ELECTRON TRANSPORT PROPERTY IN ORGANIC MOLECULAR WIRES

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Nanoarchitectures of organic molecules, particularly organic molecular layers on solid surfaces, are highly attractive in view of the future applications of nanotechnology. It is important both to control their electrical conduction and to evaluate their conduction mechanism. Polydiacetylene (PDA) is one of the candidate materials for conducting molecular wires used in the interconnection of devices, because it is a fully π-conjugated conducting polymer [1]. In the conjugated conducting polymers, the charges generated upon doping or photoexcitation are stored in localized defects, which are solitons, polarons, or bipolarons. They function as charge carriers and their electronic states appear within the band gap. They degenerate upon further doping and promote the formation of a half-filled metallic band consisting of the polaron lattice [2]. However, in an individual polymer backbone, i.e., an isolated polymer wire, the capability and mechanisms of electrical conduction are still controversial.

We evaluated the electrical conduction of PDA thin films in the region under 20 μm using a laboratory-built independently-driven double-tip scanning tunneling microscope (DT-STM) [3]. The 10,12-nonacosadiynoic acid molecule ($CH_3(CH_2)_{15}C{\equiv}CC{\equiv}C(CH_2)_8COOH_3$) was used as a diacetylene compound. The Langmuir-Blodgett method was used for sample preparation. After the three layers of the polydiacetylene thin film was prepared, the resistance was obtained from the current with fixed applied voltage between two tips when the tip-tip distance is changed under 20 μm using the DT-STM [4]. It was indicated that the resistance of the PDA thin films was proportional to tip-tip distances, suggesting one-dimensional conduction along the PDA backbones. The conductivity of the PDA thin film was estimated to be 4×10^{-6} S/cm, which was 5 orders of magnitude higher than that in the previous report. Moreover, we measured the conductivity of the intentionally iodine-doped PDA thin films using the DT-STM. The obtained results showed that one-dimensional conduction was maintained after iodine doping and a significant increase of the conductivity (3×10^{-3} S/cm) was observed [5]. These results strongly suggested that the intrinsic conductivity of PDA thin films could be observed because the tip-tip distance was sufficiently small for detecting the conductivity of highly ordered regions without domain boundaries.

We have also succeeded in controlling the fabrication of a linear PDA wire using a scanning tunneling microscope (STM) probe tip on a self-assembled monomolecular layer (Fig.1) and evaluated its electronic structure [6,7]. Spectroscopic results of the individual polydiacetylene nanowire revealed the theoretically predicted π-band and band edge singularities, which are characteristics of the one-dimensional π-conjugated polymer. Furthermore, under a high electric field applied on the polymer wire, the spectrum perceives a narrow band gap due to the polaron injection [7]. When much further high field was applied on the wire (> 4.5 V/nm), we observed that an avalanche current flow arised abruptly (Fig.2) [8]. This large current flow in the STM system means a sudden decease of the resistance betwen tip and substrate. We consider that such large current flow is originated from an

electrical property of the polymer wire, which was generated by dynamic modulation of polaron/bipolaron injections. The high density of polaron injection into polymer wires might modulate the wire electronic property into high conductivity like transition to a metallic phase.

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Figures:

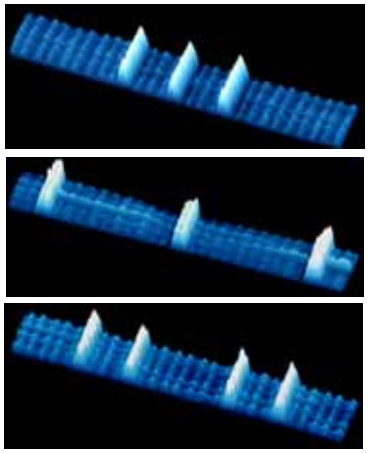

Figure 1. STM images of PDA molecular arrays fabricated with different intervals.

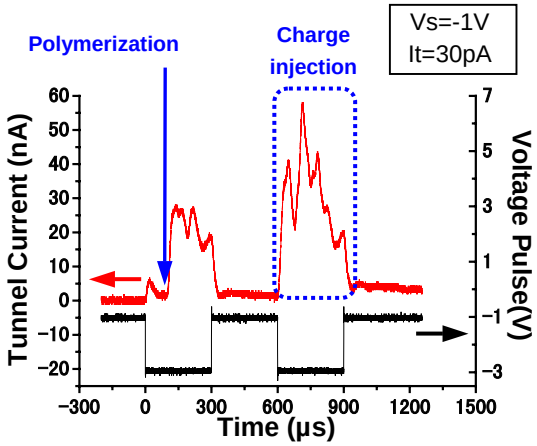

Figure 2. Large current flows by applying high voltage pulses