

## 論文の内容の要旨

### 論文題目

Effect of Molecular Vibration, Orbital, and Rotation on Electron Transport in  
Single and Double Molecule Transistors  
(単一および二重分子トランジスタの電気伝導における分子振動と軌道、回転の効果  
に関する研究)

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In this dissertation, we have investigated electron transport through single molecules in transistor geometry. The interest in this field is motivated by the idea that single molecules will form building blocks for future electronic devices. The advantages are their small sizes that make quantization energy larger than other artificial nano-structures, and their chemical versatility that allows the molecules to be designed with particular functionality. Several techniques have been developed to form single molecule junctions: scanning tunneling microscopy, mechanical break-junction technique, and electrical break-junction technique via electromigration. Among them, only electrical break-junction technique can fabricate molecular junctions with gate electrodes, i. e., single molecule transistors. The gate electrode allows not only oxidation and reduction of the molecule, but also accurate determination of charging energies and quantization energies for electrons, vibration and spin states by bringing molecular levels in and out of resonance with Fermi energy of lead electrodes. This makes studies of electron transport through single molecules particularly interesting. As an introduction to this thesis, we briefly describe experimental progress in this field, called “single molecule electronics”, and recent striking progress in single molecule transistors.

Theoretical background needed to understand the results of this dissertation is given in chapter 2. The theory includes some basic concepts related to electron transport in single molecule scale and detailed concepts of single electron transistors. It has been demonstrated that single molecule transistors operate as single electron transistors. Characteristics of such single electron transistors, which consist of current-voltage characteristics as a function of gate voltage, reveal important spectroscopic information about molecules of interest.

In chapter 3, we describe in detail the experimental setup used throughout this dissertation; fabrication of metal nanowires, deposition of molecules, electrical break junction technique including fast feedback controlled electromigration technique by using FPGA, three terminal measurements, and low

temperature insert. The chapter explains not only simple experimental processes but also the consideration for the design of experimental setups.

The discussion of experimental results starts in chapter 4 with the measurements on mechanism of electromigration. We have investigated elementary process of electromigration in detail for the purpose of improving the fabrication process of single molecule transistors and finding technological solution to EM reliability in LSI interconnects. Our experiments showed that once the number of atoms across metal nanojunctions becomes less than 100 and electron transport enters the ballistic regime, junction conductance shows successive drops by one conductance quantum, corresponding to one by one removal of metal atoms, only when the junction voltage exceeds certain critical values. The peak position in the histogram of the observed critical voltages agreed with the activation energies for the surface diffusion of metal atoms (Au, Ni and Cu). This fact indicates that the elementary process of electromigration in such small junctions is the self-diffusion of metal atoms driven by microscopic kinetic energy transfer from a single conduction electron to a single metal atom. It was also demonstrated that ballistic Cu nanojunctions could support current densities on the order of  $10 \text{ GA/cm}^2$ , as long as the junctions are biased below the critical voltage. These results suggest that both high current densities and high EM reliabilities can be achieved when the dimension of the metal interconnects is reduced to several tens of atoms.

The first molecule investigated in this dissertation is fullerene ( $\text{C}_{60}$ ), which is presented in Chapter 5. This chapter focuses on effects of molecular vibration on electron transport through single molecules. As reported in literature, tunneling electron in single molecule transistor is coupled to molecular vibration. While this phenomenon, called electron-vibration coupling, has been intensively studied in single molecule transistors, it remains elusive in double molecule transistors due to difficulties in obtaining stable samples and lack of analytical method. In order to extend our studies of electron-vibration coupling into double molecule transistors, we have investigated electron transport through double  $\text{C}_{60}$  molecule in series experimentally and theoretically.  $\text{C}_{60}$  molecule is chosen because vibration of this molecule in transistor geometry is well understood. In order to analyze transport characteristics of double molecules in series with a single gate structure, detailed modeling is presented with calculation of the Coulomb stability diagram based on a rate equation approach. Our analysis and calculations well explained the experimental data in detail, and it is found that high vibronic states can be excited via inelastic electron tunneling process between the two molecules. We believe that these observations will open a way to complete control of molecular vibration.

Chapter 6 discusses effects of molecular orbital and rotation on electron transport through single molecules, using tetra-phenyl-porphyrin (H2TPP) molecules. Electron transport through a single molecule is determined not only by intrinsic properties of the molecule but also by the configuration of the molecule with respect to the lead electrodes. In this chapter, we present how

electron transport through a single H2TPP molecule is modulated by the configuration change. The Coulomb stability diagram of a single H2TPP molecule transistor exhibited a few different patterns when a relatively large bias voltage was applied to the sample. Furthermore, the sample exhibited a negative differential resistance, the magnitude of which changed with the pattern of the Coulomb stability diagram. Such behavior can be explained by rotation of the molecule with anisotropic molecular orbitals in the gap electrodes induced by electrical stresses. Moreover, we found that energy separations between molecular orbitals are also affected by the rotation, confirming that metal-molecule interface configuration renormalizes electronic levels in the molecule. We believe that the present result has brought important implications on realization of nanomechanical molecular devices.

At the end of this dissertation, the conclusion and future prospects of this field are described. The effect of molecular vibration, orbital and rotation of the molecules are all intrinsic to the molecules. Therefore we believe that these effects on electron transport through single molecule will be useful for realization of functional single molecule devices in the future.