

Electronic Structure of a Polydiacetylene Nanowire Fabricated on Highly Ordered Pyrolytic Graphite

M. Akai-Kasaya,^{1,2} K. Shimizu,¹ Y. Watanabe,¹ A. Saito,^{1,4} M. Aono,^{1,3} and Y. Kuwahara^{1,4}

¹*Department of Precision Science & Technology, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan*

²*SORST, Japan Science and Technology Corporation (JST), Kawaguchi, Saitama 332-0112, Japan*

³*Nanomaterials Laboratories, National Institute for Materials Science (NIMS), 3-13 Sakura, Tsukuba, Ibaraki 305-0003, Japan*

⁴*Harima Institute, The Institute of Physical and Chemical Research (RIKEN), 1-1-1 Kouto, Mikazuki, Hyogo 679-5148, Japan*

(Received 22 April 2003; published 17 December 2003)

A molecular wire candidate, the polydiacetylene chain, fabricated in a substantial support layer of monomers self-assembled on a highly ordered pyrolytic graphite surface, was studied using scanning tunneling microscopy and spectroscopy. The density of states of individual polymers and constituent monomers were observed on the same surface, and then compared with the calculated results. The spectrum delineating the density of states of the polydiacetylene wire clearly reveals the theoretically predicted π -band and band edge singularities of the one-dimensional polymer.

DOI: 10.1103/PhysRevLett.91.255501

PACS numbers: 81.07.Nb, 31.15.Ct, 36.20.Kd, 68.37.Ef

The nanoscale fabrication of organic molecular layers on solid surfaces is an attractive subject with respect to future applications of nanotechnology. The use of organic molecules as molecular switches and wire connections is viewed by many as a possible way of overcoming the size constraints imposed by silicon-based technologies. We have succeeded in controlling the fabrication of linear polydiacetylene (PDA) wire by using a scanning tunneling microscopy (STM) probe tip on a self-assembled monomolecular (SAM) layer [1]. The fabricated PDA wire grows out in a straight line and extends to a submicrometer length on the surface. The fully extended conjugated backbone of the PDA is not only expected to function as an electrically conducting nanowire but is also interesting in terms of exploring physics in one-dimensional (1D) systems.

It is well known that the conjugated conducting polymers, e.g., polyacetylene, achieve extraordinarily high conductivity upon doping. PDA is already known as one of the conjugated conducting polymers [2]. The high conductivity of PDA, which is 8 orders of magnitude higher than that of its pristine crystal, has been attained upon elaborate iodine doping [3]. Furthermore, the values of the carrier mobility of PDA are higher than or comparable to those of the leading conductive polymers [2,4]. 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 band consisting of the polaron lattice [5]. However, in an individual polymer backbone, i.e., an isolated polymer wire, the capability and mechanisms of electrical conduction are still controversial. In this Letter, we report the results of scanning tunneling spectroscopy (STS) of an individual PDA wire. The results could provide a key to

the exploration of the conductivity of our fabricated "nanowire."

Diacetylene monomers form PDA through additive polymerization under ultraviolet (UV) light irradiation or thermal treatment, as described by $n(RC\equiv C-C\equiv CR') \rightarrow (=RC-C\equiv C-CR'=)_n$, where $C\equiv C-C\equiv C$ is the diacetylene moiety and R and R' are the substituents [6]. In this work, we employ 10,12-nonacosadiynoic acid, whose R and R' are $-[CH_3(CH_2)_{11}]$ and $-[(CH_2)_8COOH]$. The molecules, which were purchased from Tokyo Kasei Co. Ltd., were filtered and deposited onto a freshly cleaved highly ordered pyrolytic graphite (HOPG) substrate by means of the Langmuir-Blodgett method. The STS measurements were performed in both air and under ultrahigh-vacuum (UHV) conditions at room temperature. A tunneling current-voltage (I - V) curve was acquired at a point within the disabled feedback loop. The conductance spectra, dI/dV , were numerically differentiated from I - V or obtained using a lock-in technique which was capable of detecting small signal changes.

The PDA wires [Fig. 1(II)] were fabricated by applying a voltage pulse. The voltage pulse initiates additive polymerization, which proceeds instantaneously to both sides of the monomer array. The fabricated wires were retained between the monomer arrays. The STS spectra were acquired on the areas of (A) PDA wire, (B) diacetylene moiety, and (C) alkyl chain, as shown in Fig. 1. In spectrum (A), a dominant peak was observed at around $V_s = -0.5$ V. On the monomer, the difference between (B) and (C) was barely detected using the lock-in technique. Spectra (B) and (C) showed a minute disruption at around $V_s = -1.5$ V and a smooth curve without any peaks, respectively. However, all spectra shown in Fig. 1 had to be averaged from ten or more spectra, which were very noisy and diverse. On the molecular adsorbed surface, a serious problem for STS measurements arose in

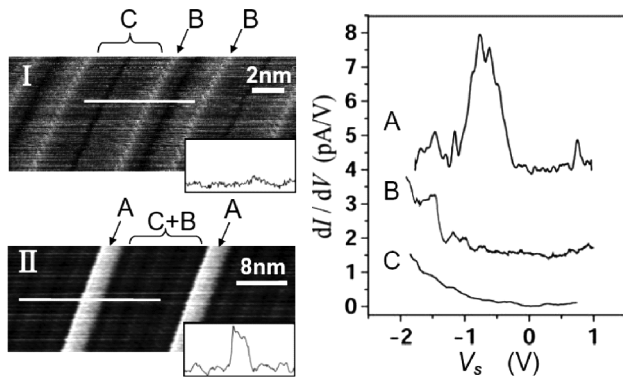


FIG. 1. Topographic STM images of (I) diacetylene SAM surface and (II) fabricated PDA wires in the SAM, taken in air with $V_s = -1$ V, $I_t = 40$ pA. The sections of white lines are shown at the same vertical scale of 0.4 nm. The dI/dV spectra were acquired for the regions (A)–(C) indicated in the images. Spectra (B) and (C) were obtained using a lock-in amplifier with bias modulation ($f = 4$ kHz, $V_{ac} = 10$ mV), and their vertical intensities have been conformed to those of I - V derivatives and multiplied by a factor of 0.5. Curves (A) and (B) are offset vertically by 4 and 1.5 (pA/V), respectively.

terms of the incidental collapse of the SAM structure. A small current, e.g., 30 pA or less, during the STS measurements was able to prevent a large collapse, but it yielded noisy current curves with a very low S/N ratio.

In the next step, we obtained many individual STS spectra on the UV-irradiated surface permitting sufficient current flow. The UV light promotes the polymerization at random and thus generates PDA wires of various lengths, as shown in Fig. 2(I)–(II). The STS measurements were performed for several specimens, which were irradiated with 253 nm UV light for 0–100 min, in UHV with a high tunneling current setting, e.g., $V_s = -1$ V, $I_t = 0.5$ –1 nA. Under these conditions, the SAM structure was hardly observed by STM. Then a few hundred STS spectra were arbitrarily obtained over a large area on each specimen. The I - V curve and dI/dV spectrum derived from the lock-in amp are acquired simultaneously. Each spectrum was obtained within only one voltage sweep, and examined without any averaging procedures. We assume that a large number of STS current stimulations must destroy the molecular arrangement on the surface. Indeed, accidental prominent noisy peaks and abrupt jumps were frequently seen in the spectra with rates of approximately 40%–60% for each specimen. Such inferior spectra were eliminated in advance. The remaining spectra could be classified into three kinds of characteristic spectra. Figure 2 shows typical dI/dV spectra. The categorizing criteria were simple: (a) a large peak emerging at approximately $V_s = -0.5$ V, (b) a peak at $V_s = -1.5$ V, and (c) no peak. On the sample that was UV-irradiated for 60 min, the population rates of the spectrum types of (a), (b), and (c) were 22%, 30%, and

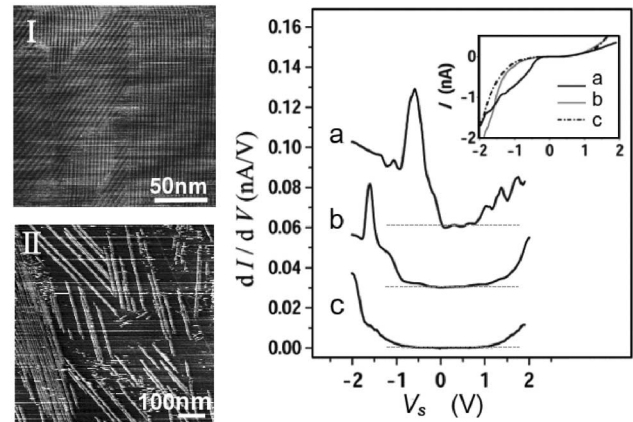


FIG. 2. Topographic STM images of diacetylene SAM, (I) before and (II) after UV irradiation for 10 min, taken in air with $V_s = -1$ V and $I_t = 40$ pA. The dI/dV spectra (a), (b), and (c) were acquired on the UV-irradiated sample using a lock-in amplifier with bias modulation ($f = 4$ kHz, $V_{ac} = 50$ mV), and the I - V curves are shown in the inset. The vertical intensities of dI/dV have been conformed to those of I - V derivatives. (a) and (b) are offset by 0.03 and 0.06 (nA/V), respectively, and (b) and (c) are multiplied by a factor of 0.5 vertically.

15%, respectively. In the residual 33% spectra, no concrete characteristic feature was ascertained. On the non-UV-irradiated specimen, only (b) and (c) spectra were acquired, with the populations of 52% and 28%, respectively. The population of the (a)-type spectrum depended on the UV irradiation time, although the ratio of (b) to (c) was almost constant. The features of spectra (a), (b), and (c) in Fig. 2 are similar to those of spectra (A), (B), and (C) in Fig. 1, respectively. We consider that the individual tunneling spectra of (a), (b), and (c), which were obtained on the UV-irradiated surface, have been identified to be those of the PDA wire, the diacetylene moiety, and the alkyl chain, respectively.

Next, the molecular orbital (MO) of the monomer and oligomeric PDA with R and R' , which were treated in our experiments, were calculated by the semiempirical Austin Model 1 method [7]. Figure 3 shows the calculated MO of the monomer and oligomers. All MOs in the energy range from -11 to 1 eV are π orbitals. In the monomer, the π orbital localizes at the diacetylene moiety. In all of the oligomers, the respective π orbitals delocalize over the PDA backbone. It is clear that the full π conjugation proceeds along the oligomer backbone upon increasing the number of polymer units. The decrease of the highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO-LUMO) gap upon increasing the number of polymer units agrees with the 1D electron gas Kuhn model [8]. This agreement suggests that the frontier orbitals at infinite length converge to within 0.01 eV from the HOMO-LUMO gap of the 18-oligomer PDA (PDA18-mer). At the frontier orbitals, the

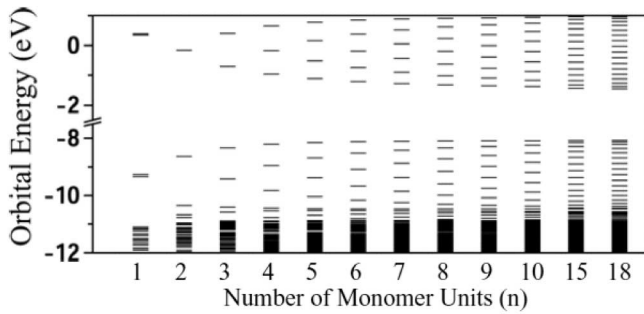


FIG. 3. Calculated MO of (1) 10,12-nonacosadiynoic acid and (2–18) oligomeric PDA. The molecular backbone length of the PDA18-mer ($n = 18$) is approximately 9 nm.

intervals between the MO levels become narrower, which is analogous to the singularities at the π -band edge [9]. We assume that the PDA18-mer has sufficient molecular length to represent the electric structure of the PDA wire. In order to compare the calculated results and STS spectra, the energy axis of the calculated MO is shifted to match the ionization energy (-5.1 eV [10]) and the band gap inferred from the optical absorption edge, E_a (680 nm [11]), of the PDA. In this way, the calculated density of states (DOS) of the monomer and PDA18-mer are deformed as shown in Fig. 4(II), where a Gaussian distribution with $\sigma = 0.2$ eV was applied to the respective MOs. The MOs are shown in the energy range of ± 2 eV centered on the Fermi energy (E_F) of a HOPG, -4.8 eV [12].

Figure 4 shows the normalized conductance spectra, $(V/I)dI/dV$, which were numerically derived from respective I - V curves [13]. Spectrum (A) was taken on the STM image of the PDA wire, and spectra (a1), (a2), (b), and (c) were obtained on the UV-irradiated surface. The $(V/I)dI/dV$ of (A) and (a1) show an analogous semiconducting gap and sharp peaks at $V_s = -0.5$ and 0.8 V. We consider that they are essentially identical spectra delineating a DOS of the linear PDA wire adsorbed on a HOPG surface. The difference between them is considered to be due to the low S/N ratio of (A). Particularly in (a1), the zero DOS gap, sharp peaks, and entailing gentle ramps appear to resemble the calculated DOS shape of the PDA. The sharp peaks are suggestive of the theoretically predicted singularities at the π -band edges in the conjugated 1D polymer system.

The $(V/I)dI/dV$ of (b) and (c) indicate a metallic nature with the finite DOS at $V_s = 0$, and they are similar to each other, with the exception of a small peak at $V_s = -1.5$ V in (b). On the basis of the calculation results for the monomer in Fig. 4(II), it is considered that only the occupied π orbital localized at the diacetylene moiety participates in the STS energy range. The tunneling spectrum results from the tunneling current passing through the molecule to the substrate. Then, on the diacetylene moiety, the occupied π orbital and HOPG DOS should

combine as in spectrum (b), and only the influence of the HOPG metallic nature should remain in spectrum (c). On the other hand, $(V/I)dI/dV$ of (a1) shows an obvious semiconducting gap. The reason for this difference is considered to be the tip-to-HOPG distance on the PDA, which is significantly greater than that on the monomer, as evident in Fig. 1.

The $(V/I)dI/dV$ spectrum of (a2) shown in Fig. 4 was derived from an (a)-type I/V spectrum. The spectra accounts for roughly 70% of the (a) type, which were labeled as (a2), showed a narrower gap than that of (a1). Spectra (a1) and (a2) were distinguished by their slight difference within the gap, though they have been categorized in an (a) type. The gap width scatterings of original I/V curves are shown in Fig. 4(I). The $(V/I)dI/dV$ spectra of (a1) show the peak-to-peak gap E_{p1} of 1.3 ± 0.1 eV and zero gap E_{g1} of 0.5 ± 0.05 eV. The $(V/I)dI/dV$ spectra of (a2) show E_{p2} of 0.8 ± 0.2 eV and small E_{g2} . It is interesting that the (a2) spectra have not been observed from the imaged PDA wire. On the UV-irradiated surface, the linearity of PDA wires has not been verified because we did not obtain the STM image coincidentally with the STS measurement. However, it is considered that the energy gap narrowing seen in (a2) is not due to the structural change of the polymer backbone. It is well known that the straight PDA with an acetylenic structure is known as the “blue phase,” and, hence, the disordered “red phase” shows a blueshifted E_a due to the disruptions of conjugate length [14]. A butatrienic structure showing a redshifted E_a has been reported [15], although the gap narrowing of this phase is due to the shorter unit length, which is rigidly restricted by the substituent lattice.

In our case, one possible reason for gap narrowing of the PDA wire is the adsorption effect entailing an electron transfer between the polymer and substrate. For the PDA wire fabricated in a SAM structure, we propose a model in which the PDA backbone is raised from the surface [16]. It is reasonable to assume that the PDA wire, which was measured as (a2) on the UV-irradiated surface, was not raised and interacted strongly with the surface. For corroborating evidence of the electron transfer, $(V/I)dI/dV$ of (a2) shows not only the gap narrowing but also finite $\rho(E_F)$. E_F alignment in the system of the semiconducting adsorbate on a metallic surface has been observed [17]. In the 1D π conjugated polymer, when a charge is added to or taken from a chain, minimal structural deformation should take place in the polymer backbone for energy relaxation. It is highly likely that these topological changes cause the formation of polaronic states within the parent band gap. The charge transfer process bears a close resemblance to the chemical doping process onto the polymer backbone.

As another possibility, it is considered that $(V/I)dI/dV$ of (a2) delineates not the DOS but the energy dependence of charge-carrier injections. The measurement of threshold energies for charge-carrier (polaron) injections into

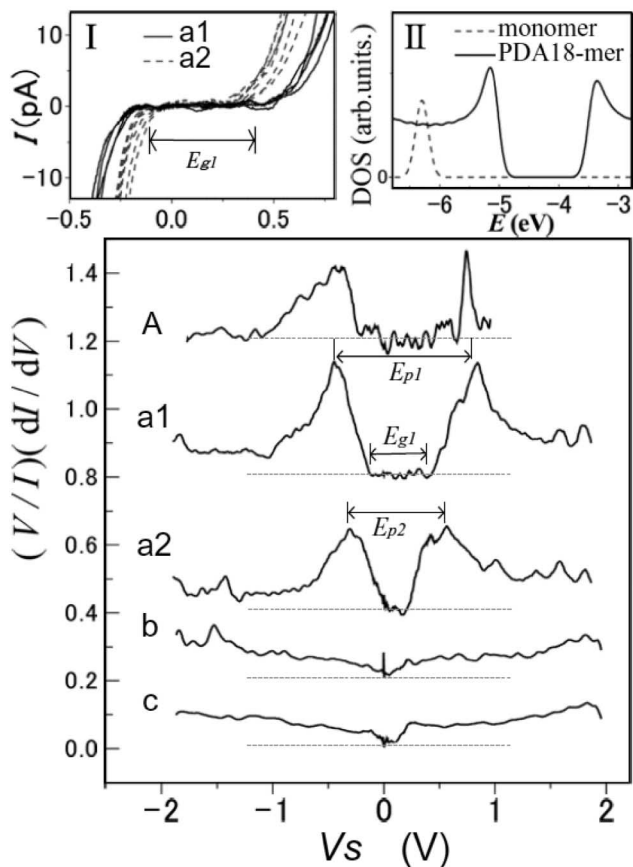


FIG. 4. Normalized conductance of (A) and (a1), (a2) PDA wire, (b) diacetylene moiety, and (c) alkyl chain. (A) was acquired on the imaged PDA wire, and (a1), (a2), (b), and (c) were acquired on a UV-irradiated sample. The vertical axis of $(V/I)dI/dV$ was calculated in (nA, V). (b) and (c) are multiplied by a factor of 0.2, (b) is offset by 0.2, and (A) and (a1), (a2) are offset by multiples of 0.4 vertically. (I) The original I - V curves of (a1) and (a2) focused on the energy range of E_{g1} . (II) The calculated DOS for monomer and PDA18-mer.

the polymer, so-called single-particle gap, E_{gsp} , by using STM was reported by Alvarado *et al.* [18]. The spectra (a2) have been observed only during large tunneling current flow. It is likely that such charge-carrier injections take place only when the tip-polymer distance is sufficiently small due to the strong field intensity at the polymer [19]. The values of E_{gsp} for organic materials used in light emitting devices are larger than E_a , whereas the smaller value of E_{gsp} has been exceptionally measured for CuPc [20]. The development of carrier injections within the forbidden gap of molecule, i.e., E_a , is still unclear. Here, for the conductive polymers, the charge-carrier generation mechanism by dopant material is simply charge addition or extraction. We consider that, for the organic materials, which have high conductivity and high carrier mobility, e.g., the conjugated conductive polymers and CuPc, the slight charge transfer from or to the STM

tip can create the polaronic state within the gap. While this theory is somewhat controversial, it must be given serious consideration. Either way, the narrow gap state is a very fascinating finding in terms of exploring the charge transfer system of an isolated conjugated polymer wire.

In conclusion, we have identified the tunneling spectra for the PDA wire and the diacetylene monomer adsorbed on a HOPG surface. The spectrum of the polymer wire represents very clearly the π -band and band edge singularities expected in the 1D conjugated polymer system. We have also observed a fascinating spectrum with a narrow gap, which is suggested to be due to the existence of charge-carrying polaron states on the polydiacetylene molecular wire.

- [1] Y. Okawa and M. Aono, *Nature (London)* **409**, 683 (2001).
- [2] *Handbook of Organic Conductive Molecules and Polymers*, edited by H.S. Nalwa (John Wiley, New York, 1998).
- [3] M. Sakamoto *et al.*, *J. Appl. Phys.* **60**, 2788 (1986).
- [4] R.J.O.M. Hoofman *et al.*, *J. Chem. Phys.* **109**, 1885 (1998).
- [5] S. Kivelson and A.J. Heeger, *Phys. Rev. Lett.* **55**, 308 (1985); S. Stafstrom and J.L. Brédas, *Phys. Rev. B* **38**, 4180 (1988).
- [6] D. Bloor and R. R. Chance, *Polydiacetylenes*, NATO ASI, Ser. E, Vol. 102 (M. Nijhoff, Dordrecht, 1985).
- [7] M.J.S. Dewar, E.G. Zoebisch, E.F. Healy, and J.J.P. Stewart, *J. Am. Chem. Soc.* **107**, 3902 (1985).
- [8] G.J. Exarhos, W.M. Risen, Jr., and R.H. Baughman, *J. Am. Chem. Soc.* **98**, 481 (1976).
- [9] J.L. Brédas, R. R. Chance, R. Silbey, G. Nicolas, and Ph. Durand, *J. Chem. Phys.* **75**, 255 (1981).
- [10] K. Seki *et al.*, *Thin Solid Films* **179**, 15 (1989).
- [11] Y. Lu *et al.*, *Nature (London)* **410**, 913 (2001).
- [12] M. Shiraishi and M. Ata, *Carbon* **39**, 1913 (2001).
- [13] In the numerical derivation of $(V/I)dI/dV$, the semi-conducting spectra (A), (a1), and (a2) were compensated according to a procedure described by M. Prietsch, A. Samsavar, and R. Ludeke, *Phys. Rev. B* **43**, 11850 (1991). An adequate small constant c has been added to V/I to prevent divergent noise within the gap.
- [14] A. Saito, Y. Urai, and K. Itoh, *Langmuir* **12**, 3938 (1996).
- [15] K. Kuriyama, H. Kikuchi, and T. Kajiyama, *Langmuir* **12**, 6468 (1996).
- [16] Y. Okawa and M. Aono, *J. Chem. Phys.* **115**, 2317 (2001).
- [17] J.W.G. Wildöer, L.C. Venema, A.G. Rinzler, R.E. Smalley, and C. Dekker, *Nature (London)* **391**, 59 (1998).
- [18] S.F. Alvarado, P.F. Seidler, D.G. Lidzey, and D.D.C. Bradley, *Phys. Rev. Lett.* **81**, 1082 (1998).
- [19] M. Kemerink *et al.*, *Phys. Rev. Lett.* **88**, 096803 (2002).
- [20] S.F. Alvarado, L. Rossi, P. Müller, and W. Rieß, *Synth. Met.* **122**, 73 (2001).