

Nonlinear electrical dipolar switching at single molecular scale

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Abstract

At the single molecular scale (less than $2 \text{ \AA} \times 2 \text{ \AA} \times 9.8 \text{ \AA}$), the nonlinear electrical dipolar switching behavior from crystalline two-monolayer polyvinylidene fluoride films was measured using a scanning tunneling microscope (STM). The atomic structure of the polymer chain was clearly imaged by the STM. The nonlinear switching behavior at the single molecular scale appears as the hysteresis in the tunneling current–voltage relationship with switching onset voltage of 0.19 V/monomer. The nonlinear dipolar switching behavior at the single molecular scale has many potential applications including single molecular scale switching devices and re-writable non-volatile memories.

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The fundamental unit of nonlinear electrical dipolar switches could be as small as a physical primitive cell possessing non-centrosymmetry in a regular array or a crystal. To our knowledge, no one, however, has observed the nonlinear switching behavior at such a small scale. Generally, it is believed that the nonlinear switching behavior is limited by a critical size, below which the nonlinear switching behavior disappears. It is known that the critical size is far larger than the crystalline primitive cell [1]. In this Letter, we report the nonlinear electrical dipole switching behavior at a smaller scale ($2 \text{ \AA} \times 2 \text{ \AA} \times 9.8 \text{ \AA}$) than the primitive cell ($8.6 \text{ \AA} \times 2.6 \text{ \AA} \times 4.9 \text{ \AA}$) [2] of a crystalline polyvinylidene fluoride film with the thickness of less than 1 nm. This was accomplished by the combination of a local probe method – scanning tunneling microscope (STM) and an organic thin film epitaxy method – the Langmuir–Blodgett (LB) monolayer deposition method.

Polyvinylidene fluoride (PVDF) is an interesting linear polar group polymeric system for single-molecular switching devices because of its unique electrical, opti-

cal, mechanical and thermal response properties [2–5]. The repeating unit of the polymer chain is the polar group CH_2CF_2 . A two-monolayer PVDF film was prepared by the vertical Langmuir–Blodgett monolayer deposition method on a silicon substrate [6]. Silicon substrates are technically very important in electronic devices including non-volatile memories. By employing silicon substrates, we can avoid the convolution of the atomic structure of the substrate in imaging the atomic structure of PVDF using STM. In the past, the observed structures of PVDF on highly ordered pyrolytic graphite (HOPG) substrates are complicated because the convolution of the HOPG atomic structures with almost the same lattice constant to the PVDF images cannot be ignored [4,7,8]. The substrate is p-type silicon (100) with a resistivity of 1–10 Ωcm . The atomic image of PVDF (Fig. 1a) was obtained at room temperature by an OMI-CRON micro-VT-UHV STM using constant height mode with 4 V of the tip bias voltage, and the feedback set current was 280 pA. The scanner was calibrated with a cleaved HOPG. The tunneling current was measured at a specific point by scanning voltage from +5 to –5 V and then by reversibly scanning voltage from –5 to +5 V at the same point. A semiempirical method was employed to calculate geometrical molecular

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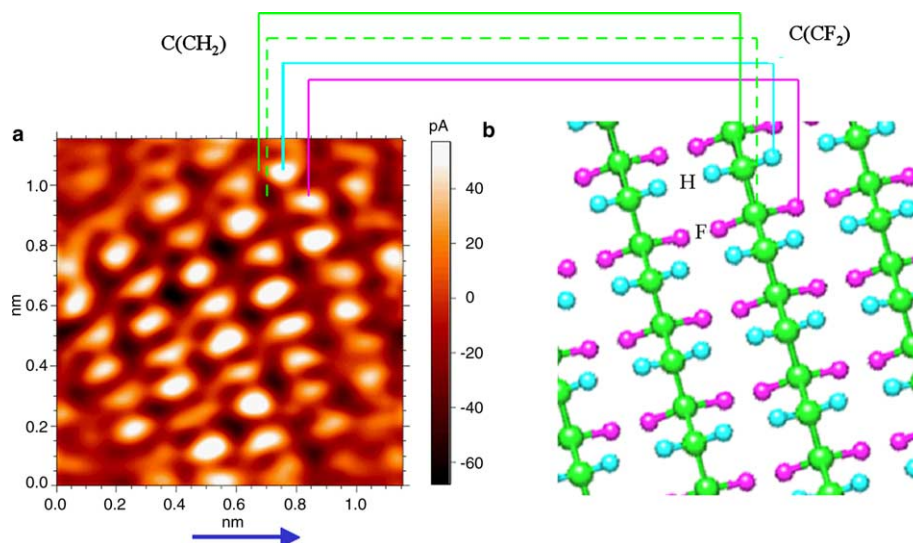


Fig. 1. (a) Atomically resolved image of polyvinylidene fluoride films with a two-monolayer thickness on a silicon substrate taken by a scanning tunneling microscope (STM tip scanned laterally). The image size is $1.15 \text{ nm} \times 1.15 \text{ nm}$. (b) Plausible molecular structures based on the STM image of (a). The each chain of molecular structures was simulated using semiempirical package program and the layer structures are manually composed based on the STM image of (a).

structures, molecular orbitals, and charge density distribution of linear polymer chain with 10 monomer units ($\text{CH}_2\text{-CF}_2$) using (PM3 method) a commercial molecular simulation package program, Molecular Orbital Package Program (MOPAC), Fujitsu Limited.

The first atomic image of PVDF on silicon substrate taken by a scanning tunneling microscope is shown in Fig. 1a. Surprisingly, the crystalline molecular structures are different from what is generally expected. What we have observed were two hydrogen and two fluorine atoms with one carbon atom barely visible in each monomer unit. The pairs of two dots with larger separation in Fig. 1a correspond to fluorines, and the pairs of two dots with shorter separation correspond to hydrogens. The observed atomic structure is largely correlated to the response of the external potential due to its intrinsic polar properties. As we can see in Fig. 1b, the observed atomic image corresponds to the top view of the crystalline all-trans structures.

The electronic charge at each constituent atom is positive for hydrogen and negative for fluorine. The charge amount of fluorine is higher than that of hydrogen. The calculated bond length ($1.38 \text{ \AA}$) between backbone carbon and fluorine is longer than ($1.10 \text{ \AA}$) that of between backbone carbon and hydrogen. The image of fluorine has an almost equal contrast to that of hydrogen. This is attributed to the moving of fluorine atoms toward the top surface by rotation around the polymer chain and the larger charge density than that of hydrogen atoms. The image indicates that the top surface of PVDF films was more likely terminated with hydrogen.

Since the bonding of PVDF consists of single bonding, the CH_2 or CF_2 units of each monomer can easily be rotated by external perturbations. Specially, the per-

turbation at an atomic scale can be achieved by applying an electrical potential to a single atom or a small portion of the molecules using an atomically sharp STM tip. During imaging with a gap voltage between an STM tip and the polymer chain, the rotation of CH_2 or CF_2 units happens. Due to the rotation of fluorine atoms around the backbone chain under the electric field from the STM tip, the image shape of the fluorine atoms is stretched in the direction perpendicular to the chain in Fig. 1a. This clearly indicates that the fluorine is rotating as the STM tip scans over the films.

The backbone carbon atom images of the PVDF are not clearly shown in Fig. 1a. There are two types of carbon atoms. The carbon atoms attached to CF_2 are positively charged while the carbon atoms attached to CH_2 are negatively charged. The carbon atom in CH_2 is more visible than that in CF_2 . This is due to the fact that carbon atom in CH_2 is close to the surface and is negatively charged.

The atomic image can be matched with molecular structures, which are obtained by the MOPAC semiempirical calculations shown in Fig. 1b. The calculated bond lengths are 2.60 , 1.38 , and $1.10 \text{ \AA}$ for C–C, C–F, and C–H bonds, respectively. As shown in Fig. 1b, the hydrogen-to-hydrogen distance is less than the fluorine-to-fluorine distance. Along the polymer chain, the difference in these distances is apparent in the scanning tunneling microscopic image (Fig. 1a).

After the imaging of the PVDF atomic structure, a single molecular nonlinear tunneling current was measured as a function of voltage at a fixed point (Fig. 2). Hysteresis behavior in the tunneling current–voltage curve was observed and it crosses the zero current at $\sim \pm 3 \text{ V}$ external voltage (Fig. 3a). As shown in

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