration of our energy scale with known spectroscopic lines indicates that our spectrograph and detector together has an absolute energy accuracy of 3-4 cm^{-1}. When the spectrograph is not scanned, our run-to-run spectroscopic accuracy is generally better than 0.5 cm^{-1}. Spatially resolved Raman scattering along the length of a single carbon nanotube FET was measured by focusing the laser to a near diffraction limited spot through an optical microscope with a 100X, f0.8 objective, and collecting the scattered light through this objective. The sample was mounted on a piezo-electric x-y stage where it could be moved with nanometer resolution to place the laser spot at a given position on the CNT-FET. The laser power on the sample was kept below 500 microwatts

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to minimize heating. The devices were characterized electrically through source drain current measurements as a function of the source drain voltage, V_d, and V_g.

Our results were obtained on individual, long carbon nanotubes with total lengths greater than 300 ③m. Multiple metal contacts were made to these long tubes. With these metal contacts taken in pairs, each long tube could be operated as several distinct, shorter FETs. The Raman spectra from most of the CNTFETs used in this work were dominated by a single sharp G^+ line at about 1584 cm^{-1} for V_g=0 [2]. Typically, they showed an RBM line at about 104 cm^{-1}, consistent with a tube diameter of about 2.4nm, and our observed G^+-G^- splitting of about 10 cm^{-1}. The intensity of the G^+ emission is fairly uniform as we scanned our laser spot along an individual device. The Raman spectra obtained at many different positions along our devices showed either weak or undetectable D line scattering near 1350 cm^{-1}. G' Raman scattering was observed near 2700 cm^{-1} in all of our CNTFETs. In other devices, we observed G line Raman scattering at V_g=0V consistent with a metallic tube with a broadened G^- line, and a weak G^+ line.

THEORETICAL MODELING

Interband electron-phonon coupling for the LO and TO modes in carbon nanotubes

To calculate the inteband electron-phonon matrix elements for LO and TO modes in semiconducting and metallic nanotubes we use the Su- Schrieffer- Heeger model [3, 4]. The results are shown in Fig. 1S. In metallic tubes, we find that the electron-phonon coupling for both the TO and LO modes are nearly momentum independent with a negligibly small interband electron-phonon coupling for the TO mode, see Fig. 1S-c. On the other hand, in semiconducting tubes, the electron-phonon couplings for both LO and

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TO modes are energy dependent with the coupling to the LO mode vanishing at the top of the valence (bottom of the conduction) band. The energy dependence of the electron-phonon couplings in semiconducting tubes can be best described by the following expression:

$$\begin{aligned} D^2_{k,LO} &= D^2_{k=0,TO}\,\alpha \frac{\varepsilon_k - \Delta}{\Delta}\left(\beta + \frac{\varepsilon_k - \Delta}{\Delta}\right)^{-1} \\ D^2_{k,TO} &= D^2_{k=0,TO}\left(1 - \alpha \frac{\varepsilon_k - \Delta}{\Delta}\left(\beta + \frac{\varepsilon_k - \Delta}{\Delta}\right)^{-1}\right) \end{aligned} \qquad (1S)$$

where ε_k is the carrier energy and Δ is the half the bandgap, while α, β are the fit parameters. Note, that the sum of $D^2_{k,LO} + D^2_{k,TO} \approx D^2_{k=0,TO}$ is nearly independent of the wavevector k as shown in Fig. 1S-a and 1S-b (green squares). As seen from Fig. 1Sa and b, Eq. (1S) gives an excellent fit to the calculated electron-phonon couplings. However, the values of α and β depend on the family of the tube. To model the experimental data in Fig. 1c and Fig. 1f we chose average values of α=1.1 and β=0.4.

Using the SSH electron-phonon coupling g=5.3 eV/ Å [5], we calculate $D_{k=0,TO}$ in semiconducting tubes to be approximately equal to $D_{k=0,LO}$ in metallic tubes, and to vary in the range 10.5 - 11.5 eV/ Å depending on the tube chirality.

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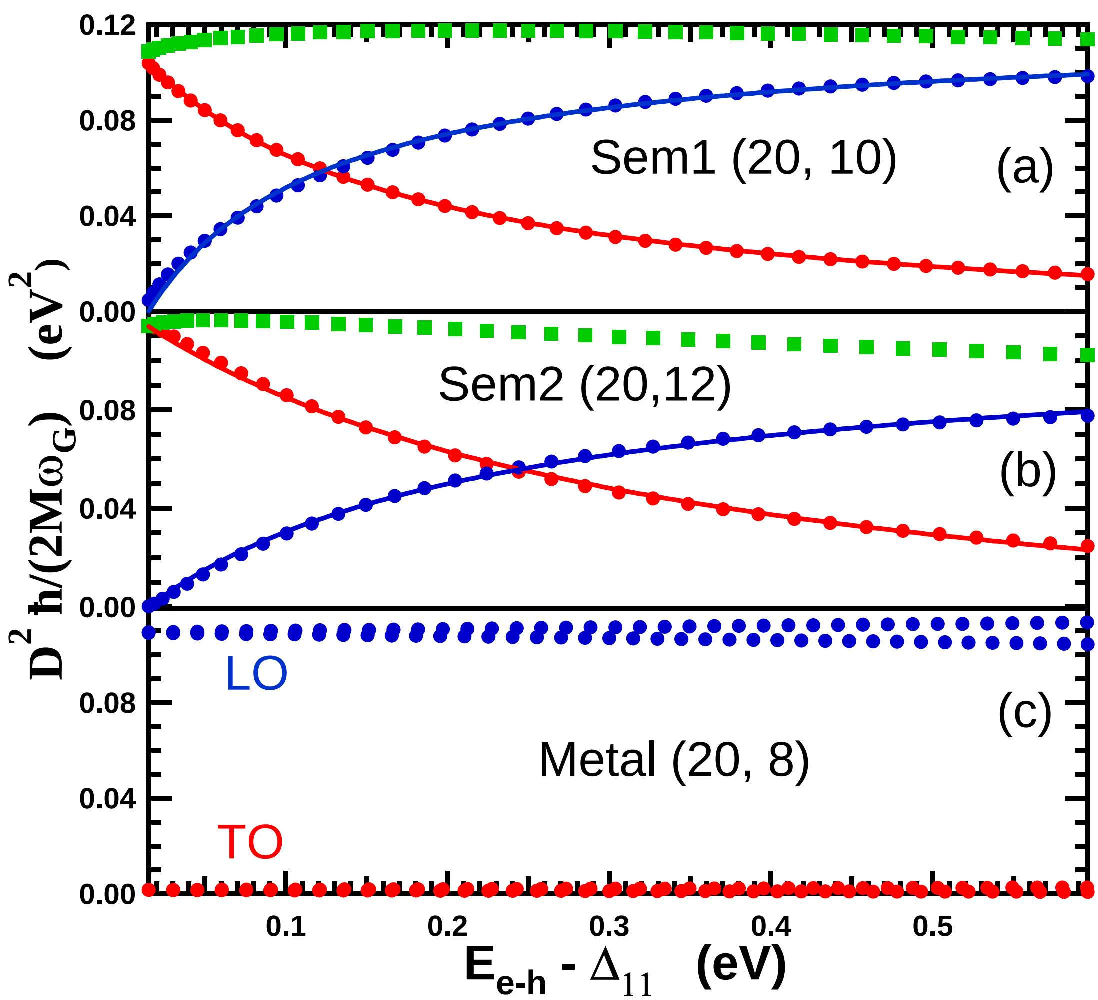

FIGURE 1S Inter-band electron-phonon matrix elements for LO (blue circles) and TO (red circles) modes as a function of electron-hole energy in semiconducting and metallic tubes with diameter of about 2.1 nm. (a) (20, 10) semiconducting tube of mod(n-m,3)=1 family, (b) (20, 12) semiconducting tube of mod(n-m,3)=2 family, (c) (20, 8) metallic tube. Note, in semiconducting tubes $\Delta_{11}=2\Delta$. The sum of the electron-phonon couplings for LO and TO modes, shown by green squares in (a) and (b), are nearly momentum

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independent. The solid curves in (a) and (b) are best fits according to Eq. (1S) with (α, β) = (1.13, 0.28) and (1.10, 0.43) for LO and TO modes in the (20, 10) tube, and (α, β) = (0.96, 0.56) and (1.26, 0.86) for the LO and TO modes in the (20, 12) tube.

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