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THE POSSIBILITY OF NANOSCOPIC MOLECULAR ARCHITECTURE WITH NOVEL ELECTRIC FUNCTION

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Abstract The possibility to construct the molecular assembly in a nanoscopic scale and with novel electric functions is discussed based on recent STM (scanning tunneling microscopy) and *in-situ* X-ray diffraction studies on the organic evaporated films. It is suggested that the nanoscopic operation with a STM tip can be utilized to change ethylene structure into acetylene structure, inducing the insulator-conductor transformation and to construct organic superlattice by arranging the molecules at the desired positions. In addition, the nanoscopic manipulation of each polar molecule will become possible by imposing an electric field to the STM tip. Furthermore, the suggestion is made that the molecular assembly with a super structure, which contains uniaxially oriented electric dipoles and exhibit piezo-, pyro- and ferroelectric activities, can be created by fabricating two kinds of non-polar molecular layers.

Keywords: molecular electric device, scanning tunneling microscope, molecular architecture, polar molecule, super structure, superlattice

INTRODUCTION

Recently, organic molecules have drawn many researchers' interest as candidate materials for the electric devices of the next generation. Especially, Carter's proposal[1] on molecular electric devices (MED) inspired one the

possibility to build the organic electric devices in a nanoscopic level and with novel functions, replacing conventional silicon-based inorganic devices. Since then, various ideas on the molecular as well as electric circuit designs have been proposed and considered. However, the issues on how to produce such nano-scale devices and to recognize the electric states on a single molecule have been remained as practical difficulties.

Meantime, the STM developed by G.Binning and H.Rohrer[2] was revealed to have the capability to visualize atoms and molecules in real space under various atmosphere including an air. In addition, it was proven that the STM can be utilized as nanoscopic tools for individual manipulation of atoms and molecules,[3] thus promoting the realization of the "MED" as well as the "nanotechnology".

On the other hand, the substantial progress in the science and technology on the organic molecules have made possible to control the molecular structures in nanoscopic level. Langmuir-Blodgett (LB) method may be one of successful processes to construct such controlled molecular layers. However, it has been recognized that the dry processes such as vacuum-evaporation method is superior to such the wet process as the LB method for building electric devices, because the problems arising from residual water or moisture is essentially eliminated and the high-quality characteristics can be expected for the dry process. Moreover, recent progress promoted by applying molecular beam epitaxy (MBE) technique[4] demonstrated such possibilities, and encouraged the further interesting proposal for MEDs.[5-7]

In this paper, we discuss the possibility to construct the molecular assembly in a nanoscopic scale and with novel electric functions, based on our recent achievements concerning the STM as well as the *in-situ* X-ray diffraction studies on the molecular structures in the ultra-thin films prepared by a vacuum evaporation method.

MOLECULAR MODIFICATION UTILIZING STM PROBE

Insulator-Conductor Transformation and Superlattice

The application of the STM to imaging organic molecules has been of great interest in these years, and succeeded in revealing directly atomic images of molecular arrangements of some simple molecules such as *n*-alkanes[8] and

liquid crystals.[9-12] Although the STM images were reported to be influenced by the STM tip through its electric force acting on the molecules, the attempt to manipulate the organic molecuis themselves has never been succeeded.

Figure 1 shows the STM image of n-paraffin molecule, *n*-tritriacontane (*n*-$C_{33}H_{68}$), prepared by a vacuum evaporation method on the HOPG (highly oriented pyrolytic graphite) substrate, which had been cleaved and baked at 150 °C for 5 hrs to get smooth and clean surfaces.[13] It is obvious that the molecules arranges quite regularly, probably in a mono layer, forming two-dimensional crystal, differing from usual three-dimensional ones. Also, the molecular arrangement and crystal domains are revealed to be affected by the substrate crystal of HOPG, namely by an epitaxial effect.

The fact that the organic molecules can be imaged with the high-resolution of atomic level gives us the expectation of the capability to modify the molecular structure using the STM tip. One of the most significant achievements in electric field will be the drastic transformation from insulator to conductor by the simple molecular reorganization, as schematically shown in Figure 2. When the hydrogen atoms in *n*-

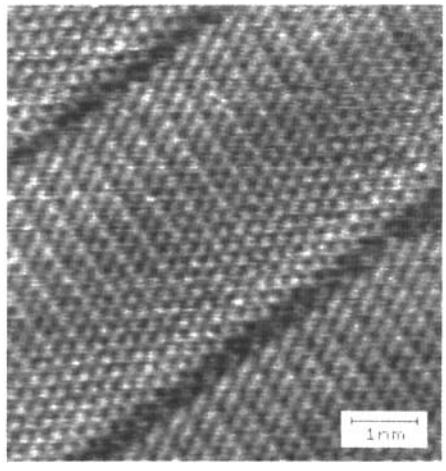

FIGURE 1 STM image of n-paraffin molecule on HOPG substrate. See Color Plate I.

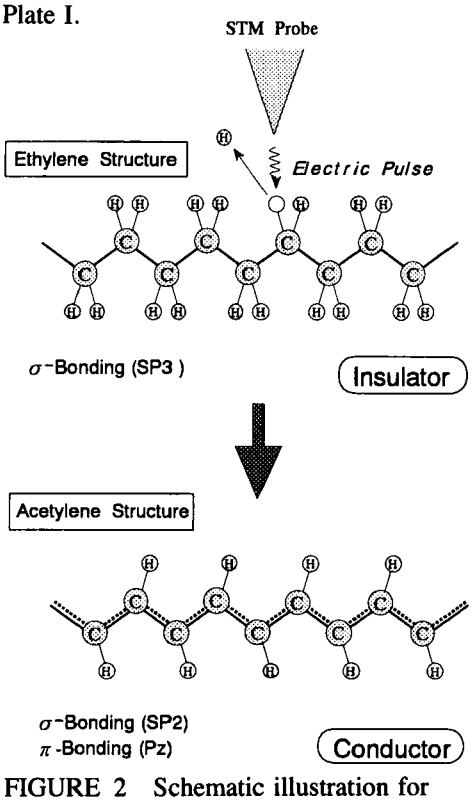

FIGURE 2 Schematic illustration for the removal of hydrogen atoms from ethylene molecules, inducing the insulator-to-conductor transformation, with the application of electric pulses.

paraffin with ethylene structure are removed by the action of electric pulses imposed on the STM tip, the structure changes to acetylene structure. While the ethylene structure composed of σ-bonding (sp^3 orbital) with localized electrons is insulator, the acetylene structure including the π-bonding (p_z orbital) electrons with non-localized characteristics. Therefore, the removal of two hydrogen atoms from each ethylene unit results in the induction of the insulator-to-conductor transformation.

Furthermore, when the acetylene molecules are created regularly at the positions with a suitable separation by the method described above, we can construct the ethylene-acetylene "superlattice". Since the energy structures in these insulator and conductive molecules are quite different, the energy band structure with "quantum well"s may be formed, as shown in Figure 3. If the separation between the wells, that is the width of the array of ethylene molecules is narrow enough, the electrons in the wells can tunnel through the potential barrier upon the application of electric field. Thus, the construction of the superlattice and the control of the lattice constants provides characteristic and artificial energy band structures, by which notable electric functions and various high-quality devices can be expected to be created.

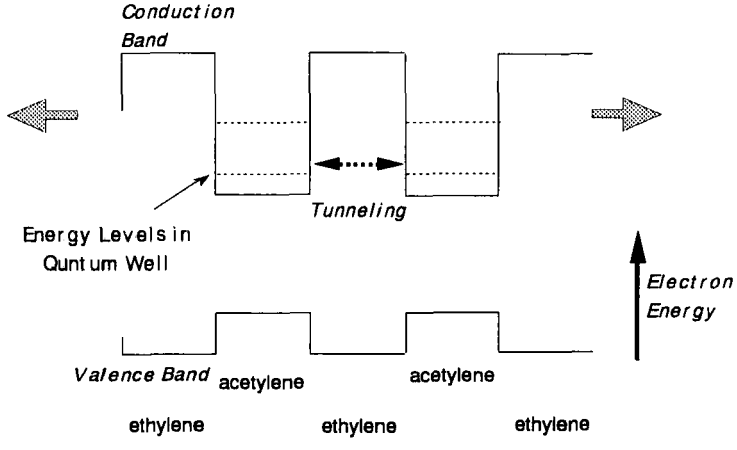

FIGURE 3 The energy band structure with "quantum well"s in the ethylene-acetylene "superlattice".

Tentative Impulse Experiment for Evaporated Paraffin Films

The possibility of the molecular reconstruction was examined by applying the electric pulses with various energies to evaporated *n*-paraffin films. The surface

features of the samples received such electric pulses were examined with the STM to detect the induced changes. When the film was monolayer, any change was admitted for the pulses with relatively small amplitudes, but the molecular arrangement in the two-dimensional paraffin crystals was destroyed for the pulses with high amplitude. This is probably due to the situation that the interaction between the molecules is too strong and larger than that between the molecules and the substrate graphite crystals.

On the other hand, the sample was much thicker, namely double or multi-layers, apparent changes were observed for the STM images, as shown in Figure 4. In this case, the electric pulse of 0.3 μm in width and 2.0 V was superimposed on the STM probe with the vias voltage of 0.5 V. In this image, the rise of molecules was detected at the places where the pulses were applied. Figure 5 shows the cross-sectional profiles for the heap regions of a, b and c in Figure 4, revealing that the rise of molecules ranges about 0.6 nm in diameter and 0.2 nm in height. This fact suggests that the application of electric field causes the distortion of samples in molecular level. Although the present tentative experiments did not demonstrate the atomic reconstruction and further detailed

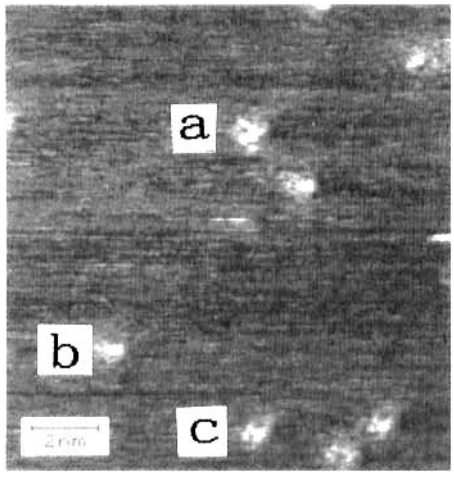

FIGURE 4 STM image of evaporated paraffin film observed after the application of electric pulses. See Color Plate II.

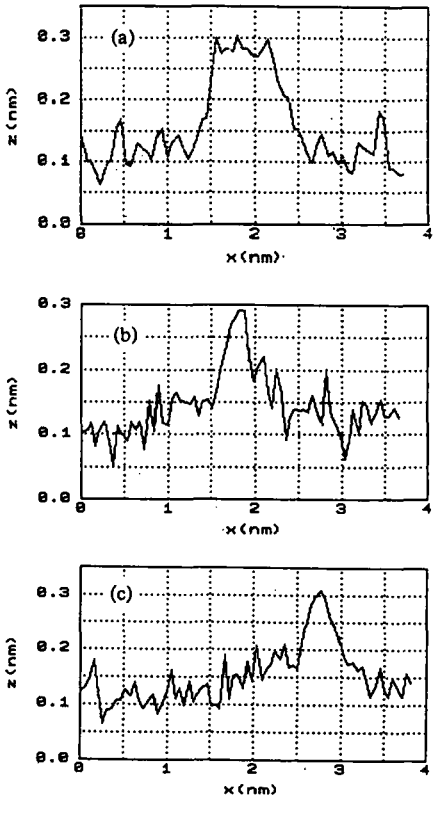

FIGURE 5 Cross-sectional profiles for the heap regions of a, b and c in Fig. 4.

trials are certainly necessary to conduct, it became conceivable that the nanoscopic modification to organic molecules can be performed by these methods.

Molecular Manipulation for Polar Molecules

Among the organic molecules, polar molecules especially attract our interest because various electric functions such as piezo-, pyro- and ferroelectricities can be expected for these substances. These polar molecules form liquid crystalline phases and their STM images have been observed several research groups.[9-12]

We conducted the STM observation for a new type of liquid crystalline molecule, 5-(p-dodecyloxyphenyl)pyrazine-2-carbonitrile (DOPPC), which has large dipole moments along the molecular axis and was adsorbed on HOPG.[14] Figures 6 and 7 show one of the STM images obtained, revealing a novel interdigitated double-rows structure, and the molecular arrangement simulated based on electrostatic multipole-multipole interaction. The image as well as the fine agreement of the simulated images suggest the important role of the electric interaction upon the molecular arrangement in this polar molecule.

If the STM tip can be employed to manipulate such the polar molecules by utilizing the electric interaction, several possibilities exist, as illustrated in Figure 8. The action of the

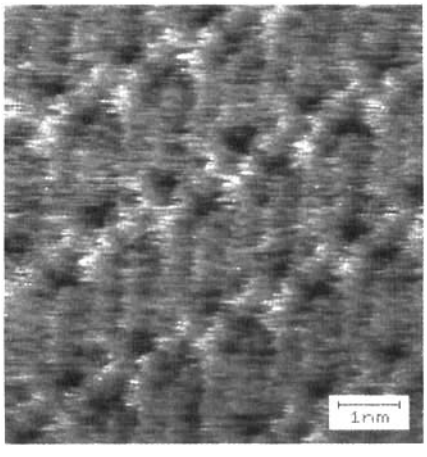

FIGURE 6 STM image of DOPPC molecules evaporated on HOPG. See Color Plate III.

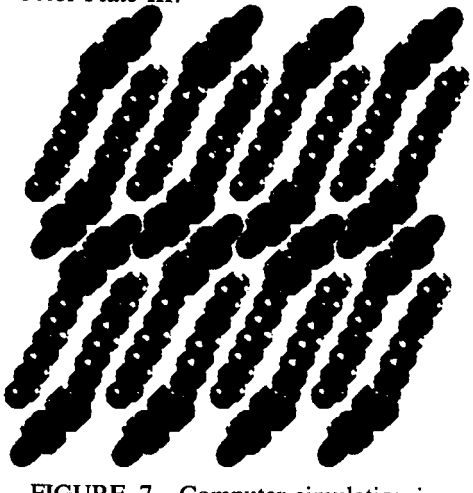

FIGURE 7 Computer simulation image for DOPPC molecular arrangement shown in Fig. 5. See Color Plate IV.

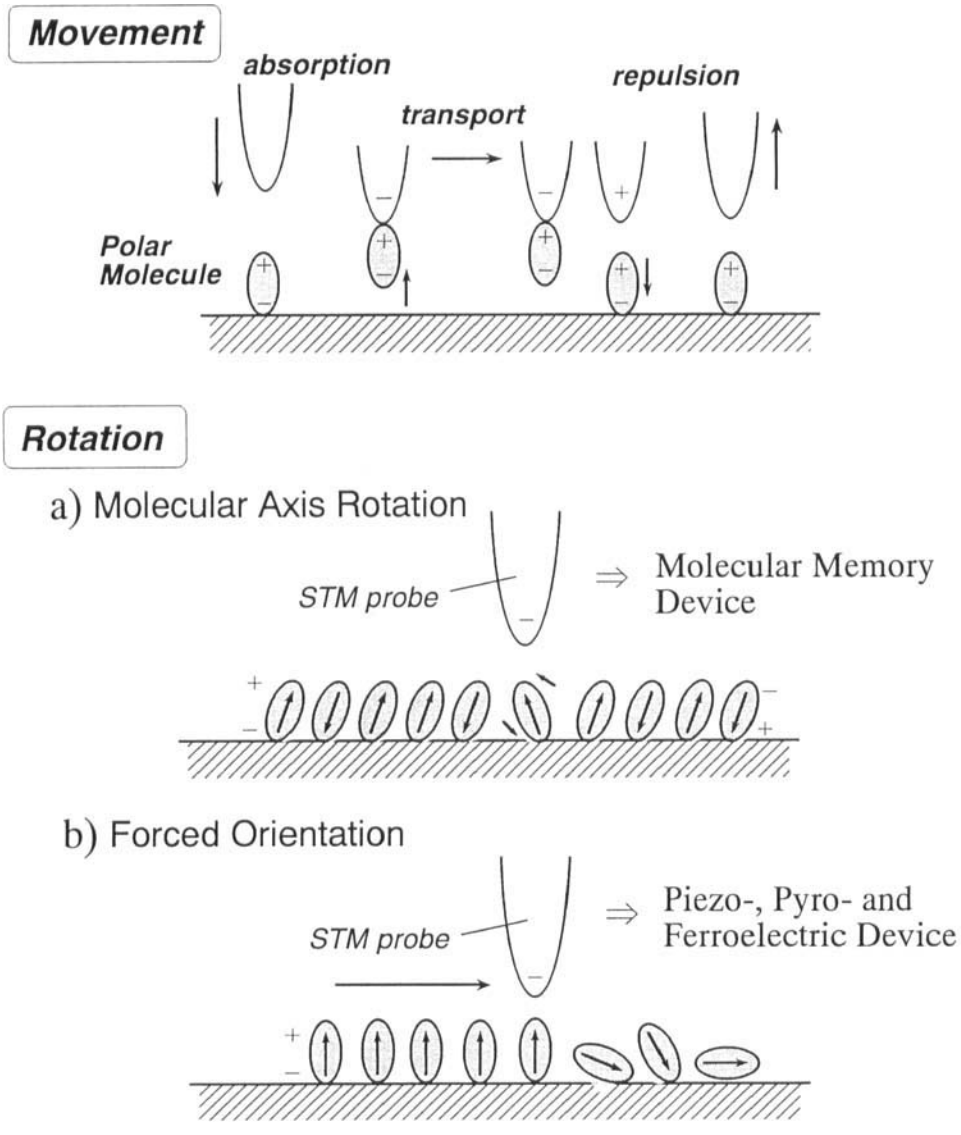

FIGURE 8 Possible nanoscopic manipulation for polar molecules with the electric interaction by utilizing a STM tip.

absorption, attachment and repulsion will be induced to the molecules with the electric interaction between the STM tip and polar molecule, and thus the individual molecules can be moved toward desired positions. While, the rotation of molecules to desired directions can be utilized to construct the ferroelectric molecular layer with memory functions and piezo-, pyro- and ferroelectric activities.

Some trials have been conducted, but so far satisfactory result has not been obtained yet. In order to achieve the molecular manipulation, the following items became apparent to be considered; some of them are the thermal stability of the molecules, suitable degree of interaction between the molecules, substrate and STM tip, and the locarization of effective electric field.

SUPER STRUCTURE BY MOLECULAR LAYER ARCHITECTURE

Next, we discuss on the formation of organic super structure. The application of the technique of the beam epitaxy to organic materials (OMBE) made possible to fabricate high quality thin films.[4] Recently, we developed the total reflection X-ray diffraction apparatus incorporated with a vacuum evaporation chamber in order to monitor the structural changes during the evaporation process, [15-17] as illustrated in Figure 9. The results revealed that the crystal structures and molecular orientations vary drastically depending on the kinds of substrate, temperature, evaporation speed, and so on. Figure 10 shows the orientation change in *n*-paraffin molecules; as-deposited film contains the molecules whose orientations are parallel and perpendicular to the SiO_2 substrate, and the heat treatment induces the orientational change from parallel to perpendicular, resulting in the well-ordered molecular assembly in the annealed film. Also, the application of electric field during the evaporation process was proven to serve effectively for controling the dipole moment in the evaporated polar films.[18] These knowledge may be utilized to control the molecular structures and orientations, and to form the super structure with notable electric functions.

One of such organic super structures is illustrated in Figure 11. If the single layer of non-polar *n*-paraffin with ethylene structure is over-layed by that of non-polar perfluoroalkane molecules, one can construct the molecular superlattice, which contains dipole moments directing from perfluoroalkane to ethylene molecules. By piling these molecular layers, one can fabricate the

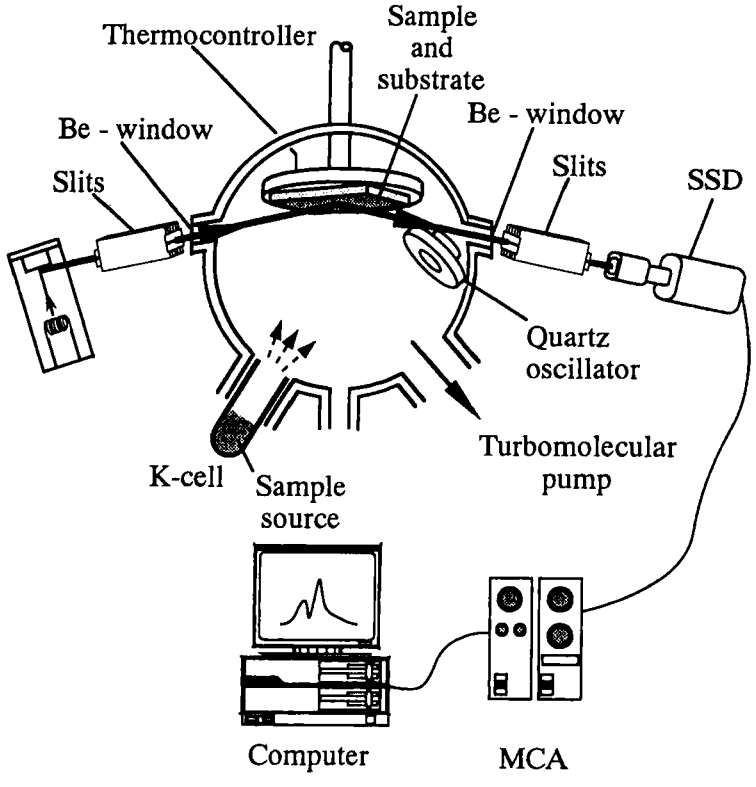

FIGURE 9 A schematic illustration of *in-situ* total reflection X-ray diffraction apparatus for organic evaporated films.

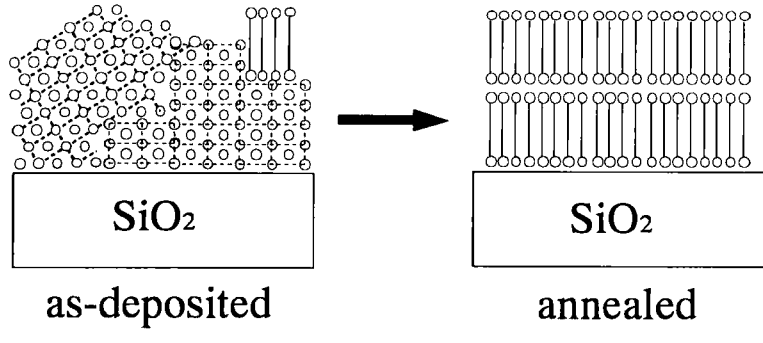

FIGURE 10 Orientational changes taken place in *n*-paraffin as-evaporated films by a heat treatment.

molecular assembly with the extremely high activities of piezo-, pyro- and ferroelectricities.

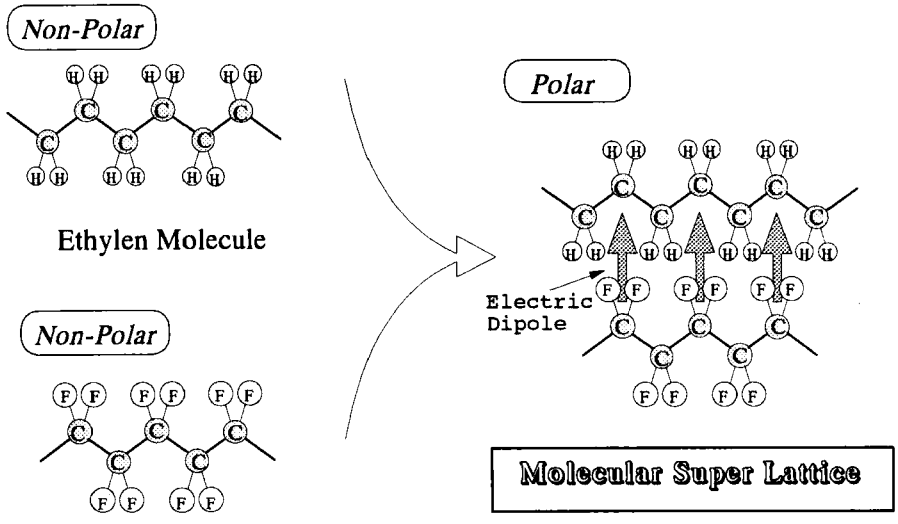

FIGURE 11 Formation of the super structure with highly-oriented electric dipoles by piling two different non-polar molecular layers.

ACKNOWLEDGEMENTS

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