Electrochemical Control of Coherent Phonon Generations in Single-walled Metallic Carbon Nanotubes

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Abstract: Coherent phonons in single-walled metallic carbon nanotubes were measured under the application of a gate voltage through ionic liquid. We found that the frequencies, amplitudes and phases of the phonons strongly depend on the voltage.

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1. Introduction

Carbon nanotubes (CNTs) consist of graphene sheets rolled up to form one-dimensional cylinder structure, which results in unusual electronic structures such as van-Hove singularities in the density of states. CNTs can either be semiconductors or metals, depending on the structure specified by the so-called chiral vector [1]. Metallic CNTs are of particular interest because they exhibit strong electron-phonon coupling due to Kohn anomaly, and thus the phonon properties shows drastic dependence on the Fermi energy and the non-equilibrium electron distribution [2-4]. However, the Fermi energy dependence on the dynamics of carriers and electron-phonon coupling has not been reported until now, partly because the control of the Fermi energy requires micro-sized devices such as FETs that are difficult to apply to the ultrafast measurement. Here, we use a more convenient approach to investigate the Fermi energy dependence on the ultrafast carrier and phonon dynamics in CNTs, in which we apply a voltage through an ionic liquid and CNT electrodes [5]. The observed coherent phonon signals depend strongly on the applied voltage, which are inaccessible with the conventional Raman spectroscopy.

2. Experiments

Metallic single-walled CNTs (SWCNTs) with average diameters of 1.4 nm were obtained from purification of initial SWCNTs produced by an arc-discharge (Arc-SO, Meijo nano-carbon Co.). The purifications were performed by using density-gradient ultracentrifuge method using deoxycholate sodium salt for a surfactant in a dispersion step to obtain high-purity metallic SWCNTs in a manner similar to that in Ref. [6]. The thin films were formed on glass substrates by using a method reported in Ref. [5]. From the optical absorption spectra, purity of metallic SWCNT is confirmed to be greater than 95%. We used an ionic liquid (N, N, N-trimethyl-N–propylammonium bis(trifluoromethanesulfonyl) imide (TMPA-TFSI), Kanto-Kagaku Co.) for electrolyte solution, which is known to exhibit large electrochemical window, high transparency, low volatility, and high environmental stability. A 7.5-fs Ti-sapphire laser (center wavelength of 800 nm, repetition rate of 80 MHz, and output power of 200 mW) was used for pump-probe transmission measurements. The output of the laser was separated into pump and probe beams. The pump pulse is delayed by an optical shaker with a scanning range of 15 ps, and focused on the sample together with the probe pulse. The probe pulse transmitted through the sample was delivered to a photodiode for detecting the probe signal. To balance the current of the photodiode for the probe signal, the reference signal was also detected. The difference between the probe and reference signals was amplified and collected by an analogue-to-digital converter [7].

3. Results and Discussion

Figure 1 shows the coherent phonons in metallic SWCNTs with different gate voltages. The amplitudes and phases of the observed coherent phonons in SWCNTs depend strongly on the gate voltage. The Fourier transformed spectra obtained from the time-domain data show specific high-frequency phonons in SWCNTs up to 100 THz: radial

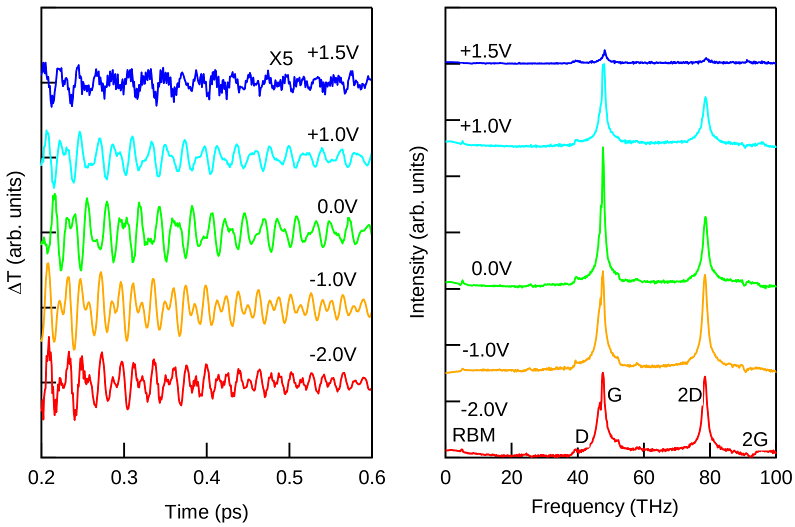

Figure 1: Observed transmission change of high frequency coherent phonons in metallic SWCNTs at different gate voltages. The slow responses due to the transient absorptions of SWCNTs are subtracted by filtering out the low frequency components. The Fourier transformed spectra are shown in the right.

breathing mode (RBM), D-mode, G-mode, 2D-mode, and 2G-mode. We also note that the frequencies of these peaks slightly change upon the gate voltage, which are consistent with those of the micro-Raman measurement [3].

The decrease of the coherent phonon amplitude at the high gate voltage can be understood as the change of Raman scattering cross section due to the Pauli blocking. When the electronic states at the van Hove singularity are occupied by applying the gate voltage, the resonant transition would be suppressed, and subsequently, gives the smaller coherent phonon signal. We also observed an effect of Kohn anomaly to the resonant frequencies and dephasing times of the G modes, in which the phonon softening and enhanced dephasing are observed at the Dirac point. Time-dependent frequency-shift of the G-mode was also observed by applying the windowed Fourier transformation on the time profiles. These results demonstrate that our method for measuring the Fermi energy dependence will open a new possibility to observe novel ultrafast phenomena in materials.

4. Conclusion

We observed the coherent phonons in metallic SWCNTs up to 100 THz under the application of a gate voltage through ionic liquid. The amplitudes, frequencies, and phases of the observed coherent phonons show strong dependence on the gate voltage, which can be explained by considering the Pauli blocking and Kohn anomaly. The results demonstrate that our method for applying the gate voltage is promising for investigating ultrafast dynamics of materials with different chemical potentials.

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