STM visualization of site-specific adsorption of pyridine on $TiO_2(110)$

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Pyridine molecules adsorbed on a $TiO_2(110)$-(1 × 1) surface were visualized by scanning tunneling microscopy (STM). Direct evidence of coordination-controlled adsorption on a metal oxide surface is reported for the first time. A pyridine molecule was more strongly adsorbed on a four-fold coordinated Ti atom exposed at single-atom-height step edges than on the five-fold coordinated Ti site over the perfect (110) terrace. Furthermore, the activity of the four-fold coordinated Ti sites at step edges was strongly dependent on the orientation of the step in azimuth. Sequential imaging of the pyridine-exposed surface revealed that terrace-adsorbed molecules were transformed to step-bonded species and vice versa even at room temperature.

Keywords: acid–base interaction, STM, pyridine, $TiO_2(110)$, surface diffusion

1. Introduction

Understanding and controlling the acidic property of oxide surfaces are the key issues for the development of industrial catalysts [1]. However, the inherent compositional and structural inhomogeneity of oxide surfaces makes the problem of identifying the essential issues for their catalytic performance extremely difficult. Scanning probe microscopy has particularly great potential to overcome the difficulty of heterogeneity and great advantages to structural study of heterogeneous surfaces, discriminating and visualizing surface atoms and molecules at each site with different properties [2,3]. Following the invention of scanning tunneling microscopy (STM), several transition metal oxides have been subjects of real space imaging with atomic-scale resolution [4–11]. A promising ability of STM in visualizing surface reactions on metal oxide has been demonstrated even at elevated temperatures [12] and in the presence of reactant atmospheres [13].

The adsorption state of pyridine specific to single-atom height steps resident on a metal oxide surface is visualized in the present study. Pyridine is a typical Lewis-base compound and employed as a probe for the acidic properties of oxide catalysts. The quality and quantity of acidic sites have often been analyzed with thermal desorption and infrared absorption spectroscopy. Despite a number of studies with the macroscopic techniques, the atomic-scale structure of acid sites is still unclear. For example, our previous study [14] revealed that pyridine was only physisorbed on the (110)-(1 × 1) surface of rutile TiO_2 without definite N–Ti bonding, although the highly ionized Ti atoms exposed on that surface could be assumed as Lewis acid sites favorable for pyridine chemisorption. Visualization of individual probe molecules adsorbed on different parts of a metal oxide surface, which is performed in the present study for the first time, is indispensable for rational design of acid sites with controlled reactivity.

2. Experimental

The experiments were performed with an UHV compatible scanning tunneling microscope (JSTM-4500VT, JEOL) equipped with an Ar^+ gun and LEED-AES optics. A polished $TiO_2(110)$ wafer of $6.5 \times 1 \times 0.25$ mm^3 (Earth Chemicals) was annealed in air at 1100 K for 1 h. Nickel film was then deposited on the back side of the wafer for resistive heating on the microscope stage. The temperature of the surface was monitored with an IR radiation thermometer. After cycles of Ar^+ sputtering (3 keV, 0.3 μA) and vacuum annealing at 900 K, a sharp (1 × 1) LEED pattern was observed on the surface. The (1 × 1) surface was cooled to room temperature and then exposed to pyridine (research grade, Wako Pure Chemicals) vapor. Constant current topography of the pyridine-exposed surface was continuously determined at room temperature with an electro-chemically etched W tip. A positive sample bias voltage (V_s) of +2.5 V, and a tunneling current (I_t) of 0.05 nA were employed in imaging.

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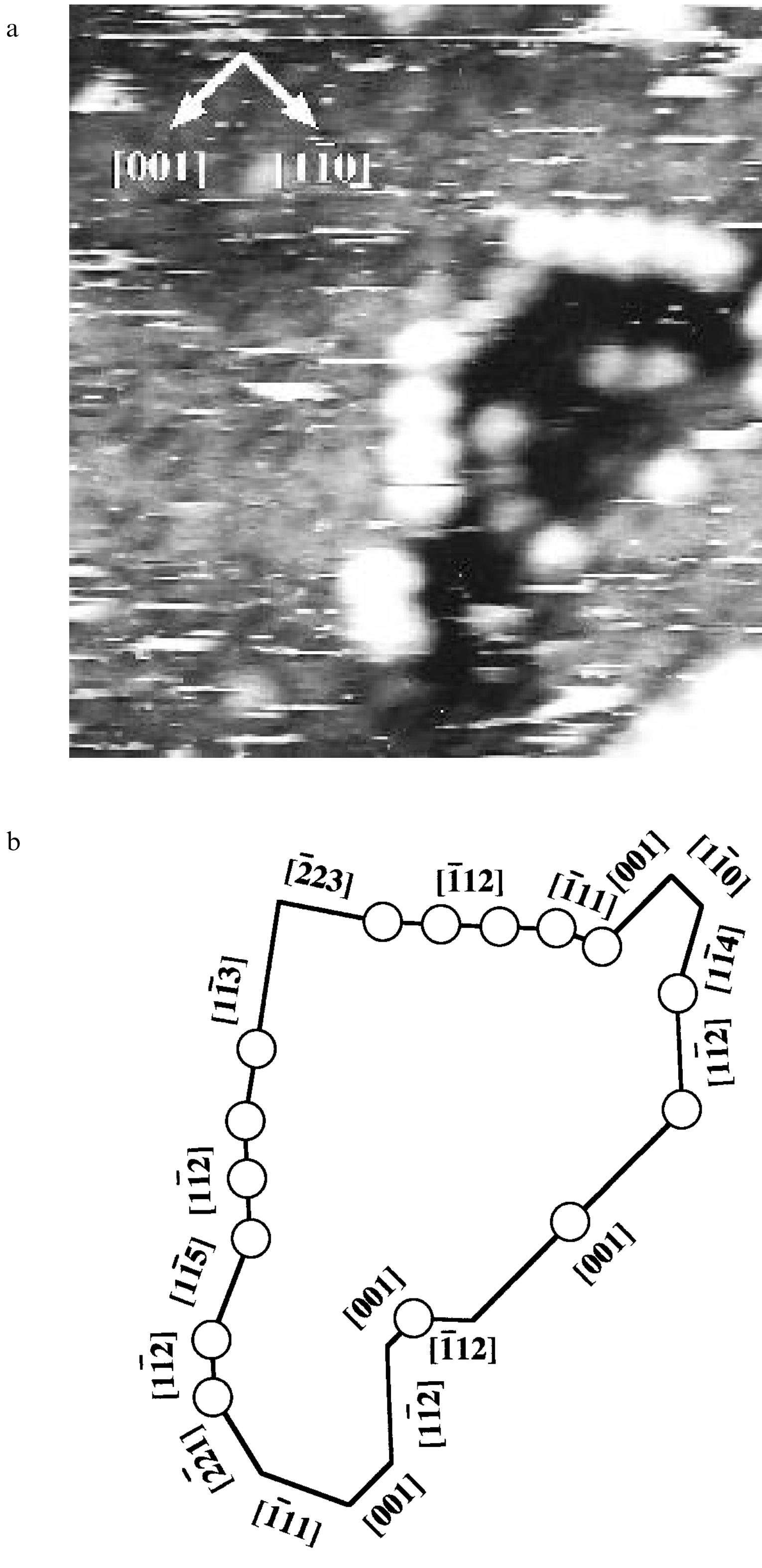

Figure 1. (a) An STM image of the pyridine-exposed $TiO_2(110)$-(1×1) surface. 15×15 nm^2, sample bias voltage: +2.5 V, tunneling current: 0.05 nA. (b) A schematic drawing of the single-atom height steps in (a). The positions of pyridine molecules adsorbed on the steps are shown by dots.

3. Results and discussion

The annealed (1 × 1) surface was exposed to pyridine vapor of 0.01 L at room temperature in the treatment chamber and then transferred to the microscope stage. Figure 1a shows a typical STM topography of the pyridine-exposed $TiO_2(110)$-(1 × 1) surface, where two terraces separated with single-atom height steps were imaged. Figure 1b illustrates the position and azimuthal orientation of the step edges. Fifteen protrusions of complete circular shape were observed on the edges. These protrusions were assigned to individual pyridine admolecules. The step-bonded molecules were imaged completely, whereas many images of fragmented shapes were observed over the upper terrace. The fragmented shapes of molecular image suggest vital migration of pyridine molecules adsorbed on the terrace, because a quickly migrating molecule cannot stay at a position long enough to be properly imaged with scanning microscopy. Indeed, terrace-adsorbed pyridine molecules frozen at about 100 K could be resolved as isolated protrusions of the complete shape [15]. Our previous work showed that the five-fold coordinated Ti^{4+} sites exposed on the (110)-(1 × 1) terrace are incapable of making stable Ti–N bonds with pyridine admolecules [14]. The step-bonded species of the complete shape were less mobile at room temperature and thus more strongly bound to the surface, than the terrace-adsorbed species were. The residence time at the step edges was the order of 100 s, as shown later.

The rows of the five-fold coordinated Ti^{4+} atoms (Ti-rows) were resolved as lines of slight contrast on the upper terrace in figure 1a. It has been well established that the exposed Ti atoms are imaged as small protrusions in STM topography determined with positive sample bias voltages [5]. The step-bonded pyridine molecules were always observed at positions where the steps truncated Ti-rows. Four-fold coordinated Ti atoms should be exposed at those intersections. The Ti atom originally five-fold coordinated loses one oxygen ligand at a step edge. A step parallel to the [$1\bar{1}2$] direction is illustrated in figure 2 as an example. The coordination number around Ti atoms was maximized in the model with the least number of four-fold coordinated Ti atoms and no three-fold coordinated Ti atoms. A bulk truncation without any reconstruction or relaxation was assumed. It is thus concluded that a pyridine molecule is adsorbed more strongly on a coordinatively unsaturated (four-fold coordinated) Ti atom exposed on the step edge, than on a five-fold coordinated Ti atom over the (110)-(1 × 1) terrace.

A possible interpretation of the adsorption state specific to the step edges is that the unsaturated (four-fold) coordination promotes the Lewis-acid strength of the Ti site. A molecular dynamics (MD) calculation considering electrostatic and van der Waals forces between the step site and a single pyridine molecule failed to reproduce the observed state [15], while a weakly bonded state on a perfect (110) terrace was well presented in the calculation [14]. Hence, chemical bonding interaction, i.e. acid–base type interaction in this case, may play a role in the adsorption at the step edges.

On the other hand, the step-bonded state exhibited topography very similar to that of the terrace-adsorbed species, when the surface migration of the latter was frozen out at 100 K [15]. The image height of both the states at 100 K was determined to be 0.25 ± 0.01 nm. The MD calculation of a single pyridine molecule adsorbed on a perfect (110) terrace revealed that the adsorbed pyridine was most stable when the aromatic ring is parallel to the surface [14]. If the step-bonded pyridine molecule is adsorbed with a N–Ti chemical bond, the aromatic ring should stand up relative to the terrace plane. Pyridine adsorbed in this manner was found on a ZnO ($10\bar{1}0$) surface in an X-ray absorption study [16]. The topographical similarity of the step-bonded and terrace-adsorbed species does not suggest the upright geometry of the step-bonded state. The adsorption geometry stable at the step site and the contribution of N–Ti chemical bond are now being examined with a density functional method [15].

It has been pointed out that the multiplicity of coordination vacancy is a key factor controlling the reactivity of the metal centers of metal oxides [17]. The present study yields direct evidence of coordination-controlled adsorption on a metal oxide surface for the first time. Furthermore, the affinity of the four-fold coordinated Ti atoms was dependent on the azimuthal orientation of the step edges. The steps in figure 1 on which pyridine molecules were adsorbed run parallel to the [$1\bar{1}2$] direc-

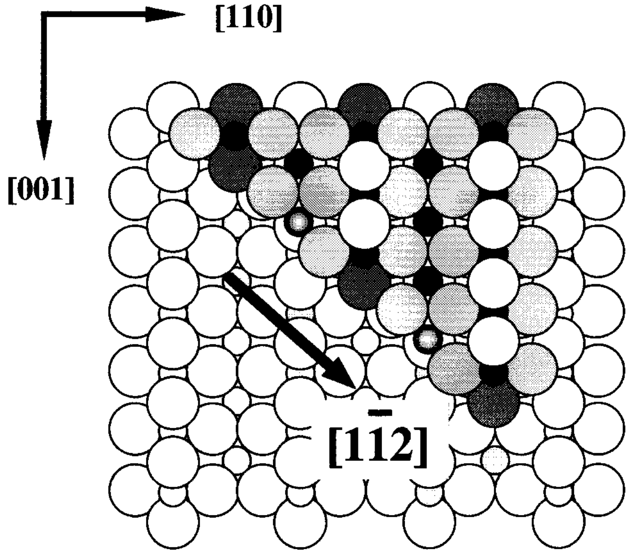

Figure 2. A ball model of a step along the [$1\bar{1}2$] direction. Small and large symbols represent Ti and O atoms.

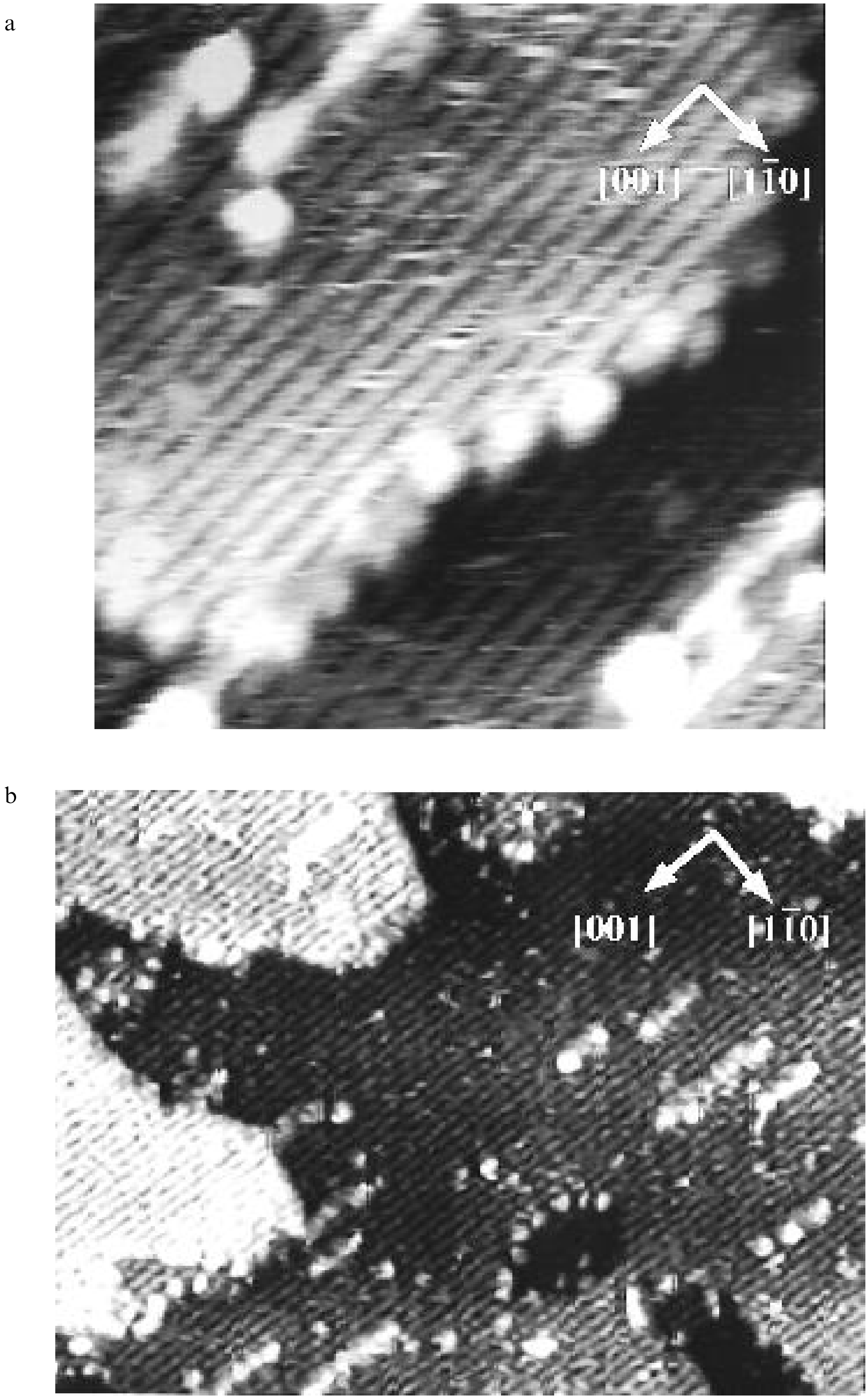

Figure 3. (a) An STM image of a pyridine-adsorbed step along the [1$\bar{1}$5] direction. 17 × 17 nm^2, sample bias voltage: +2.5 V, tunneling current: 0.05 nA. (b) A wide area image of the surface in figure 1. 40 × 30 nm^2, sample bias voltage: +2.5 V, tunneling current: 0.05 nA.

tion. Similar activity was observed on the steps parallel to $[1\bar{1}3]$, $[1\bar{1}4]$, and $[1\bar{1}5]$ directions. Figure 3a shows an STM image of three pyridine molecules adsorbed on a $[1\bar{1}5]$ step, as an example. Ti-rows were well resolved on the terrace and the step-bonded molecules were again adsorbed on the intersections of the step edge and Ti-rows. In contrast, steps parallel to $[1\bar{1}1]$, $[1\bar{1}0]$, and [001] orientations were not active for the adsorption. Figure 3b shows a wide-area (40×30 nm^2) image of the pyridine-exposed surface. Step-bonded species were not observed on the steps terminating the upper terrace, which were parallel to $[1\bar{1}1]$, $[1\bar{1}0]$, and [001] directions, while short segments of $[1\bar{1}2]$ and $[1\bar{1}3]$ steps on the lower terrace were covered with eight pyridine molecules of the complete shape.

Steps capable and incapable of pyridine adsorption are modeled in figure 4, where we assume the non-reconstructed, ideal structures truncated along desired orientation. The lack of the strongly adsorbed species is not surprising on steps along the [001] and $[1\bar{1}0]$ directions. Those steps only contain five-fold and six-fold coordinated Ti atoms. In contrast, the absence of the adsorption activity on the $[1\bar{1}1]$ step is quite interesting, because four-fold coordinated Ti atoms are still exposed as shown in figure 4c. The nearest-neighbor coordination of the Ti atoms active at the $[1\bar{1}2]$ step and inactive at the $[1\bar{1}1]$ step is equivalent, four-fold. How does a pyridine molecule distinguish the step of one orientation from the other and hate the $[1\bar{1}1]$ step? Site-specific state of adsorbed benzene was found on single-atom-height steps on Cu(111) at 77 K [18]. However, preference of step-orientation was not observed in that case. The activity of the four-fold coordinated Ti center must be affected by the arrangement of atoms at second-nearest positions or further. A four-fold coordinated Ti atom at the inactive $[1\bar{1}1]$ step has two Ti neighbors on both sides along the step, and each of which neighbors is five-fold coordinated with oxygen atoms (figure 4c). At the active $[1\bar{1}2]$ step in figure 2, one of the neighbors is missing. The pair of the extra O atoms being coordinated to the Ti neighbor may sterically obstruct close approach of a pyridine molecule to the four-fold coordinated Ti center at the $[1\bar{1}1]$ step. The missing Ti neighbors may also perturb the electronic states of the adsorption site through the bridging O atoms. Anyway, this orientation-dependent affinity is beyond the simple coordination vacancy argument.

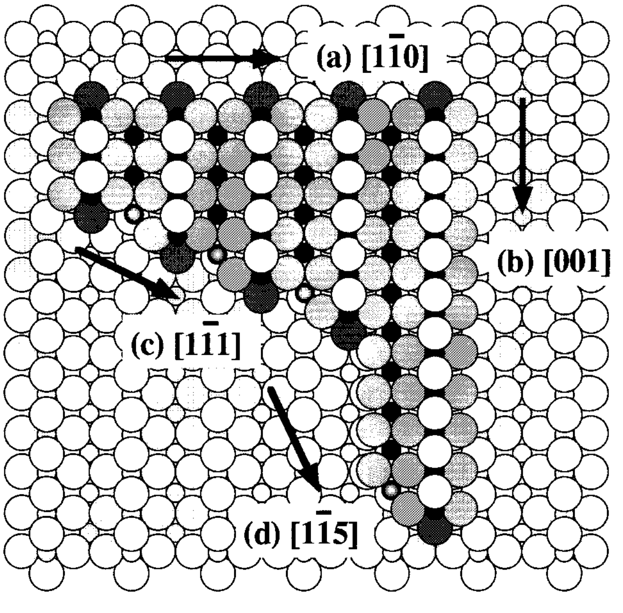

Figure 4. Bulk truncated models of steps along (a) $[1\bar{1}0]$, (b) [001], (c) $[1\bar{1}1]$, and (d) $[1\bar{1}5]$ directions.

Sequential imaging of the pyridine-exposed surface revealed that terrace-adsorbed molecules were transformed to step-bonded species and vice versa. Figure 5 shows sequential six frames recorded on the surface of figure 1 at an interval of 18.3 s/frame. The number and position of step-bonded pyridine molecules fluctuated through frames (a) to (f). The frame-by-frame fluctuations suggest that the residence time on a step site is comparable with the image acquisition time (order of 100 s).

The observed exchange allows us to draw a picture that the terrace-adsorbed state is a precursor to produce the step-bonded species. First, pyridine molecules in the gas phase are adsorbed on the five-fold coordinated Ti sites on terraces. The terrace-adsorbed species migrate over the surface to be trapped at the step sites. A gas-phase pyridine molecule can also strike and adsorb directly on the step site. However, the direct adsorption should be an infrequent event due to the minor population of step sites. Thereby, surface diffusion of the terrace-adsorbed state plays an essential role to form the step-bonded species.

It has been contended that metal oxides are the place to find strong analogies with organometallic chemistry and homogeneous metal-complex catalysis [17]. The metal cations in oxides are compared to the metal centers in mononuclear metal complexes in solution in that scheme, because the cations are isolated from each other by bridging oxygen anions. However, the exchange visualized in figure 5 demonstrates that two-dimensional transport of adsorbates promotes the interactions among physically isolated metal sites. Remind that the step-direction dependent affinity is also out of the simple coordination vacancy argument of an isolated metal center. These findings lead to the chemistry characteristic of heterogeneous catalysis beyond analogies with organometallic chemistry and homogeneous catalysis. Scanning probe microscopy including STM is a powerful technique to visualize such chemical phenomena on solid surfaces of heterogeneous compositions and structures.

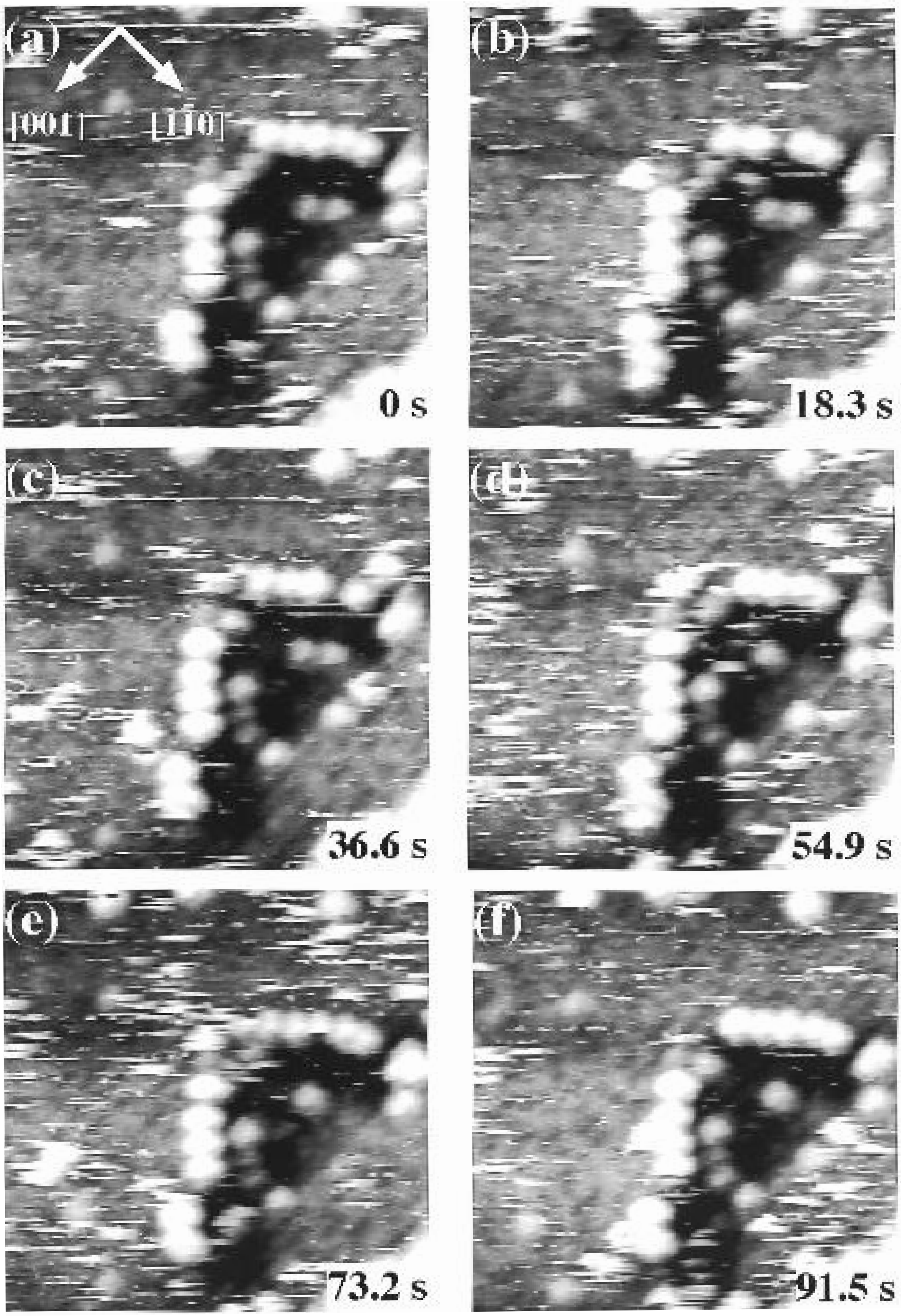

Figure 5. Sequential STM images of the surface shown in figure 1. The frames (a)–(f) were determined at a rate of 18.3 s/frame. 15 × 15 nm^2, sample bias voltage: +2.5 V, tunneling current: 0.05 nA.

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