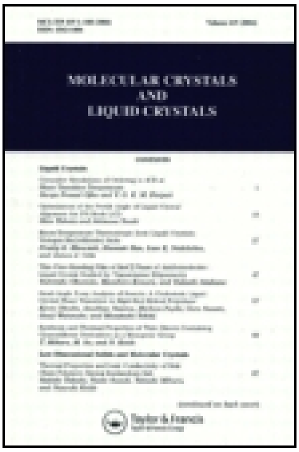

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Inelastic Electron Tunneling Spectroscopy in Single Monolayers and Hetero-Structured Films by Using a Polyimide Barrier

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INELASTIC ELECTRON TUNNELING SPECTROSCOPY IN SINGLE MONOLAYERS AND HETERO–STRUCTURED FILMS BY USING A POLYIMIDE BARRIER

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Abstract Using 9–layer polyimide Langmuir–Blodgett films as a tunneling barrier, Current Voltage (I–V) characteristic and inelastic electron tunneling (IET) spectra of the junctions in corporating 1–layer organic monolayer were investigated. The I–V characteristics exhibited a typical I–V characteristic of ideal tunnel junctions with a noble metal/tunnel barrier/superconductor. Several peaks originating in the excitation of the vibrational modes of constituent molecules of the 1–layer monolayers were clearly observed in the IET spectra. Further we examined the electric phenomena occurring in hetero–structured films by using IETS and thermally stimulated displacement–current–measurements.

1. INTRODUCTION

In order to apply organic molecules to electronic devices, functional ultra–thin films and hetero structured films have been investigated by many researchers. Hetero–structured films have great potential for electronic device applications, e.g., electrical rectifier devices using electron accepting and electron donating elements in molecules[1], and pyroelectric devices using hetero structured films having permanent dipole at the molecular interface[2]. It is essential to gain any informations on the junction at molecular level.

Inelastic electron tunneling spectra (IETS) measurement is useful to investigate the electron phenomena of molecular junction, because the measurement is very sensitive in the detection of the energy of vibrational modes of molecular element constructed at the hetero–structured interface[3,4].

In the present study, we fabricated Au/PI/C20/ODA/Pb junctions with PI LB films as a tunnel barrier, and then examined the electrical phenomena originating in hetero–structured interface from current–voltage (I–V) and IET measurements. Finally, we

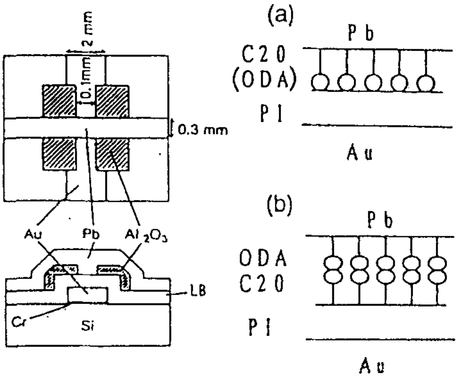

FIGURE 1
Electrode configuration of the junction used I–V and IETS measurement.
(a) Au/PI/C20/Pb or Au/PI/ODA/Pb
(b) Au/PI/C20/ODA/Pb junction

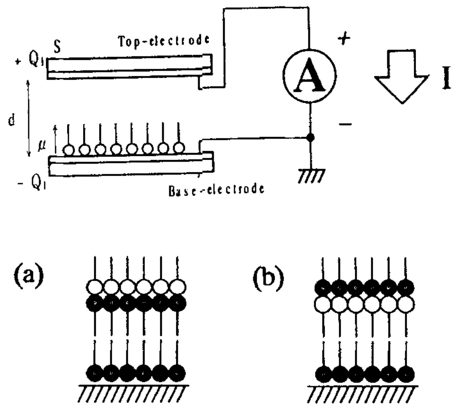

FIGURE 2
Sample description of thermally stimulated displacement current measurement
(a) Au/C20/C20/ODA/air gap/Au sample
(b) Au/C20/ODA/C20/air gap/Au sample

examined the electrical phenomena originating in hetero structure interface by using thermally stimulated displacement–current–measurement.

2. EXPERIMENTALS

2.1. Sample description

Figure 1 shows the configuration of the junctions used for IET and I–V measurements. All junctions were fabricated on silicon substrate in the same manner as described in previous papers[3,4]. LB films were composed of a tunnel barrier and mono– or hetero–structured LB films as shown in Fig. 1. 9–layer PI LB films were used as a tunnel barrier. Arachidicacid (C20) and Octadecylamine (ODA) were used as mono– and hetero–structured LB films. The junction area of each samples was about 0.03 mm^2.

Figure 2 shows the sample configuration used for thermally stimulated displacement–current–measurement. Bottom and top Au metal electrodes were evaporated on glass slide. Hetero–structured LB films composed of C20 and ODA were deposited on bottom Au electrode as shown in Fig. 2. The working area of each sample was 6.25 cm2 and the distance between the two electrodes was about 0.1 mm.

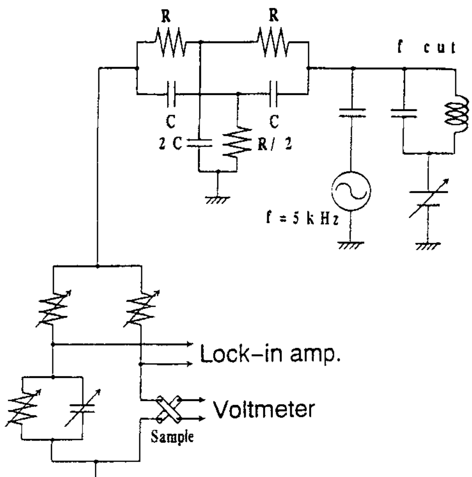

FIGURE 3
Measurement circuit of IETS measurement

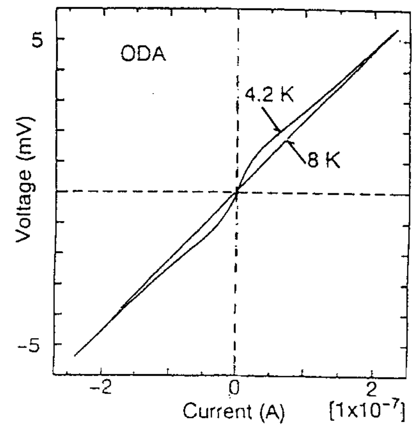

FIGURE 4
A typical I–V characteristic of the Au/PI/ODA/Pb junction at a temperature of 4.2K and 8.0K.

2.2. Measurements

Figure 3 shows the circuit used for the IETS measurements. Each junction was placed in a liquid helium bath in which temperature was 4.2 K and were connected in a standard four terminal arrangement. The IET spectra were measured with the application of a DC biasing voltage coupled with a small modulation current with a frequency of 5.0 kHz. In the IET measurement, it is possible to determine the energy of vibrational modes originating from C20 and ODA molecules. The IET spectra and I–V measurement were performed in a manner similar to that in our previous study[3,4].

The circuit used for the thermally stimulated displacement–current–measurement is shown in Fig. 2. The two electrodes were connected to each other through the ammeter A. The details of the measurement were the same as in our previous study[5]. In this measurement, it is possible to detect the orientational change of the dipole moment of a polar molecule and the displacement of electrons at the interface.

3. RESULT AND DISCUSSION

Figure 4 shows a typical example of the I–V characteristic of the Au/PI(9L)/ODA(1L)/Pb junction observed at temperatures of 4.2K and 8.0K. The I–V characteristic at a temperature of 4.2K deviates from a liner relationship and exhibits a typical I–V characteristic of a tunnel junction with a metal/insulator/superconductor

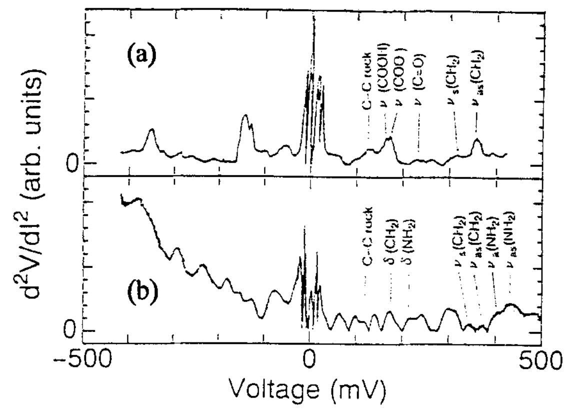

FIGURE 5
IET spectra of the junctions in the energy range between 0 and 500 mV at a temperature of 4.2K.
(a) Au/PI/C20/Pb and
(b) Au/PI/ODA/Pb junctions.

structure. Half of the energy gap (Δ/e) of Pb superconductor, about 1.2 mV, is clearly seen. At the temperature of 8.0K, above the critical temperature of Pb (7.2K), an almost linear relationship is seen between I and V. Similar experimental results were obtained for about 30% of the junctions we fabricated. These results suggest that 9-layer PI LB films whose thickness is about 3.6 nm function as a good tunneling barrier.

Figure 5 shows the IET spectra of Au/PI(9L)/C20/Pb (a) and Au/PI(9L)/ODA/Pb (b) junctions at energies between 0 and 500 mV. Several peaks appeared at voltages between 130 mV and 360 mV due to the excitation of the vibrational modes of C20 molecules, and at voltages between 110mV and 420 mV due to the excitation of the vibrational modes of ODA molecules. The peak at around 160mV is assigned due to the excitation of –COOH vibrational mode of C20 molecule, and the peak at around 420 mV is due to the excitation of $-NH_2$ vibrational mode of ODA molecule. As shown in Fig. 4, IET measurement is useful for detecting the electronic phenomena originating in mono-layer molecules.

Figure 6 shows the IET spectra of a Au/PI(9L)/C20/ODA/Pb junction. Many peaks appeared at voltages between 110 mV and 440 mV. As shown in Figs. 4 and 5, the IET spectra of a Au/PI(9L)/C20/ODA/Pb junction differs from that of Au/PI(9L)/C20/Pb and Au/PI(9L)/ODA/Pb junctions. That is, for example, the 160 mV peak originating from –COOH element of C20 and the 420 mV peak originating from $-NH_2$ element of ODA were disappeared. In the hetero-structured C20/ODA junctions, the energy of vibrational modes originated from –COOH and $-NH_2$ elements of C20 and ODA molecules shifts to the energy of vibrational modes originated from $-COO^-$ (170mV) and $-NH3^+$, because protons transfer between –COOH element in C20 molecules and $-NH_2$ element in ODA molecules[6] if molecular junction

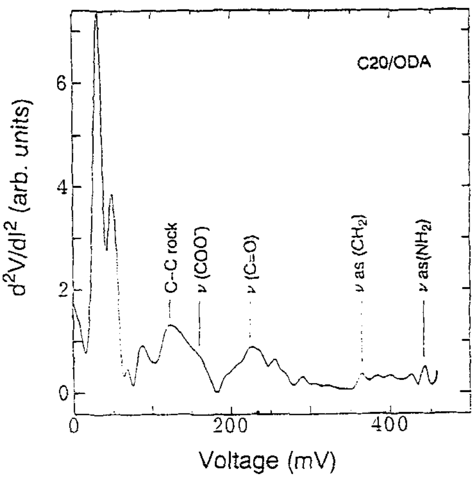

FIGURE 6
IET spectra of the Au/PI/C20/ODA/Pb junctions at a temperature of 4.2K.

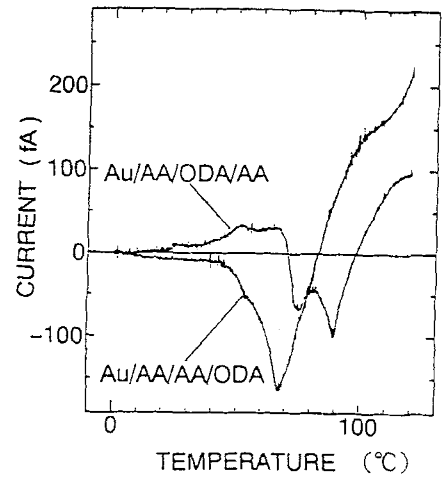

FIGURE 7
Thermally stimulated displacement current spectra of Au/C20/C20/ODA/ air gap/Au and Au/C20/ODA/C20/air gap/Au junctions.

is constructed at the interface. In our experiment, chemical shift of the energy of vibrational modes was not clearly seen. However, the IET spectra of monolayer films differed from that of hetero-structured molecular junction. The IET measurement is useful to investigate the electronic phenomena in the molecular junctions.

Figure 7 shows an example of the thermally stimulated displacement current generated from three-layer hetero-structured films with Au/C20/C20/ODA and Au/C20/ODA/C20 structures. The displacement current flows in positive direction at a temperature of about 50 C as shown in the spectra of C20/ODA/C20 structure. In contrast, the displacement current flows in the opposite direction at a temperature of about 50 C in the spectra of C20/C20/ODA structure. The current peaks around 70 C and 90 C maybe assigned to the break-up of C20 and ODA layers caused by heating[5]. The displacement current peaks appearing at a temperature of 50 C correspond to the melting point of C20/ODA and ODA/C20 hetero structures[6]. The displacement current flows in the direction estimated from the orientation of dipole moment established as a result of proton transfer in a single hetero structure. It is possible to determine the direction of the charge transfer by means of thermally stimulated displacement current measurement.

Finally, we conclude that IET and thermally stimulated displacement current measurements are very useful measuring techniques to investigate the electronic phenomena occurring at hetero-structured interface. It is possible to determine the vibrational modes energies of the molecular elements consisting of the molecular junction by means of IETS measurement, whereas it is possible to determine the direction of charge transfer at the interface by means of thermally stimulated displacement current measurement.

4. CONCLUSIONS

We fabricated Au/PI/C20/ODA/Pb junctions using 9-layer PI LB films as a tunnel barrier, and investigated the electron phenomena in the C20/ODA hetero-structured interface by means of I-V, IETS, and thermally stimulated displacement current measurements. It was found that the 9-layer PI LB films which thickness is about 3.6 nm function as a good tunneling barrier. And the IET and thermally stimulated displacement current measurements are very useful to investigate the electronic phenomena at the hetero structured interface.

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