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Reactive rearrangements of step atoms by adsorption and asymmetric electronic states of tetrafluoro-tetracyanoquinodimethane on Cu(100)

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We investigated the local adsorption structure and electronic states of 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ) on Cu(100) at low coverage using scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS). F4-TCNQ molecules, which are preferentially adsorbed at a lower step edge, induce the reactive rearrangements of Cu atoms, including the formation of periodic kinks and step etching. The cyano groups of F4-TCNQ adsorbed at the step edge interact with not only the Cu(100) terrace but also Cu atoms at an upper step edge. This extra interaction results in the asymmetric electronic states in F4-TCNQ species, which are evidenced by STM and STS.

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The development of organic electronic devices such as organic light-emitting diodes, organic field-effect transistors, and photovoltaic cells requires an in-depth understanding of both electronic states and structures at organic-metal or organic-organic interfaces. In order to modify interfaces electronically, organic molecules having a strong electron affinity are expected to be useful materials for the organic electronic devices described above.[1] In particular, tetrafluoro-tetracyanoquinodimethane (F4-TCNQ), which has a high electron affinity ($E_A = 5.24$ eV), has been studied on various substrates from the perspective of the p-type doping of organic films,[2–6] the energy-level alignment on metal surfaces,[7–9] and the surface-transfer doping of semiconductor surfaces.[1,10–13]

The electronic modification of organic-metal interfaces often involves structural transformations in organic molecules and/or metal surfaces. Recently, structural rearrangements by molecular adsorption have been reported on Cu surfaces.[14–22] Scanning tunneling microscopy (STM) and density functional theory (DFT) studies show that tetracyanoethylene (TCNE) molecules form ordered straight chains in the [110] and [$\bar{1}$10] directions on Cu(100) and induce the periodic buckling of the Cu surface.[14,15] Romaner *et al.* reported that the adsorption of F4-TCNQ on Cu(111) induces a strong molecular distortion using x-ray standing wave and DFT.[16] In this system, the combination of adsorption-induced geometric distortion of F4-TCNQ and charge redistribution between the molecule and the surface leads to a net work-function change. Very recently, Tseng *et al.* reported that the adsorption of TCNQ on Cu(100) involves both the structural distortion of the organic molecule and the substrate buckling.[17] Thus, the present interface between F4-TCNQ and the Cu(100) surface is considered as a model system for the interfaces between strong acceptor molecules and metal surfaces.

Recently, we investigated the electronic and vibrational states of F4-TCNQ on Cu(100).[18] At 300 K, F4-TCNQ adsorbs on the Cu(100) surface via both the charge transfer from the surface to F4-TCNQ (back donation) and the rehybridization between cyano groups and the surface (donation). In this Brief Report, we focus on the local interaction between F4-TCNQ and a step on Cu(100) at an initial stage of adsorption using STM and scanning tunneling spectroscopy (STS). We found the direction of steps was drastically changed, including the periodic kink formation upon adsorption of F4-TCNQ at a lower step edge. In addition, reactive etching of Cu atoms from a step was observed.

All experiments were carried out in an ultrahigh vacuum chamber. The chamber was equipped with a low-energy electron diffraction (LEED) apparatus, a quadrupole mass spectrometer, and scanning tunneling microscopy (STM, Createc). The Cu(100) surface was cleaned by cycles of Ne ion sputtering and annealing to 700 K. The orderliness of the Cu(100) surface was confirmed by LEED and STM, and the cleanliness of the Cu(100) surface was checked by STM. The observed terrace width ranged from 4 to 40 nm. F4-TCNQ molecules were evaporated at 370 K from a homemade miniature effusion cell and deposited on the Cu(100) surface at 300 K. Details of the cell were described elsewhere.[12,18,23] After F4-TCNQ deposition at 300 K, the sample was transferred to the STM unit at 6 K, and STM observation was carried out at 6 K.

Figure 1(a) shows a typical STM image of the clean Cu(100) surface, including a few steps where the terrace width is relatively narrow. Straight steps with some kinks were usually observed. The inset in Fig. 1(a) shows an atomic-resolution STM image of the Cu(100) terrace. Based on this image, the azimuth of the Cu(100) surface was determined. It was confirmed that the direction of the step in Fig. 1(a) was mostly parallel to [110] or [$\bar{1}$10]. Figure 1(b) shows an STM image of F4-TCNQ adsorbed near a step edge. F4-TCNQ was observed as a bright elliptic protrusion. The local coverage on this surface was estimated to be 3.9×10^{13} molecules/cm^2 by counting the number of F4-TCNQ molecules. Figure 1(b) shows that F4-TCNQ molecules assemble from lower step edges. These results indicate that thermal diffusion of F4-TCNQ occurs on Cu(100) at 300 K, and F4-TCNQ prefers to adsorb at a negatively charged lower step edge (Smoluchowski effect).[24–27] Since F4-TCNQ is a strong electron accepter, it is logical that it adsorbs at such an electron-rich site. In Fig. 1(b), F4-TCNQ molecules show two different contrasts. One is F4-TCNQ species inside the small domain growing from the lower step edge. The other is F4-TCNQ species outside the step domain, which is relatively less packed. In the case of TCNQ on Cu(100),[17] it was reported that the adsorption energy was larger in the densely packed domain than in the isolated TCNQ.

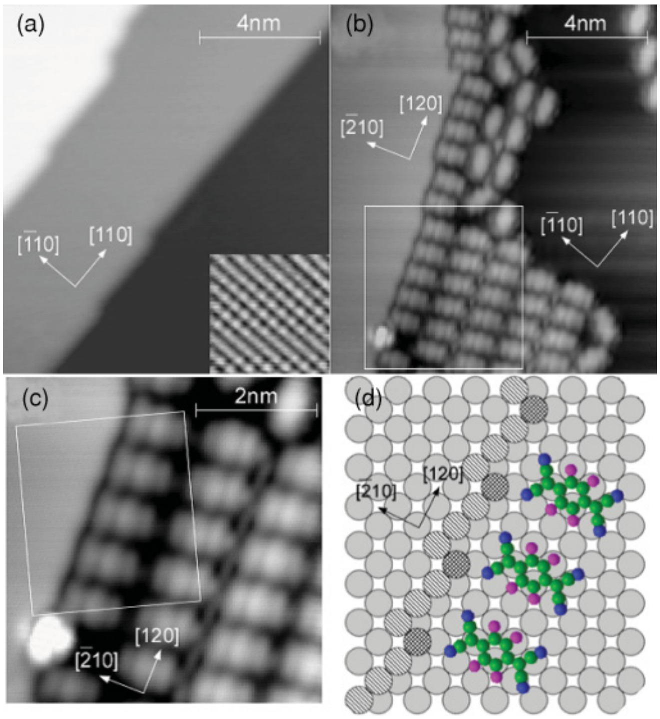

FIG. 1. (Color) (a) An STM image of the Cu(100) clean surface. The inset shows an atomic-resolution STM image of the Cu(100) terrace (2.3 × 2.3 nm^2). (b) An STM image of F4-TCNQ adsorbed at a lower step edge. (c) The close-up image of the indicated rectangle in (b). (d) A proposed structure model of F4-TCNQ adsorbed at a lower step edge (terrace Cu, gray circles; step Cu, hatched circles; kink Cu, cross-hatched circles; C, green circles; N, blue circles; F, magenta circles). The range of this structure model corresponds to the rectangle in (c). V_s and I_t are 0.4 V and 0.1 nA in (a), −0.2 V and 0.08 nA in (b), and 0.2 V and 0.08 nA in (c).

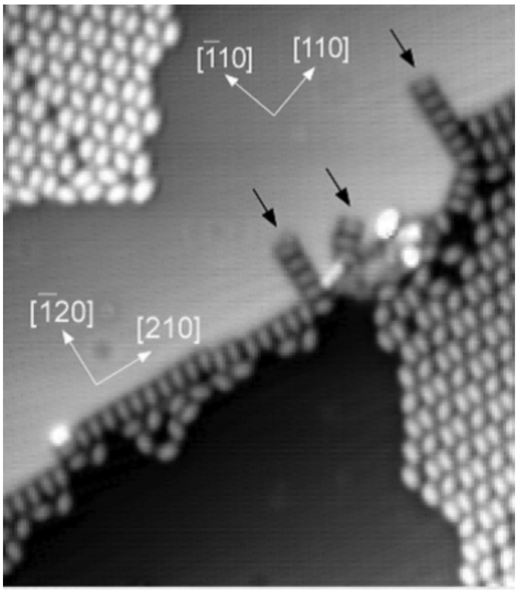

FIG. 2. An STM image of F4-TCNQ adsorbed at a lower step edge. The black arrows show the area etched by F4-TCNQ. V_s and I_t are −1.3 V and 0.08 nA.

Thus, the observed contrast difference in Fig. 1(b) indicates that the adsorption states are different in these two types of F4-TCNQ. In this Brief Report, we focus on F4-TCNQ species attached to the lower step edge. Figure 1(c) shows a close-up STM image of Fig. 1(b). F4-TCNQ aligns with its long axis nearly perpendicular to the step edge, and the periodic kinks were observed at the step edge. The periodicity of these kinks is 0.806 nm, which agrees with the distance between F4-TCNQ molecules adsorbed at the lower step edge. Figure 1(d) shows a structure model of the F4-TCNQ species adsorbed at the lower step edge. The step edge in Fig. 1(c) is oriented at about 18.5° relative to [110]; the direction of the step edge has been changed to [120] by adsorption of F4-TCNQ, where the [120] step consists of the periodic single kinks and short step sections of 3 atom lengths.

Figure 2 shows an STM image of F4-TCNQ adsorbed at another lower step edge. The black arrows show the step edges etched by F4-TCNQ molecules. The direction of these etched steps corresponds to [$\bar{1}$20]. The width of these etched areas is nearly equal to the long axis of F4-TCNQ, and it corresponds to four Cu atoms (1.02 nm). Thus, the four cyano groups of F4-TCNQ inside the etched "gulf" closely face the step-edge atoms. The periodic-kink structures are also observed in the etched gulf (Fig. 2); again, single kinks and short step sections of 3 atom lengths form the step edge inside the etched gulf. These results indicate that the step etching is incorporated with F4-TCNQ species. These rearrangements of step atoms would offer energetically more stable bonding sites for F4-TCNQ than the straight [110] steps.

Previous STM studies have reported that the steps of Cu surfaces frizz at 300 K because of kink diffusion,[28–31] which is a thermally activated process. At low temperature, the steps become smooth, and the direction is parallel to the atomically close-packing rows because the smooth-step configuration is energetically more stable [see Fig. 1(a)]. Thus, during deposition of F4-TCNQ at 300 K, Cu atoms at steps are always fluctuating. In addition, recent studies have reported that buckling of the Cu(100) surface is induced by the adsorption of TCNE or TCNQ on Cu(100).[14,15,17] These rearrangements of surface atoms are caused by the strong bidirectional interaction between Cu atoms and acceptor molecules (donation and back donation). We think that the present step rearrangements including the formation of periodic kinks and step etching are induced by the strong interaction between F4-TCNQ and Cu atoms at the step edge. In the case of F4-TCNQ adsorbed at the lower step edge, the electronic states of cyano groups near the lower step edge are rehybridized with not only the Cu(100) terrace atoms but also Cu atoms at the upper step edge. We think that such a configuration offers energetically more stable bonding between F4-TCNQ and Cu atoms than the case at [110] or [$\bar{1}$10] steps; thus, the periodic kinks are formed. In the case of F4-TCNQ embedded inside the etched gulf (Fig. 2), all four cyano groups closely face the Cu atoms at the upper step edges and are thus stabilized. However, the very limited number of gulf formations at a step suggests that this process is kinetically hindered. It is noted that the modification of morphology through step faceting and bunching was reported upon the full-monolayer deposition of glycine and alanine on Cu(100) at ∼400 K.[19,20]

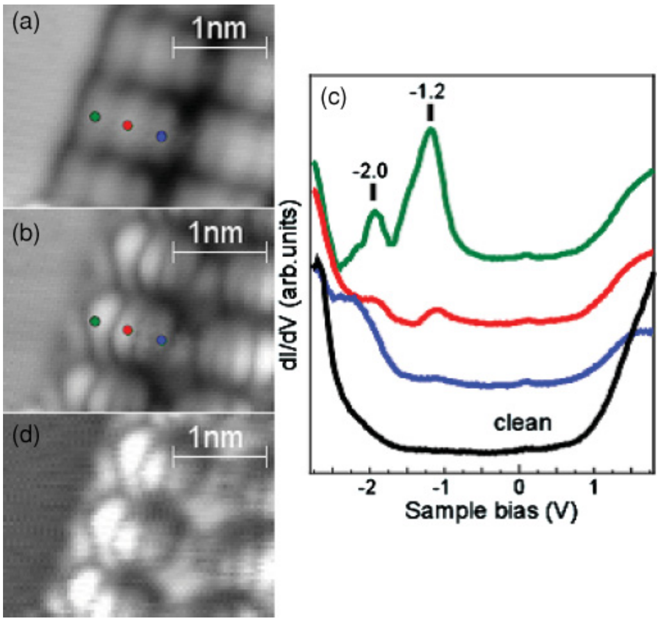

FIG. 3. (Color) (a) Unoccupied-state and (b) occupied-state STM images of F4-TCNQ adsorbed at the lower step edge. V_s and I_t are 0.2 V and 0.08 nA in (a) and -1.2 V and 0.08 nA in (b). (c) The dI/dV spectra measured at indicated positions in F4-TCNQ adsorbed at the lower step edge. The Fermi level corresponds to 0 V. (d) A dI/dV mapping measured at $V_s = -1.2$ V and $I_t = 0.08$ nA.

The local electronic states of F4-TCNQ attached to the lower step edge were investigated using STS. Figures 3(a) and 3(b) show the typical unoccupied- and occupied-state STM images of F4-TCNQ adsorbed at the lower step edge, respectively. At $V_s = +0.2$ V, the shape of each F4-TCNQ molecule is fairly symmetric in Fig. 3(a). On the other hand, at $V_s = -1.2$ V, it becomes asymmetric, as shown in Fig. 3(b). The observed difference is further investigated by STS measurements. Figure 3(c) shows dI/dV spectra measured at indicated positions of F4-TCNQ at the lower step edge and that on the clean Cu(100) surface. Two peaks are observed in the occupied states at -1.2 and -2.0 V. Since these peaks were not observed on the clean Cu(100) surface, these states are attributed to the adsorbed F4-TCNQ species. According to the theoretical study of F4-TCNQ on Cu(111),[16] the "occupied" lowest unoccupied molecular orbital (LUMO) and "relaxed" highest occupied molecular orbital (HOMO) are located at ~1 and ~2 eV below the Fermi level, respectively. In addition, the "occupied" LUMO states of F4-TCNQ on various surfaces were observed in the region from 1.2 to 0.45 eV below the Fermi level using photoelectron spectroscopy.[7,12,18,32] Thus, the observed peaks at -1.2 and -2.0 V are attributed to occupied LUMO and relaxed HOMO states of F4-TCNQ, respectively.

The peaks at -1.2 and -2.0 V are more distinct at the green dot in Figs. 3(a) and 3(b). On the other hand, at the blue dot, the peak at -1.2 V is weak, and the peak at -2.3 V is broad. At the red position, small peaks are observed at -1.2 V and -2.0 V. The intensities of "occupied" LUMO are different at each position in the molecule. This indicates that the local density of state (LDOS) distribution of this state in F4-TCNQ is not symmetric along the molecular long axis. Figure 3(d) shows a dI/dV mapping recorded at -1.2 V and 0.08 nA. The scan region is identical to the STM images in Figs. 3(a) and 3(b). The symmetry of the observed molecule adsorbed at the lower step edge becomes C_1 (including the surface) from D_{2h} (the symmetry of free F4-TCNQ). Note that one side of the molecule near the step edge is brighter than the other side in Fig. 3(b). Asymmetric molecular images that are not only along a long axis but also along a short axis indicate the different electronic states around CN groups near the step and kink atoms [see a structure model in Fig. 1(d)]. On the other hand, such asymmetric distribution of LDOS inside the molecule was not observed in Fig. 3(a) because there is little difference in the unoccupied states [Fig. 3(c)].

This asymmetric distribution of electronic states is caused by two factors, as discussed below. One is the "Smoluchowski effect" at a step on Cu(100).[24–27] At the lower step edge, the LDOS near the Fermi level is higher than that of the clean surface. When the cyano groups of F4-TCNQ interact with such electron-rich sites, the degree of back donation from the substrate becomes asymmetric along the molecular long axis. As a result, the LDOS of "occupied" LUMO becomes asymmetric along the molecular long axis. The second factor is the chemical environment of cyano groups in F4-TCNQ. At the lower step edge, the two cyano groups of F4-TCNQ near the step interact with both the Cu(100) terrace and Cu atoms at the upper step edge. Note that kink Cu atoms may provide stronger bonding sites for F4-TCNQ than the case of a straight step. However, other cyano groups of F4-TCNQ away from the step do not directly interact with the upper step edge. The extra interaction between the cyano groups near the step and Cu atoms at the upper step edge induces the stronger back donation than that from the other side of F4-TCNQ. This difference in the degree of the charge transfer causes asymmetric LDOS of F4-TCNQ along the molecular long axis.

In summary, we investigated the local adsorption states of F4-TCNQ adsorbed at steps on Cu(100). The adsorption of F4-TCNQ induces the reactive rearrangements of step atoms; the periodic kinks and step etching are observed. These processes are induced by strong interaction between F4-TCNQ and Cu atoms, involving thermal migration of F4-TCNQ and thermal fluctuation of step atoms on Cu(100) at 300 K. The cyano groups of F4-TCNQ near the step interact with not only the Cu(100) terrace but also the upper step edge. This extra interaction may cause the stronger back donation to the nearest cyano groups in adsorbed F4-TCNQ; the LDOS mapping of "occupied" LUMO shows an asymmetric image along the molecular long axis.

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