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Anisotropic Water Chain Growth on Cu(110) Observed with Scanning Tunneling Microscopy

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We report a novel structure of water aggregate by means of scanning tunneling microscopy. Water molecules are self-assembled into one-dimensional chains on Cu(110) at 78 K. The chain exhibits a zigzag structure with a period of 7.2 Å and grows to a length of ~ 1000 Å. We propose that water hexamers are arranged alternately along the chain. Interchain repulsion due to dipole interaction facilitates the 1D chain growth. A two-dimensional overlayer develops only at high coverage.

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Water-solid interaction has been intensively studied both experimentally and theoretically during the past two decades, since it plays crucial roles in a variety of chemical processes, such as corrosion and heterogeneous catalysis [1,2]. Numerous studies have been performed with single-crystalline close-packed metallic surfaces [3–9], due to their structural similarity to the truncation of hexagonal I_h ice. Water molecules diffuse and aggregate on the surfaces above ~ 40 K, forming a two-dimensional overlayer [6]. The overlayer is comprised of water hexagonal units which are hydrogen-bonded to each other (conventionally designated as a water bilayer). The details of the overlayer structure, such as proton orientation [4,5,9] and the presence of partial dissociation [7], have been argued.

In contrast to the comprehensive studies on close-packed metallic surfaces, the structure of a water overlayer on open surfaces is less understood. It has been believed that water molecules form a distorted hexagonal bilayer on Cu(110) based mainly on the $c(2 \times 2)$ superstructure commonly observed with low-energy electron diffraction (LEED) [10–14]. Further information was obtained for proton orientation [13], molecular symmetry [15], and vibrational states [12]. While partial dissociation of water molecules was suggested by x-ray photoemission study [14], it was recently disproved and ascribed to x-ray- and electron-induced effects [16].

The structure of a water network is determined in the interplay of water-water and water-substrate interaction. An anisotropy in the water-substrate interaction may give rise to unique network growth [3]. From this point of view, we studied water adsorption on Cu(110) using scanning tunneling microscopy (STM). Reflecting the twofold symmetry of the surface, water aggregates into a one-dimensional (1D) chain. The chain exhibits a zigzag structure in the STM images, and we propose that water hexamers constitute the zigzag 1D network. Furthermore, the dipole repulsion between the chains inhibits the formation of a two-dimensional (2D) network and facilitates the anisotropy in the growth. The 2D overlayer is observed at high coverage, although it is not in registry with Cu(110).

The experiments were carried out in ultrahigh-vacuum chambers. The STM images were obtained in constant current mode at 78 K. The sample bias during the scanning (V_s) was 0.1–0.5 V for imaging water adsorbates. Scannings with $|V_s|$ lower than 0.1 V induced uncontrollable restructuring of water adsorbates at 78 K. An electrochemically etched tungsten tip was used as an STM probe. LEED experiments were conducted in a separate chamber equipped with a quadrupole mass spectrometer for thermal desorption measurements. The beam energy of 49 eV and incident current of 70 nA were used for the LEED observation to minimize the electron irradiation effect. The water-adsorbed sample was heated only by radiation from a hot filament. The single-crystalline Cu(110) was cleaned by repeated cycles of sputtering with 500 eV Ar^+ ions for 15 min and annealing at ~ 800 K for 1 min. The surface was exposed to D_2O gas via a tube doser positioned ~ 1 cm apart from the sample surface at 78 K (STM) or 120 K (LEED).

Figure 1(a) shows an atomically resolved STM image of clean Cu(110). The arrows indicate two high-symmetry crystallographic orientations along the surface. The surface consists of atomic rows aligned along $[1\bar{1}0]$. We represent the atomic distances along $[1\bar{1}0]$ (parallel to the row) and $[001]$ (perpendicular to the row) by a_0 (2.56 Å) and b_0 (3.62 Å), respectively. The surface was exposed to increasing amounts of D_2O at 78 K [Figs. 1(b)–1(d)]. Initial adsorption occurs preferentially at step sites [bottom right of Fig. 1(b)]. On the terrace, linear chains are observed to grow along the direction perpendicular to the Cu rows. Since water is adsorbed intact on Cu(110) at 78 K [16], the chain is ascribed to an assembly of water molecules. With increasing exposure, three-dimensional (3D) ice starts to develop on the chains before the terrace is completely covered with water [Fig. 1(d)].

A magnified image of two parallel chains is shown in Fig. 2(a), where zigzag structures are observed with a period of $2b_0$. The zigzag corners are protruded in the topographic image. The chain width is estimated to be $(3.2 \pm 0.2)a_0$ from the distance between the adjacent protrusions projected to $[1\bar{1}0]$. The registry of the zigzag chain

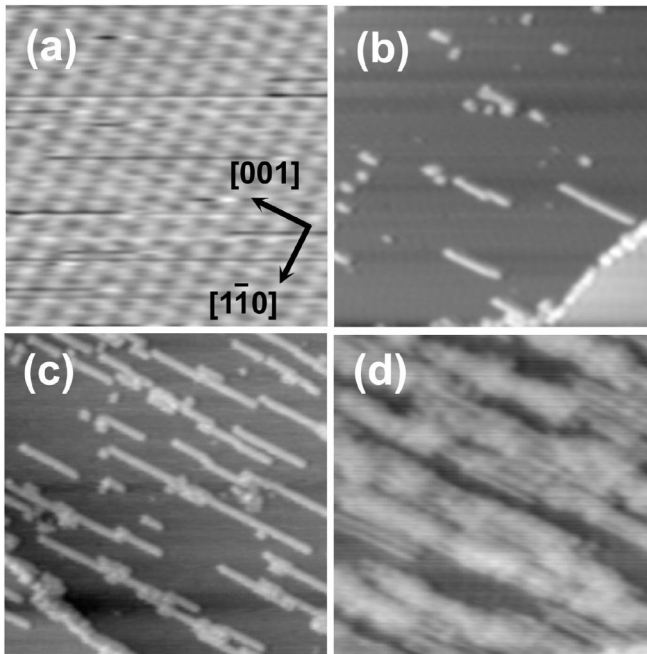


FIG. 1. (a) Atomically resolved topographic STM image of clean Cu(110) ($44 \times 44 \text{ \AA}^2$). The image was acquired at 0.4 nA tunneling current and 0.02 V sample bias. The arrows indicate two high-symmetry directions along the surface. The surface consists of atomic rows aligned along $[1\bar{1}0]$. (b)–(d) STM images of Cu(110) after being exposed to increasing amounts of water at 78 K. The image (b) was obtained at 0.02 nA and 0.1 V ($640 \times 640 \text{ \AA}^2$). Water adsorbs preferentially at the step (bottom right). On the terrace, linear chains grow along the direction perpendicular to the Cu rows. The image (c) was obtained at 0.05 nA and 0.5 V ($640 \times 640 \text{ \AA}^2$). There is a step in the bottom left. The image (d) was obtained at 0.05 nA and 0.25 V ($800 \times 800 \text{ \AA}^2$). Three-dimensional ice starts to grow on the chains, while there still exist bare regions on the surface.

with the substrate is shown in Fig. 2(b). The upper and lower parts were recorded with $V_S = 0.3$ and 0.03 V to image the chain and the substrate, respectively. The solid lines indicate the location of the Cu rows; the corners of the chains lie on the trough of Cu(110). The location along the row cannot convincingly be determined. Figure 2(c) shows a line scan along the dashed line in Fig. 2(a). The apparent height of the water chain is 1.3 Å above the surface plane. The height is comparable to that of 2D water clusters on Cu(111) [8], suggesting one molecule in height in the chain.

Thermal activation induces the restructuring of water aggregates. The surface was covered with an ice multilayer at 78 K [corresponding to the coverage of Fig. 1(d)] and then gradually heated ($\sim 2 \text{ K/hour}$). The images were acquired after cooling down the substrate to 78 K to reduce thermal drift (heat and quench). After being heated up to 120 K, the surface is free from 3D ice and 2D overlayers appear [Fig. 3(a)]. Water chains are also observed in the gap. In the 2D overlayer, a periodic structure of $(6.9 \pm$

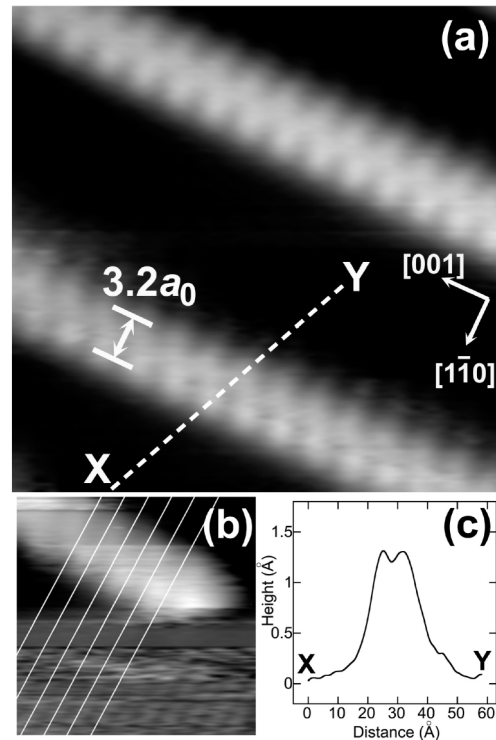


FIG. 2. (a) STM image of two parallel chains ($90 \times 90 \text{ \AA}^2$). The image was obtained at 0.03 nA and 0.1 V. The chains exhibit a zigzag structure with the corners protruded along the direction perpendicular to the Cu rows. The period along the chain is $2b_0$. The width of the chain is $(3.2 \pm 0.2)a_0$, as estimated from the distance between the adjacent protrusions projected to $[1\bar{1}0]$. (b) The registry of the zigzag chain with the substrate ($45 \times 45 \text{ \AA}^2$). The upper and lower parts of the image were acquired at 0.3 and 0.03 V to observe the chain and the substrate, respectively. The tunneling current was 0.3 nA. The solid lines show the location of the atomic rows of the substrate, indicating that the corners of the zigzag chains lie on the trough of Cu(110). (c) A line scan along the dashed line in (a). The apparent height of the water chain is 1.3 Å above the surface plane.

$0.3)a_0$ is seen along $[1\bar{1}0]$. A magnified image of the 2D island is shown in Fig. 3(b), where the zigzag structures are observed along $[001]$. They correspond to the 1D chains, although they are broken and disordered. This implies that the 2D overlayer is composed of the 1D chains which are hydrogen-bonded to each other. The interaction between the chains may affect the 1D network and cause the disordering along the chains. Note that the 2D overlayer was not observed in the adsorption process at 78 K (Fig. 1), suggesting that its formation requires thermal activation. The corresponding LEED pattern [Fig. 3(c)] shows $(6.6 \pm 0.4)^{-1}$ order spots in the $[1\bar{1}0]$ direction. The overlayer-induced LEED spots disappeared in ~ 1 min after starting the observation due to the irradiation of electron.

After being heated to 140 K, the dense 2D overlayer almost disappears as a result of desorption, and the chains arranged at nearly regular intervals are observed

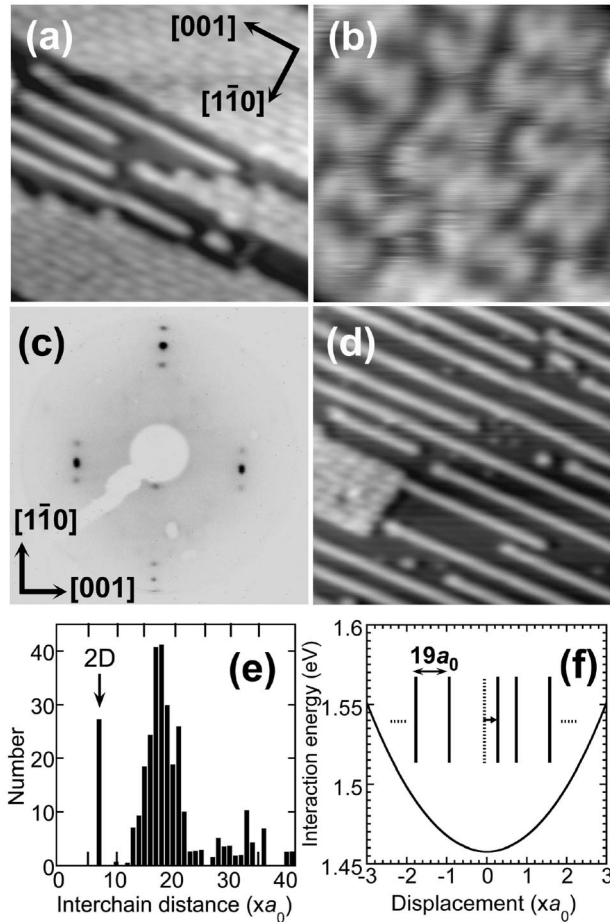


FIG. 3. (a) STM image of Cu(110) covered with multilayer water and subsequently heated to 120 K ($440 \times 440 \text{ \AA}^2$). The image was obtained at 0.03 nA and 0.5 V. The multilayer disappears, and the 2D overlayer and chains coexist on the surface. The 2D overlayer shows a periodic structure of $(6.9 \pm 0.3)a_0$ along $[1\bar{1}0]$. (b) STM image of the 2D island ($90 \times 90 \text{ \AA}^2$). The image was obtained at 0.05 nA and 0.2 V. The 2D overlayer is composed of the 1D chains which are broken and disordered along the chains. (c) LEED pattern for the 2D overlayer, where $\sim \frac{1}{7}$ order spots are observed near the (1×1) spots in the $[1\bar{1}0]$ direction. (d) STM image after heated to 140 K ($440 \times 440 \text{ \AA}^2$). The image was obtained at 0.1 nA and 0.3 V. Parallel chains at nearly regular intervals are observed. (e) Histogram of the distances between two adjacent chains at arbitrary 280 positions. The data were collected from five images acquired under the same condition as (d). The distances are measured between the centers of the chains. Two parallel chains are hardly observed within $12a_0$. The arrow indicates the interchain distance in the 2D overlayer. (f) A simple model to roughly estimate the dipole repulsion between long water chains (inset). The model consists of an ensemble of chains of $100b_0$ length at regular intervals of $19a_0$. We displace a chain in the direction perpendicular to the chains (arrow), and the dipole interaction energy between the displaced chain and the others is calculated as a function of the displacement (solid curve). The energies required to displace a chain by a_0 and $2a_0$ are 10 and 40 meV, respectively. The result qualitatively indicates that the dipole repulsion is strong enough to arrange the chains at nearly regular intervals.

[Fig. 3(d)]. The thermal activation facilitates the chain growth so that the length reaches 1000 \AA . A histogram of the interchain distances, measured between the centers of two adjacent chains, is shown in Fig. 3(e). In the 2D overlayer, the interchain distance is $\sim 7a_0$. Except for the 2D overlayer, the average interchain distance is $19.2a_0$, and two parallel chains are hardly found within $12a_0$. This indicates repulsive interaction between the chains, which inhibits 2D island formation at this coverage. The origin of the repulsion is discussed later.

A structural model of the chain is tentatively proposed in Fig. 4, based on the registry and dimensions determined by STM. We assume that the chain is composed mainly of water cyclic hexamers and that water is adsorbed on top of Cu atoms [17]. The water hexamer is known as a stable building block of water aggregates on Pd(111) at 100 K [9]. The model structure of the chain includes five inequivalent water molecules (A–E) on the first (B and C) and second (A, D, and E) layers of the surface. Molecule D can be considered as a “bridging” species of the hexamers [9], and each hexamer appears as a protrusion in the STM images. The distorted hexagon in boat conformation is neither a type of planar hexamer rings [9] nor a nearly flat hexagon [4] proposed on close-packed metallic surfaces. The nearest-neighbor distance of Cu atoms is 7% shorter than that of the truncated I_h structure. Thus, water molecules may be located off the center of the Cu atom along the row to release the stress. Within this model, it seems that the interchain distance of $7a_0$ is too far for the chains to form a 2D overlayer via hydrogen bondings. However, we infer from Fig. 3(b) that the chains are bonded via water molecules which are provided by breaking the 1D network.

Static interaction between water molecules is classified mainly into long-range (dipole-dipole repulsion) and short-range (hydrogen-bonding attraction) ones [1]. Is the dipole repulsion responsible for the long intervals between the chains? It is roughly evaluated using a simple model of chain array shown in the inset in Fig. 3(f). A dipole moment of adsorbed water molecules was estimated from a work function measurement to be 0.9 D [12]. For a qualitative argument, we approximate the zigzag chain with a line, along which seven dipoles are arranged per b_0 , and consider an infinite ensemble of chains of $100b_0$ length at regular intervals of $19a_0$ [18]. The approximation is justified since the interchain distance ($19a_0$) is much larger than the half width of the chain ($\sim 2a_0$). We displace a chain in the direction perpendicular to the chains, and the dipole interaction energies between the displaced chain and the others are calculated as a function of the displacement [Fig. 3(f)]. The energies required to displace the chain by a_0 and $2a_0$ from the equilibrium are 10 and 40 meV, respectively. The Boltzmann distributions of the displacement by 0, $\pm a_0$, and $\pm 2a_0$ at 140 K are 0.51, 0.45, and 0.04, respectively. Note that including the image dipoles

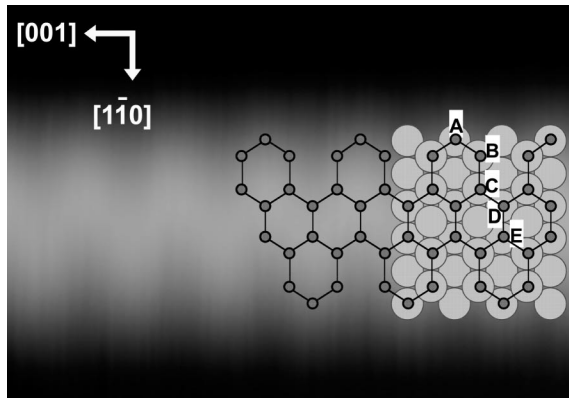


FIG. 4. A tentative model structure proposed for the water chain on Cu(110), superimposed on the STM image obtained at 0.05 nA and 0.3 V ($45 \times 31 \text{ \AA}^2$). The white circles indicate Cu atoms. Orientation of the proton in the network is unknown, and water molecules are depicted by gray circles. The chain consists of five inequivalent water molecules (A–E). The solid lines indicate hydrogen bondings between water molecules.

would further increase the repulsion. This calculation qualitatively indicates that the dipole-dipole repulsion is certainly responsible for the observed intervals between the chains. At high coverage, short-range hydrogen-bonding interaction may result in the coexistence of the chains and 2D overlayer [Fig. 3(a)].

Finally, we mention a discrepancy between the LEED results. The 2D water overlayer gives rise to the fractional-order spots in the $[1\bar{1}0]$ direction [Fig. 3(c)] in agreement with the STM result. On the other hand, the previous LEED studies commonly reported a $c(2 \times 2)$ pattern for water-adsorbed Cu(110) [10–14]. We found that this pattern results from electron irradiation during the LEED experiments. After the water-covered surface was irradiated by electron and subsequently heated to 160 K, we observed a sharp $c(2 \times 2)$ pattern. This pattern, however, did not appear when we probed an area apart from the irradiated region of the surface. This indicates that the $c(2 \times 2)$ pattern results from the electron irradiation, possibly inducing the dissociation of water molecules [16].

In summary, we observed 1D water chain growth on Cu(110) at 78 K using STM. The chain grows exclusively

in the direction perpendicular to the Cu rows and shows a zigzag structure with a period of $2b_0$. We propose that water hexamers mainly constitute the zigzag 1D chains. Dipole-dipole repulsion works between the chains, which facilitates the 1D chain growth and inhibits 2D island formation. The 2D overlayer appears only at high coverage. We conclude that the discrepancy between the LEED results arises from the electron-induced damage of the water overlayer.

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- [18] According to the model in Fig. 4, seven molecules are involved per b_0 in a chain. We adopt $100b_0$ (362 \AA) as a typical length of the chains. The interval ($19a_0$) corresponds to the average in Fig. 3(e).