Thermoelectricity in Benzenedithiol Molecular Junctions with Ni Electrodes

S.K. Lee,[*] T. Ohto, R. Yamada, H. Tada
Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyama, Osaka, JAPAN.

There has been considerable interest in the studies on thermoelectricity of atomic and molecular junctions since it is proposed that the best thermoelectric efficiency can be achieved in charge transport through a single energy level [1]. Seebeck coefficient (S) of atomic and molecular junctions is described as a function of $d\tau/dE$, where τ and E represents transmission function and energy, respectively [1,2]. As the Fermi energy level (E_F) of the electrode is usually located between the transmission peak related to the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) level, the sign of S can indicate the energy level of the E_F relative to the HOMO or LUMO levels [3]. However, this simple assumption might not be valid for ferromagnetic electrodes because the interaction between the spin-polarized electronic states (usually the partially filled d-band) of the electrode and the molecule can generate new hybridized states around E_F [4], which can cause a significant change in the value of S. In this study, we investigate the thermoelectricity of benzenedithiol (BDT) molecular junctions using Au and Ni electrodes.

The thermoelectric voltage of the molecular junctions was measured with a home-built scanning tunneling microscope (STM) (Figure 1). Temperature difference between the tip and the substrate was controlled by the substrate's temperature with a Peltier device. Si diode temperature sensors were used to monitor the temperatures of the tip and substrate. The STM tip was brought close to the substrate until the threshold current value, that was larger than the current for a single molecular junction determined by break junction measurements, was reached. Then, the voltage difference between the tip

and the substrate was measured during the retraction of the tip.

Figure 2 shows the TEV of Au-BDT-Au and Ni-BDT-Ni as a function of ΔT. Ni-BDT-Ni junctions showed negative thermopower, whereas the Au-BDT-Au junctions showed positive thermopower. First principle calculations revealed that the negative thermopower for Ni-BDT-Ni junctions is due to spin-split hybridized states generated by the highest occupied molecular orbital of BDT coupled with s and d states of the Ni electrode.
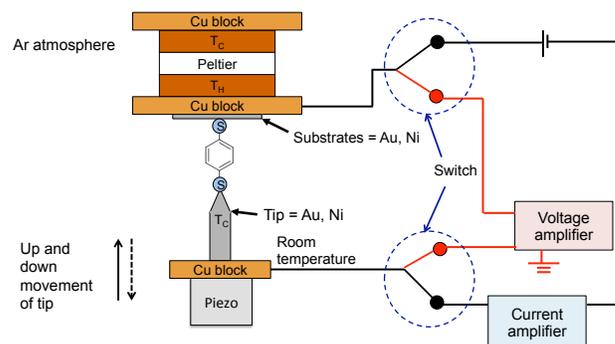

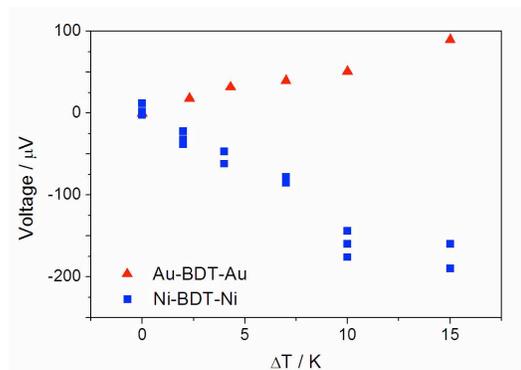Fig.1. Schematic diagram of the experimental setup.

Fig.2. Thermoelectric voltage as a function of ΔT for BDT molecular junctions.

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[*] Email: seekei@molectronics.jp