EVALUATION OF ELECTRICAL CONDUCTION OF POLYDIACETYLENE THIN FILMS BY DOUBLE-TIP STM

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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 to both control their electrical conduction and 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] that overcomes the size constraint imposed by silicon-based technology. Recently, we have succeeded in controlling the fabrication of a linear PDA wire using a scanning tunneling microscope (STM) probe tip on a self-assembled monomolecular layer [2,3]. To control the conductivity of organic polymers, impurity doping is commonly used and it causes a metal-nonmetal transition when the conductivity of these polymers markedly increases [4]. For example, iodine will remove an electron from the PDA backbone. The hole so generated is trapped in the PDA backbone to be a cation radical, that is, a polaron, which contributes to charge transfer along the backbone as a charge carrier. In this study, we measured the conductivity of PDA thin films before and after the iodine doping by laboratory-built double-tip STM (DT-STM) [5] and evaluated the effect of doping by atomic force microscopy (AFM) and visible light absorption spectroscopy (VAS).

We used filtered 10,12-Nonacosadiynoic acid (CH_3-$(CH_2)_{15}$-C≡C-C≡C-$(CH_2)_8$-COOH: MW = 430.71) as a diacetylene compound. 10,12-Nonacosadiynoic acid thin films were prepared by the conventional LB method [6]. The films were transferred to a freshly cleaved mica substrate or a water-cleaned glass substrate by the lifting method to form three layers on the substrate. The films were then irradiated with UV light (dominant wavelengths of 194 nm and 256 nm, 12.7 mW/cm^2). In the iodine doping process, the PDA thin films obtained were enclosed in a glass with iodine vapor for 2 hours. The absolute amount of iodine doped in the films was determined by chemical analysis and laser ablation analysis.

The results of VAS indicated that the blue and red phase emerged depending on the duration of UV light irradiation. AFM images of two phases showed island structures, but in the blue-phase films, rather large islands with small roughness were observed. On the other hand, in the red-phase films, we found many cracks inside the islands and the surface was not smooth. The DT-STM measurement was carried out for the blue-phase PDA film. Figure 1 shows a CCD image obtained during the conductivity measurement of PDA thin films with the Pt/Ir tips. Resistance was obtained from current at a fixed applied voltage of 1 V between the two tips when the tip-tip distance was changed less than 20μm. Figure 2 shows the variation of the resistances of the blue-phase PDA thin films depending on the tip-tip distance. Before UV irradiation, the observed currents were below the detection limit of about 0.1 pA (>8000 GΩ, shown as a dotted line in Fig. 2) for all tip-tip distances and no I-V dependence was found. In the case of blue-phase PDA thin films, it was found that the resistance was

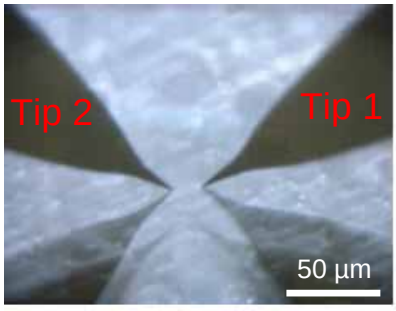

Figure 1: CCD image obtained during the conductivity measurement of PDA thin films with the Pt/Ir tips.

proportional to the tip-tip distance, as shown in Fig. 2. The relationship of resistance vs. distance between two point electrodes differs with the dimensions of the objects; that is, when the conduction between the two point contacts has two- and one-dimensional characteristics, the resistance vs. distance obeys logarithmic and linear functions, respectively. The linear characteristics of the resistance obtained for the PDA thin films indicated one-dimensional conduction along the PDA backbone.

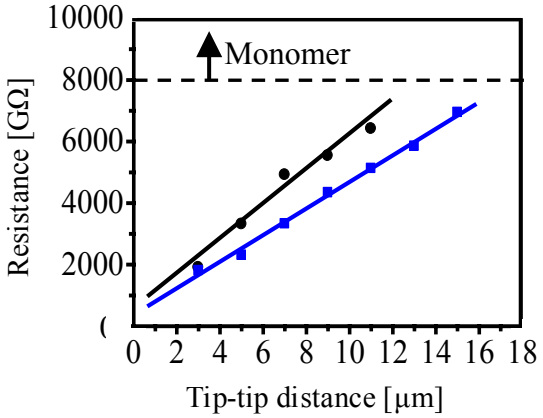

Figure 2: Variation of resistance of blue-phase PDA thin films (before iodine doping) depending on tip-tip distance.

The conductivity of the PDA thin films can be estimated from $\sigma = L / (R \cdot S)$, where L, R and S are the tip-tip distance, resistance and cross-sectional area of the contact area, respectively. The conductivity of the PDA thin films was estimated to be about (3-5) x 10^{-6} S/cm in our experiments. It is surprising that this value of the conductivity of PDA thin film is about 5 orders of magnitude higher than that in the previous report [8] and is almost the same as that of nondoped polyacetylene [4,8]. It is strongly suggested that the conductivity in this work reflects the intrinsic conductivity of pristine PDA thin films because the tip-tip distance is small enough to detect the conductivity of the highly oriented PDA thin films without domain boundaries.

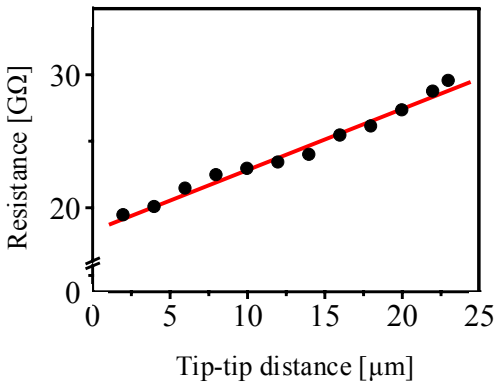

Figure 3: Variation of resistance of iodine-doped PDA thin films depending on tip-tip distance.

Figure 3 shows the variation of the resistance for the iodine-doped PDA thin film depending on the tip-tip distance. The obtained resistance between the two tips was proportional to tip-tip distance. This linear relationship between resistance and tip-tip distance for the iodine-doped PDA thin films is the same as that for the nondoped PDA thin films. This indicates that one-dimensional conduction is maintained after iodine doping. The conductivity of the iodine-doped PDA thin film was estimated using same equation as nondoped PDA thin films. The estimated conductivity of iodine-doped PDA thin film was about 3 x 10^{-3} S/cm, which was three orders of magnitude higher than that of the nondoped PDA thin films. The mobility of iodine-doped PDA could be estimated to be approximately 1.7 x 10^{-5} $cm^2/V \cdot s$, which is relatively high compared with those of other conductive polymers.

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