

博士論文（要約）

Terahertz spectroscopy of single molecules using sub-nm scale gap electrodes

（サブ nm ギャップ電極を用いた単一分子のテラヘルツ分光に関する研究）

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THz spectroscopy has been developed as a powerful tool for clarifying electronic structures and vibrational dynamics of various kinds of molecules since many vibrational modes exist in the THz frequency range. However, in the nm-scale, the long wavelength nature of the radiation prohibits THz wave efficiently interacting with nanomaterials, leaving the research on THz dynamics in nanomaterials still at a preliminary stage. With increasing requirements of cutting-edge research fields such as molecular biology and quantum information technologies, THz nanoscience has received much attention. For this purpose, we focus our work on the THz spectroscopy of single molecules and aim at bringing a breakthrough in the study of THz nanoscience at atomic scales.

As an introduction to the work, Chapter 1 reviews the development of THz spectroscopy from mm-scale to nm-scale. THz time-domain spectroscopy (THz-TDS) was invented to measure sample at mm-scale. Then, THz-TDS system was integrated into a chip to break through the diffraction limit by using THz waveguides, which allows detecting sample at μm -scale. More recently, THz-STM technique has been performed to detect 10-nm scale sample. However, all of these methods belong to ensemble measurements. Therefore, the motivation of this work is to perform THz spectroscopy of single molecules.

In Chapter 2, we proposed to use a single molecule transistor (SMT) structure to perform THz spectroscopy at single molecule level. By using this structure, we can go much beyond the diffraction limit and focus THz radiation onto a single molecule. Furthermore we can detect extremely weak absorption by measuring the THz-induced photocurrent. In the fabrication of SMT structure, first we designed two kinds of THz antennas for different frequency range with the help of the finite element method (FEM) simulation. The enhancement of THz field in the nanogap region is expected to be more than 10^5 times. Then we used the shadow evaporation and the feedback controlled electromigration as special nanofabrication techniques. By removing metal atoms one by one by electromigration, we created electrodes with a sub-nm gap to capture single molecules. To identify single molecules in the nanogap, we performed transport measurements to obtain Coulomb stability diagram. We also described single electron tunneling theory to understand Coulomb stability diagrams.

In Chapter 3, we explain how to perform THz spectroscopy on single- C_{60} molecules. Since the SMTs are very slow devices due to their high tunnel resistances, it is impossible to measure ultrafast current changes. Therefore, we adopted the time-domain THz autocorrelation measurements. By using a beam splitter, we split the laser beam into two parts and created double laser pulses. A surface of an InAs wafer was consecutively pumped by the femtosecond laser pulses and the time-correlated THz double pulses were generated. By recording the photocurrent induced by the THz double pulses as a function of the time interval between the THz pulses, we obtained interferograms of the photocurrent induced in the single molecule by THz radiation. When we illuminated the sample with THz pulses, a very small, but finite photocurrent was observed near the charge degeneracy point. Then, we measured an interferogram of the THz-induced photocurrent and calculated the Fourier spectrum to obtain a spectrum for a C_{60} SMT. Two peaks are observed at around 2 meV and 4 meV. It should be noted that a THz vibrational spectrum is obtained even for a single molecule when the SMT structure is used. The low-energy excitations observed for a C_{60} SMT originate from the vibron-assisted tunneling promoted by the THz-induced center-of-mass oscillation of the C_{60} molecule. Vibron-assisted inelastic tunneling has been observed in the tunneling spectroscopy measurements. In the THz spectroscopy, molecular vibrations are excited not only by the tunneling electrons but also by the impulsive THz fields generated by the femtosecond laser pulses. Because

of the broadband THz excitation, the center-of-mass oscillation of the C_{60} molecule is excited and creates new tunneling paths for tunneling electrons. When the lowest unoccupied molecular orbital (LUMO) level is above the Fermi level of the electrodes, an electron in the electrodes cannot enter the molecule in the dark condition. However, when the center-of-mass oscillation of the C_{60} molecules is excited by the THz radiation, an electron in the electrode can absorb a vibron and jump into the molecule (vibron-assisted tunneling). Furthermore, we can roughly estimate the quality (Q)-factor of the C_{60} molecular vibration to be approximately 3-5, although the linewidths of the sharp peaks are affected by the resolution of the experimental setup. This means that an electron that hops on the C_{60} molecule resides on the molecule at least for about 3-5 cycles of vibration and leaves the molecule.

A very interesting observation is that the vibron peaks around 2 meV and 4 meV are finely split into two. The excited-state lines due to molecular vibration in the Coulomb stability diagrams originate from the Franck-Condon effect. So far, the vibrational frequencies of the molecule for the N - and $N+1$ -charge states have been assumed to be the same. However, this may not be the case in actual systems; i.e., the van der Waals potential felt by a C_{60} molecule on the gold surface may depend on the charge state of the molecule. From the interaction energy curves for neutral and negatively charged C_{60} on a gold surface calculated by Hamada, we have found that, when C_{60} is negatively charged, the system becomes destabilized, because the antibonding state between the lowest unoccupied molecular orbital of C_{60} and the substrate state is partially occupied. Accordingly, the equilibrium distance becomes longer and the vibrational energy is lowered. The calculations suggest that the vibrational energy depends on the charge state and, thus, the splitting of the vibron assisted tunneling peak is observed. Indeed, the magnitude of the observed splitting (0.6~0.8 meV) is in good agreement with the calculated change in the vibrational energy (0.7 meV). The result reflects the difference in the van der Waals potential profile experienced by the C_{60} molecule on the metal surface when the number of electron on the molecule fluctuates between N and $N+1$ during the single electron tunneling process.

In Chapter 4, we performed THz spectroscopy of single $Ce@C_{82}$ endohedral metallofullerenes. We used a SMT structure that consisted of a single $Ce@C_{82}$ molecule and the nanogap metal electrodes as a sensitive THz detector. We used a broadband THz source (blackbody light source) from Fourier transform infrared spectroscopy (FTIR) system to excite the single- $Ce@C_{82}$ molecule. The photocurrent is large near the charge degeneracy point and gradually decreases as the gate voltage moves away from the charge degeneracy point. Furthermore we measured a color-coded map of the THz-induced photocurrent of a $Ce@C_{82}$ SMT as a function of the source-drain voltage and the gate voltage. The measured photocurrent does not depend on the polarity of the source-drain voltage, indicating that the photocurrent flows by the photovoltaic mechanism. The photocurrent distribution also suggest that the THz radiation does not simply excite an electron, but excites the electron-vibron coupled mode (the second-order process).

By measuring an interferogram of the THz-induced photocurrent and taking a Fourier transform, we have obtained a spectrum of a single $Ce@C_{82}$ molecule. Two broad peaks are observed around 6 meV and 16 meV. We conclude that the vibrational peaks around 6 meV and 16 meV are associated with the Ce atom in the C_{82} cage. From a comparison with theory, we attributed the vibrational modes of these two peaks to the ultrafast motion of the encapsulated atom. The vibrational mode at ~6 meV is due to the bending motion of Ce atom (lateral motion of the Ce atom) and the peak around 16 meV is due to the stretching mode (vertical motion). It is noteworthy that the peaks observed around 6 meV and 16 meV are very broad and the

spectral shape is not Lorentzian, suggesting that the Ce atom motion is very unharmonic. This work demonstrates that our THz spectroscopy is sufficiently sensitive to detect ultrafast motion of a single atom.

In the last chapter of this dissertation, we summarized the whole work and gave a comment on future prospects. We performed terahertz spectroscopy of single molecules by using SMT structure, and investigated THz dynamics of single molecules and single atoms. This novel scheme provides a new opportunity of investigating ultrafast dynamics of sub-nm scale systems. We have opened a door to “THz nanoscience at single molecule level”.

Shaoqing Du, Ya Zhang, Kenji Yoshida, and Kazuhiko Hirakawa, Terahertz spectroscopy of a single atom in a fullerene cage, Proceedings of 2017 42nd International Conference on Infrared, Millimeter, and Terahertz Waves (IRMMW–THz), 27 Aug.–1 Sept. 2017, Cancun, Mexico. DOI: 10.1109/IRMMW–THz.2017.8066858