論 文 の 内 容 の 要 旨

論文題目　Effect of the contact states on electron transport of single molecule systems within an STM junction
（STMジャンクション中の一分子の電子輸送特性とコンタクト状態の研究）

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Introduction

Scanning tunneling microscope (STM) is a powerful tool to investigate single molecules on a substrate. STM imaging reveals the position and configuration of the single molecule. Scanning tunneling spectroscopy (STS) reveals the electronic states of the molecule around the Fermi level (E_F). In addition, STM can be used as the nano tweezers. STM manipulation technique enables us to move, touch, pick-up and sometimes destroy the single molecule via the atomic force, electric fields and injected tunnel electrons from/by the STM tip. In this point, STM tip can be the source of external perturbation.

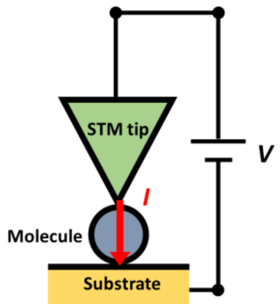

Fig. 1. Schematic image of the STM contact measurement and the single molecular junction.

Due to these exclusive characteristics, the STM contact measurement, where the STM tip contacts to the molecule on the surface (Fig. 1), provides us effective ways to (i) measure the electronic transport properties of the single molecular junction, where the single molecule is sandwiched between electrodes, (ii) control the transition of the ground states of the molecule by inducing perturbations from the STM tip. We emphasize that STM contact measurement together with STM imaging and STS makes it possible to investigate the molecular junction with characterizing the contact state; the geometrical configurations and the electronic states of the molecule in the junction. This point is an advantage to the mechanically controllable break junction (MCBJ) measurements[1], which cannot directly characterize the contact state.

In this thesis, we report the results of the STM contact measurements on three systems; (1) the fullerene (C_{60}) molecule, (2) the silicene nano ribbon (SiNR) and (3) the Iron(II) phthalocyanine (FePc) molecule. In the following paragraphs, we will introduce the brief background, the purpose of the study and the experimental results of each system.

Results and Discussion

(1) Single molecular junction (SMJ) is a model system of ultimately miniaturized electronic devices[2]. Investigating the electron transport characteristics of the SMJ is one of the central issues for the development of such nano electronics. The electron transport phenomenon in the nanoscale sample such as the SMJ is expressed by the Landauer formula[3]

$$G = G_0 \sum_{i=1}^{n} \tau_i \ ,$$

where G is the total conductance, $G_0 = 2e^2/h$ is the conductance quantum, n is the number of transport channels and τ_i is the transmission coefficient for the i-th channel. The transport channel is an electronic state of the sample which carries electrons from one electrode to another. In the case of the SMJ, electronic states of the molecule, especially states around the E_F, i.e., the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are important. For the better understanding of the electron transport phenomenon in the SMJ, it is essential to experimentally determine n and τ_i and unveil the relations between these values and the electronic/geometric configuration of the molecule.

For this purpose, we have constructed the C_{60} molecular junction with the superconducting metal electrodes of a Nb tip and a Pb(111) substrate[4]. The superconductor (S) junction enables us to determine n and τ_i; in the S/N/S junction (N indicates a normal conductor), multiple Andreev reflection occurs and it produces the subharmonic gap structure (SGS) in the current-voltage (I-V) spectra. Due to the non-linear dependence of the SGS on τ_i, we can determine n and τ_i of the junction[5].

Figure 2(a) shows an STM image of C_{60} molecules on Pb(111). Each bright spot corresponds to the single C_{60}. We found two different configuration in the image; a round shape denoted by α and a two-fold shape denoted by β. Figures 2(b) and (c) show the I-V spectra obtained when the Nb tip contact to the α- and β-C_{60} molecule at $T = 0.4$ K. The non-zero currents under the bias voltage 3 mV is the SGS. Analyzing the SGS based on the theoretical calculations [solid red lines in Figs. 2(b) and (c)], we evaluated the values: $n = 3$ and $\tau_{1,2,3} = \{0.095, 0.095, 0.095\}$ for the α-C_{60} junction, and $n = 3$ and $\tau_{1,2,3} = \{0.17, 0.075, 0.06\}$ for the β-C_{60} junction. STS spectra of C_{60} on Pb(111) show resonance peaks around the E_F, which are derived from the LUMOs of C_{60}. Hence, we concluded that the three transport channels ($n = 3$) in the C_{60} junction originates from the LUMOs of C_{60} (triply-degenerate in the gas phase). In addition, we observed that τ depends on the molecular configurations (α and β). We expect that the transmission coefficient difference is attributable to the different spatial distribution of LUMOs with respect to the electrodes caused by the different molecular configurations.

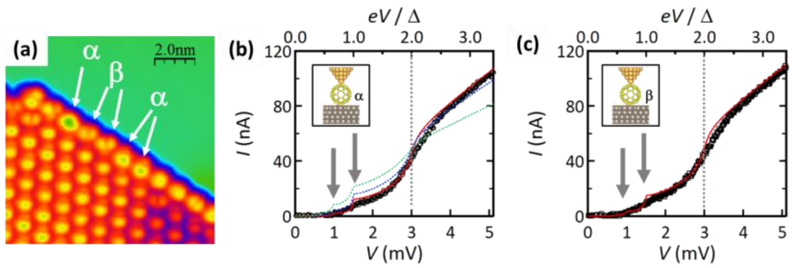

Fig. 2. (a) STM image of C_{60} molecules on Pb(111).
(b) I-V spectra of α-C_{60} junction. Inset shows the schematic model of the junction. (c) I-V spectra of β-C_{60} junction.

(2) Silicene nano ribbon (SiNR), which is an analogical material of graphene nano ribbon, is a recently discovered honeycomb nano ribbon composed of Si[6]. The honeycomb nano ribbons attract much interest due to their unique electronic properties such as the edge state. The edge state is spatially localized at a zigzag edge of the honeycomb ribbon and energetically locates at the Fermi level (E_F) with almost flat dispersion around the longitudinal direction in the k-space. Due to the band structure, the edge state is expected to provide a perfect conduction channel along the edge when the inter-valley scattering is negligible. It is essential to experimentally measure the edge state or the edge current in SiNR for the future applications of the Si-based honeycomb materials. Although silicene and SiNR have been well synthesized on Ag substrates, recent studies on silicene/Ag(111) have revealed that the interaction between Si and Ag cause the vanishment of the unique electronic properties in silicene[7]. Therefore, we tried to construct the SiNR junction and reduce the interaction between Si and Ag by lifting up the SiNR by the STM tip.

We synthesized SiNR on Ag(110). STS spectra obtained on SiNR show no peaks attributable to the edge state around the E_F. As expected, we conclude that the edge state disappears for SiNR on Ag(110). We constructed the SiNR junction and lifted up the SiNR from the Ag substrate by the STM tip. dI/dV spectra obtained when the STM tip lifted the SiNR show a sharp peak at the E_F, which are in good accordance with the characters of the edge state.

(3) Kondo effect is a many-body phenomenon, where an impurity spin is collectively screened by the bulk conduction electrons of the host metals via the exchange interaction accompanied with the spin flip scattering. The Kondo effect screens the impurity spin and the many-body ground state called Kondo resonance state is formed. We focused on one of the frontier topics in the Kondo problem; the multi-stage Kondo resonance and the competing effect such as the Fund coupling and the spin-orbit coupling (SOC) in the spin multiplet system[8]. Recent studies revealed that Iron(II) phthalocyanine (FePc) on Au(111) is an ideal test system; the spin state of FePc on Au(111) is triplet $S = 1$ (two spins in the Fe 3d orbitals) and the two-stage Kondo resonance occurs, i.e., both two spins form the Kondo resonance state with a different interaction strength. The interaction strength is expressed as the characteristic temperature called the Kondo temperature T_K; for FePc on Au(111), $T_K = 2.7$ K and $\approx$ 100 K[9]. We performed the STM contact measurement to this system in order to investigate the effect of the STM tip contact on the magnetic ground state of Fe. The external field induce by the STM tip perturb the Kondo resonance state and cause the ground state transition.

We have constructed the STM tip-FePc-Au(111) junction. The evolutions of dI/dV spectra as a function of the STM tip-Fe distance show the gradual transition of the spectral shape; when the STM tip is far from Fe, the spectra show the asymmetric narrow dip (the half-width of the resonance Γ is about 1 meV) and wide peak (Γ is about 20 meV) structure, which indicates the two Kondo resonance states of FePc on Au(111). As the STM tip approaches, the narrow dip structure transforms to a symmetric step structure (the step position is $V = \pm 5$ mV) with respect to the E_F and the wide peak structure also disappears. The origin of the symmetric step structure is assigned to the inelastic magnetic excitation process according to the magnetic dependence of the spectra.

Conclusion

By STM contact measurements, we have revealed (1) the number of electron transport channels and their transmission coefficients in the C_{60} junction by using superconducting STM tip and substrate. Three channels in the C_{60} junction are in good accordance with the number of C_{60} LUMOs, which locates near the E_F. Moreover, we obtained the result that the molecular configuration difference causes the different transport characteristics. (2) The edge state of SiNR was observed by constructing the STM junction and reducing the interaction between the SiNR and Ag substrate. (3) The magnetic ground state of FePc on Au(111) was controlled by the STM tip contact. We observed the ground state transition and the vanishment of the strong Kondo resonance state (~100 K) in the single molecule, which is almost impossible to be achieved by the temperature control measurement.

Our results demonstrated the following points; (1) STM contact measurement with superconducting tip and substrate is an effective way to investigate the transport characteristics of the SMJ. (2) STM contact measurement is useful to induce the external perturbation and control the properties of a single molecule. By the STM tip contact, the edge state of SiNR is restored and the magnetic ground state of FePc on Au(111) is controlled from the two-stage Kondo resonance state to the non-screened $S = 1$ state.

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Publications

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[4] R. Hiraoka et. al., "Direct manipulation of multi-stage Kondo resonance state in FePc on Au(111) by STM tip contact", *In preparation*.