Nanowire connection using chain polymerization

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We demonstrate that chain polymerization of molecules can be initiated by stimulating a thin molecular film with a scanning tunneling microscope (STM) tip, so that a conjugated polymer nanowire can be created at designated positions. The demonstration has been presented for a self-ordered monomolecular layer of diacetylene compound adsorbed on a graphite surface. By stimulating the molecular layer with an STM tip at a single point, a linear polydiacetylene molecule of length ranging from 5 to 300 nm was created, the length being controlled by domain boundaries or artificial defects in the molecular layer.

Introduction

The exploration of a novel device concept beyond the silicon-based transistor is one of the most important scientific and technological issues of today. Because of this, various new molecular nanoelectronic devices have recently been proposed.[1–5] However, the interconnection of such devices is often disregarded in spite of its essential importance. Here, we propose a promising new approach to address this issue.

It is known that if a thin molecular film is stimulated by a biased scanning tunneling microscope (STM) tip, a local chemical reaction or reorientation is sometimes induced, as has been demonstrated in several cases.[6–8] Therefore, when the biased STM tip is scanned, continuous modification along the scan is possible. However, we have instead explored the possibility of inducing a nonlocal or extended chain chemical reaction initiated by an STM tip, because the chain polymerization used in this work have many advantages as follows: First, the reaction products are guaranteed to have a perfect structure without any defects. Second, the obtained nanowires are stable at room temperature. Third, the entire process will occur in a short span as a single event, and finally, no additional energy is needed for the propagation of the chain reaction. We have succeeded in realizing this idea using a monomolecular layer of amphiphilic diacetylene compounds, adsorbed on a cleaved face of graphite.[9,10]

Diacetylene compounds with the general formula $\mathrm{R{-}C{\equiv}C{-}C{\equiv}C{-}R'}$, where $\mathrm{C{\equiv}C{-}C{\equiv}C}$ is the diacetylene moiety and R and R' are substituent groups, are known to polymerize by appropriate stimulation in the solid state.[11,12] The polymerization produces polydiacetylene compounds, which are conjugated linear polymers represented by the general formula $+\!\!\!\!\!(\ \mathrm{RC{-}C{\equiv}C{-}CR'}\ )\!\!\!\!\!+_n$. In the present work, we have used 10,12-pentacosadiynoic acid $[\mathrm{CH_3(CH_2)_{11}{-}C{\equiv}C{-}C{\equiv}C{-}(CH_2)_8COOH}]$ and 10,12-nonacosadiynoic acid $[\mathrm{CH_3(CH_2)_{15}{-}C{\equiv}C{-}C{\equiv}C{-}(CH_2)_8COOH}]$, where $(\mathrm{CH_2})_n$'s are alkyl side chains.

Molecular ordering

We deposited the monomer molecule on a freshly cleaved graphite substrate using a quasi Langmuir-Blodgett technique. According to STM observations of thin films of various diacetylene compounds on graphite surfaces,[13–15] a variety of molecular arrangements are formed depending on the method of film preparation, the species of substituent groups, and the incorporation of foreign molecules. In our 10,12-pentacosadiynoic acid monomolecular layer, the molecular arrangement was as follows.

A typical STM image of the layer is shown in Fig. 1(a); all STM images in this study were obtained with an STM

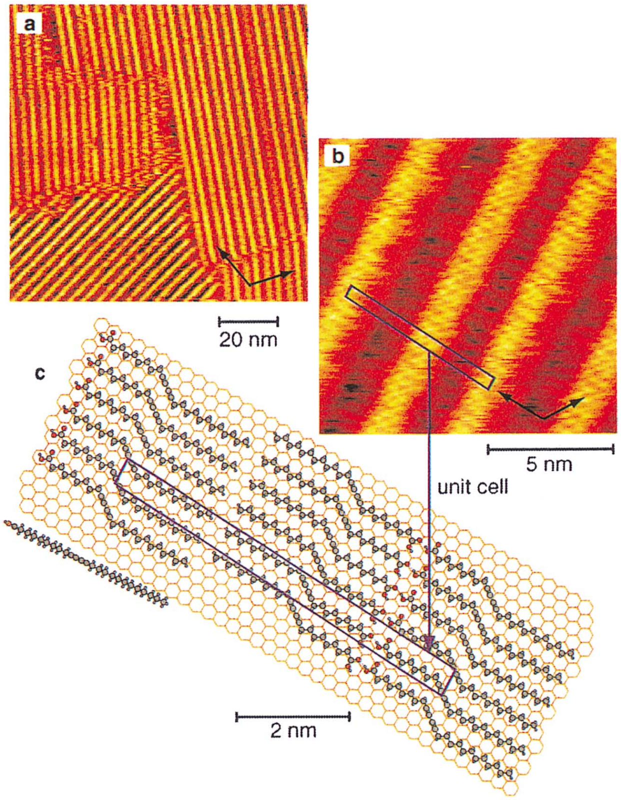

Fig. 1. (a) STM image of 10,12-pentacosadiynoic acid layer on graphite. (b) Magnified STM image of the layer. The arrows in the image indicate the main crystal axes of graphite. (c) Top and side views of a model of the molecular arrangement.

operated in air (Digital Instruments) using a Pt-Ir tip. The image in Fig. 1(a) consists of parallel bright lines separated by two different alternate spacings of about 3.0 and 3.8 nm, indicating that the 10,12-pentacosadiynoic acid molecules on the graphite surface are self-ordered. A magnified STM image of the layer is shown in Fig. 1(b), in which individual molecules are resolved. On the basis of such STM images, we can deduce the molecular arrangement shown in Fig. 1(c), where the molecules are aligned to form straight chains and the chains are arranged in a manner such that the COOH end groups of a chain are opposite those of a neighboring chain.

By comparing the images of the molecular layer with an image of the graphite substrate for the same area observed at an appropriately small sample bias and large tunneling current, it was found that the alkyl side chains of each molecule are oriented parallel to the main crystal axis in the basal plane of graphite, $\langle 1\,\overline{\tfrac{1}{2}}\,\overline{\tfrac{1}{2}}\,0 \rangle$. If we examine STM images such as in Fig. 1(b), a weak modulation of image contrast is observed as a moiré pattern due to the interference between the molecular layer and the graphite substrate. Analysis of the moiré pattern confirms the orientation of the alkyl chains discussed above and indicates that the spacing between neighboring molecules in the molecular layer is 0.47 nm.

Photopolymerization

Before carrying out experiments of STM-induced chain polymerization, we examined whether such chain polymerization could be induced by ultraviolet irradiation in the film described above. For this purpose, the molecular layer was irradiated with ultraviolet light from a low-pressure mercury lamp (254 nm in wavelength and 1.3 mW/cm^2 in power density at the sample position using a band-pass filter).

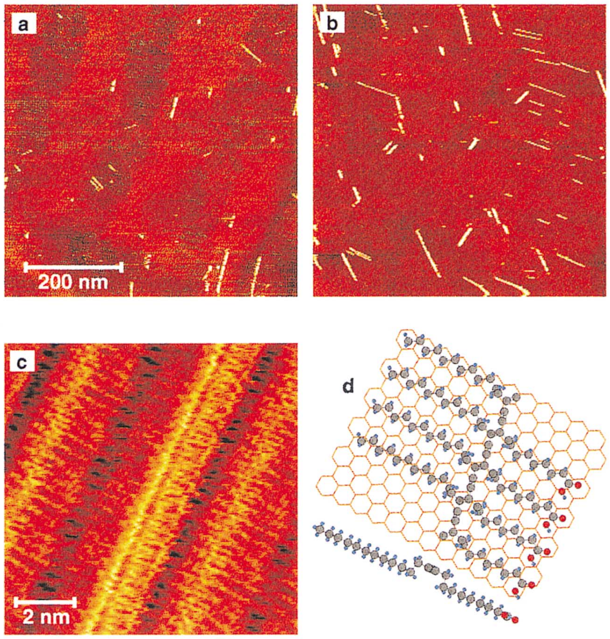

Fig. 2. (a), (b) STM images obtained after ultraviolet irradiation for (a) 10 min.; (b) 20 min. (c) Magnified image of a polymer. (d) Top and side views of the proposed structural model of a polymer.

Figures 2(a) and (b) shows typical STM images of the layer after the ultraviolet irradiation for 10 min. and 20 min., respectively. As can be seen, very bright lines have appeared, and their number density increased with increasing the duration of ultraviolet irradiation. One of the very bright lines is imaged in Fig. 2(c) on a magnified scale. Such images show that the very bright lines appeared in such a manner that part of the bright lines in STM images such as in Figs. 1(a) and (b) become increasingly brighter, particularly along a line corresponding to the linear array of diacetylene moieties. This means that the linear array of diacetylene moieties is partly photopolymerized, resulting in polydiacetylene.

The moiré pattern described above was also observed for the molecular layer after the ultraviolet irradiation, as can be seen in Fig. 2(c). An important point is that the moiré pattern is not modulated around the created polymer. This means that the orientation of the alkyl chains is maintained parallel to $\langle 1\,\overline{\tfrac{1}{2}}\,\overline{\tfrac{1}{2}}\,0 \rangle$ of graphite even after polymerization. This leads us to the following explanation of the structure of the created polymer. If all C–C bonds in the alkyl chains in the polymer have the trans conformation, as in the monomer, all carbon atoms in the polymer should lie on the same plane parallel to the surface of the substrate. If this is the case, under the experimentally observed condition that the polydiacetylene backbone of the created polymer has the same orientation as the linear array of diacetylene moieties of the original monomers, the alkyl chains cannot be parallel to $\langle 1\,\overline{\tfrac{1}{2}}\,\overline{\tfrac{1}{2}}\,0 \rangle$ of graphite, because the C–C bonds connecting the alkyl chains to the polydiacetylene backbone are restricted in direction such that they satisfy the sp^2 (for C on the polydiacetylene side) and sp^3 (for C on the alkyl chain side) bond angles. This is inconsistent with the experimental finding described above.

We therefore propose the structural model shown in Fig. 2(d) for the polymer; the alkyl chains are parallel to $\langle 1\,\overline{\tfrac{1}{2}}\,\overline{\tfrac{1}{2}}\,0 \rangle$ of graphite, but their innermost carbon atoms adjoining the polydiacetylene backbone are raised and therefore the polydiacetylene backbone is also raised. This is an energetically reasonable conformation, since the sp^2 and sp^3 bond angles are fulfilled. Furthermore, this structural model can explain the puzzle as to why the polymer is observed with exceeding brightness in STM images such as that shown in Figs. 2(a) and (b). The polymer simply protrudes geometrically in part of the polydiacetylene backbone by 0.14 nm, assuming that the C–C bond length is maintained to be the typical length of 0.154 nm.

The mechanism of the photopolymerization is considered as follows, on the basis of the case of three-dimensional crystals of diacetylene compounds.[16] At first, the diacetylene moiety of one of the molecules is excited by photoabsorption into a diradical state with an unpaired electron at either end. Then, an addition reaction occurs thermally between the excited diacetylene moiety and a neighboring diacetylene moiety. The created dimer of diacetylene moieties is also in an excited state as a diradical, so that a similar addition reaction occurs on both sides; the repetition of such addition reactions finally results in the extended chain polymerization. We can therefore expect that if the excited diradical state in the first step can be created by stimulation with the STM tip, the extended chain polymerization will follow.

Chain polymerization triggered by an STM tip

Figure 3(a) shows an STM image of the 10,12-pentacosadiynoic acid film observed from the bottom to the top at a sample bias of −1 V, but a large sample bias of 4 V was applied for a short time of 10 μs (which is shorter than the time constant of STM feedback) when the scanning tip passed the point indicated by an arrow, as shown on the left side of the figure. As can be seen, a very bright line appeared starting from the point where the pulsed sample bias was applied. This very bright line is identical with those observed in Figs. 2(a) and (b) in structure. Namely, the stimulation with the STM tip certainly induced the chain polymerization and created a polymer with polydiacetylene as its backbone. The area shown in Fig. 3(a) was imaged again and the result is shown in Fig. 3(b). It is found from this image that chain polymerization occurred on both sides of the point of stimulation. In almost all cases, chain polymerization proceeded on both sides, as in the case of Fig. 3(b). In Fig. 3(b), a structural defect is observed at the point of stimulation, as shown more clearly in the magnified image in Fig. 3(c). However, the formation of such a structural defect is not essential for inducing the chain polymerization. In fact, the probability of appearance of such a structural defect was less than 50% when chain polymerization was induced by a pulsed sample bias of 4 V in height and 10 μs in width.

As seen in the upper-right corner of Figs. 3(a) and (b), the polymers created were usually terminated at domain boundaries. In other words, the chain polymerization initiated by the STM tip propagated in the domain without any additional energy except thermal energy and terminated when it encountered the domain boundary which acted as a kind of structural defect. The length of the polymers formed in this way sometimes reaches approximately 300 nm.

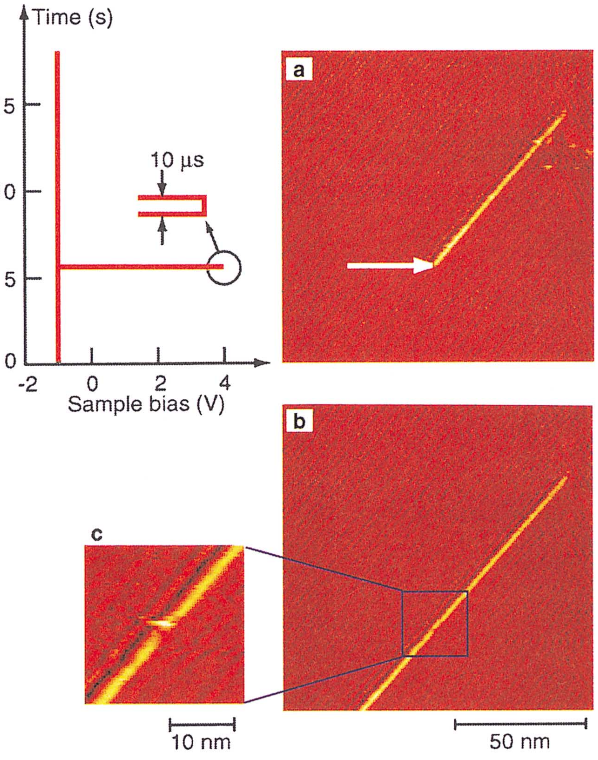

Fig. 3. STM images showing the chain polymerization triggered by an STM tip. (a) STM image of a monomer film observed from the bottom to the top. A large sample bias of +4 V was applied for a short time of 10 μs when the scanning tip passed the point indicated by the arrow. (b) STM image of the same area recorded just after (a). (c) Magnified image of the point of stimulation.

By making an artificial structural defect in advance at a position along the path of propagation of chain polymerization using the STM tip, we can also control the length of created polymers at will. A demonstration was presented for a monomolecular layer of 10,12-nonacosadiynoic acid on a graphite surface,[9] as shown in Fig. 4. First, we created an artificial defect in the form of a 6-nm-wide hole at a predetermined position in the monomolecular layer, as shown in the center of Fig. 4(a), using a previously reported method.[17] After that, a pulsed sample bias (−4 V in height, 5 μs in width) was applied at the point indicated by arrow 1. As is evident in Fig. 4(b), a very bright line appeared, which indicates that chain polymerization started at the point and ended at the artificial defect; see also Figs. 4(e) and (f). Next we stimulated the adjacent molecular array indicated by arrow 2, by applying another pulsed bias. In this case as well, chain polymerization started at the point of stimulation and ended at the artificial defect, as shown in Fig. 4(c). In a similar manner, as shown in Fig. 4(d), we created one more polydiacetylene nanowire by stimulating a molecular array indicated by arrow 3. Figs. 4(a)–(d) show that we can connect at least three nanowires to an object as small as 6 nm; thus we could wire up the three electrodes (source, drain, and gate) of a single-electron transistor, for example, even if it is nanometer sized.

Interestingly, the chain polymerization occurred at both polarities of the pulsed sample bias with the threshold kinetic energy of tunneling electrons of 2.9 ± 0.2 eV. This is close to the energy separation between the $\pi\pi$ ground state and the lowest excited $\pi\pi^*$ triplet state of the diacetylene moiety, 3.1 eV.[18]

Since the polydiacetylene backbone has a conjugated π-electron system and the highest valence and the lowest conduction bands exhibit fairly strong dispersions,[19] the polydiacetylene backbone will be a conductor when excess electrons or holes are supplied to it. In fact, excess electrons created in a polydiacetylene single crystal by light illumination move in response to an electric field with a large drift mobility,[20] and the conductivity of polydiacetylene films considerably increases upon doping with iodine which supplies holes.[21] The polydiacetylene backbone of the polymer created on the graphite substrate in the present study is also expected to be conductive if a charge transfer between the polymer and the graphite substrate exists.

Conclusion

We have succeeded in showing that an extended chain reaction of molecules can be initiated by local stimulation with an STM tip. This method will be useful for fabricating novel molecular nanoelectronic devices comprised of conjugated polymer nanowires and interconnecting them. We also believe that the method will bring about future breakthroughs

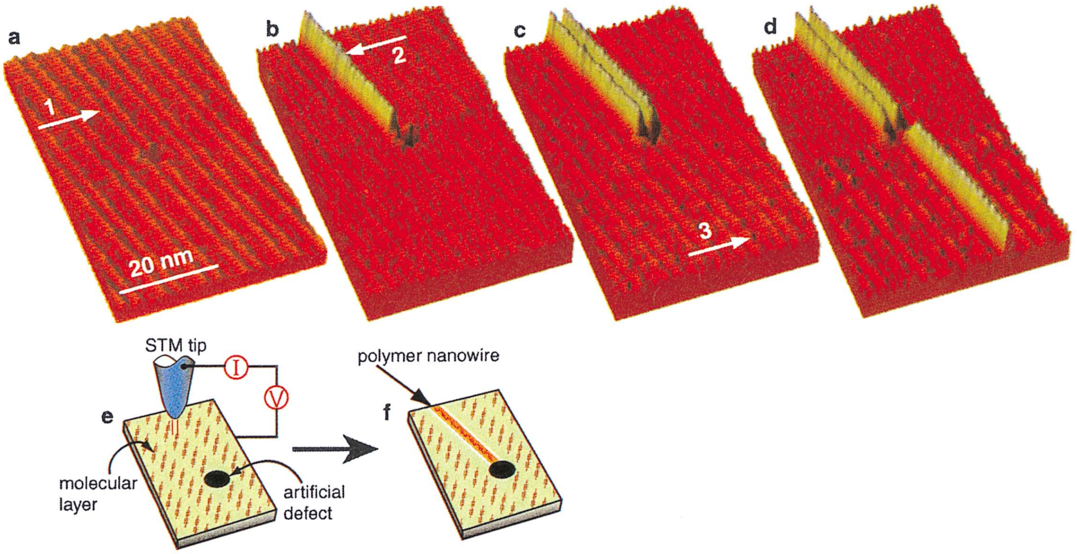

Fig. 4. STM images (a–d) and diagrams (e,f) showing the process of controlling the initiation and termination of linear chain polymerization with an STM tip. (a) STM image of the original monomolecular layer of 10,12-nonacosadiynoic acid, in which an artificial defect has been created in advance using an STM tip. (b) First chain polymerization, initiated at the point indicated by arrow 1 using an STM tip and terminated at the artificial defect. (c) Second polymer nanowire has been created by stimulating a molecular array indicated by arrow 2. (d) Third polymer nanowire has been created by stimulating a molecular array indicated by arrow 3. (e), (f) Diagrams illustrating the initiation of chain polymerization with an STM tip and the termination of the polymerization at the artificial defect.

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