Scanning Tunneling Microscopy Studies of Formaldehyde Synthesis on Cu(110)

F. M. Leibsle, S. M. Francis, R. Davis,* N. Xiang, S. Haq, and M. Bowker†

Interdisciplinary Research Centre in Surface Science, University of Liverpool, Liverpool L69 3BX, United Kingdom

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The synthesis of formaldehyde from methanol on oxygen-predosed Cu(110) surfaces has been studied using scanning tunneling microscopy (STM). Sequential STM images show the shrinking of the (2×1) Cu-O islands in the [001] direction and the formation of a (5×2) methoxy-induced reconstruction that incorporates the added-row Cu atoms of the (2×1) reconstruction. The decomposition of methoxy to formaldehyde occurs upon desorption; STM images show methoxy islands shrinking in the [001] direction and the release of incorporated Cu atoms.

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The study of reactions on surfaces can be broken down into three distinct questions: How does the reaction occur on the surface, what do the reaction products do while they are on the surface, and how do they leave the surface? The reaction of methanol on clean and oxygen-covered Cu surfaces has, in the past, been studied extensively on both single crystals [1–7] and supported catalysts [8,9], the syntheses of formaldehyde and methanol being the driving forces for such work. The work of Wachs and Madix [1] has shown that on Cu(110) the presence of surface oxygen helps to convert methanol to methoxy through a Langmuir-Hinshelwood process (a reaction between two chemisorbed species). The pathway for this reaction is

$$2CH_3OH_{(ad)} + O_{(ad)} \rightarrow 2CH_3O_{(ad)} + H_2O_{(g)}.$$

Upon heating to above 300 K, formaldehyde is produced through

$$2CH_3O_{(ad)} \rightarrow 2CH_2O_{(g)} + H_{2(g)}.$$

In this Letter, we demonstrate the use of scanning tunneling microscopy to follow the reaction pathway corresponding to the synthesis of formaldehyde from methanol on oxygen-predosed Cu(110) surfaces. Sequential images show the shrinking of the initial (2×1) Cu-O islands in the [001] direction and the evolution of a (5×2) methoxy-induced surface reconstruction. In addition, we report for the first time atomic resolution images of steps preceding the thermal desorption-decomposition process: the breakup of methoxy islands. Sequential images show directly the role of island size and crystallographic direction in this process. These images also reveal that the (5×2) methoxy-induced structure is not an ordered overlayer but an actual reconstruction of the Cu(110) surface that involves added Cu atoms.

Our scanning tunneling microscope (STM) results were obtained in an ultrahigh vacuum (UHV) chamber with a base pressure of 1×10^{-10} mbar. The STM used in this study was a commercial model from Omicron Vacuumphysik. The chamber also contained facilities for ion bombardment, low energy electron diffraction (LEED), and a quadrupole mass analyzer for checking gas purities. The sample was mounted on a Ta baseplate with Ta clips. Sample heating was accomplished by electron beam bombardment with the electrons striking the back of the baseplate. Sample cooling was achieved by bringing the baseplate into contact with a liquid nitrogen cooled cold finger. Sample temperatures were monitored by means of a chromel-alumel thermocouple mounted on the sample manipulator approximately 2 cm away from the sample. The Cu(110) surface was prepared by mechanical and electrochemical polishing and cleaned *in vacuo* by repeated cycles of argon ion bombardment and annealing to 720 K until a sharp (1×1) pattern was observed by LEED. After cooling the sample down to near room temperature, the sample was placed into the STM and dosed with oxygen to form submonolayer coverages of the (2×1)O reconstruction. STM measurements were used to calibrate the oxygen doses. The sample was then removed from the STM and placed back into the manipulator and cooled to 270 K and then dosed with 10 L of methanol (1 L = 10^{-6} Torr sec). The sample was then reinserted into the STM and reimaged. There are no facilities for heating or cooling within the STM itself, so all measurements were made with the sample either at room temperature or in the process of warming up to or cooling down to room temperature.

Figure 1(a) shows a typical area of the Cu(110) surface after dosing with 5 L of oxygen. The image shows long narrow islands of the (2×1)O added-row reconstruction which are separated by areas of the (1×1) clean surface which appear featureless in our STM images. The long direction of these islands is in the [001] direction of the substrate. The images obtained were consistent with the many previous STM results for this system [10–12]. Figure 1(b) shows a typical area after being cooled to 270 K and dosed with 10 L of methanol. In accordance with the expected chemistry of the reaction, the amount of surface area covered by the (2×1)O reconstruction has diminished significantly; furthermore in place of the featureless clean surface, we see that the surface is composed of "zigzag" chainlike structures running in the [001] direction separated by areas showing a $c(2\times2)$ periodicity. We observe zigzag chains adorning

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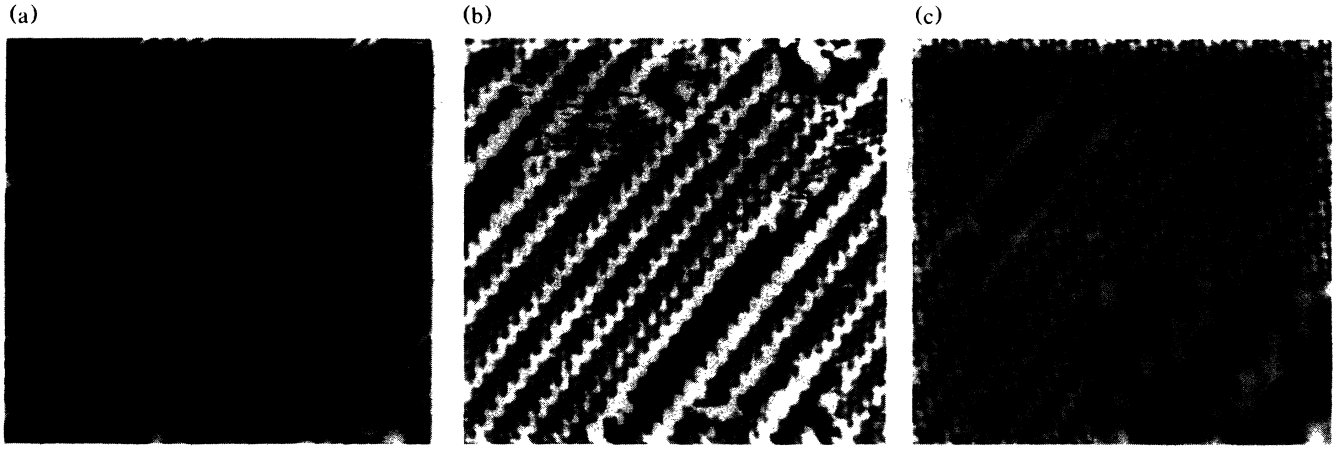

FIG. 1. 200 Å×200 Å areas of the Cu(110) surface. (a) Following 5 L dose of oxygen, this image shows areas of the clean surface and the (2×1) added-row O reconstruction (sample bias $V=3.0$ V, $I=1$ nA). (b) After cooling and dosing with 10 L methanol, this image shows (2×1) areas coexisting with methoxy-induced "zigzag" chain and $c(2\times2)$ structures. (c) Similar area as (b) after 40 min time; the amount of (2×1) area has been reduced and the surface has evolved into a (5×2) reconstruction. A (5×2) unit cell is outlined within the inset in (c).

the sides of the remaining (2×1) islands. The surface structure was also observed to evolve with time in two respects. First the number of zigzag chains on the surface increased at the expense of the $c(2\times2)$ areas. These zigzag chains were observed to grow in the [001] direction and to move laterally in the $[1\bar{1}0]$ direction until the vast majority of the surface was covered by (5×2) unit cells consisting of zigzag chains separated by $c(2\times2)$ subunits. Furthermore, areas of the (2×1)O reconstruction were still being reacted away. Figure 1(c) shows a typical area of the surface 40 min after the image taken in Fig. 1(b) was obtained; the inset in Fig. 1(c) shows the (5×2) unit cells in greater detail. If all the bright features observed in the $c(2\times2)$ and (5×2) areas are methoxy derived then the corresponding methoxy coverages for the two areas are 0.5 and 0.4 ML (monolayer), respectively. This would imply that some methoxy is lost as the surface is driven into a (5×2) configuration. The (5×2) structure was not reported in a previous LEED study [2], however, in another study, using a somewhat different sample preparation method, a heavily streaked LEED pattern, interpreted to be a (4×2) pattern, was observed [7]. We have observed the (5×2) LEED pattern from three separate Cu(110) crystals in three separate UHV systems where thermal-programmed desorption (TPD) and x-ray photoelectron spectroscopy (XPS) measurements were also performed [13]. The TPD results duplicated those of previous studies [1,3]. We note that the (5×2) LEED pattern is extremely sensitive to the electron beam lasting only about 20 s while the sample temperature was maintained at 250 K. The pattern is actually a glide line structure with systematic spot absences in the [001] direction.

This process by which remaining (2×1)O islands are reacted away can be seen in Fig. 2, where four images taken sequentially of the same area are shown. We see confined areas of the (2×1)O reconstruction shrinking over a period of 9 min and being replaced by zigzag chains and $c(2\times2)$ subunits. The (2×1) island in the upper left hand corner of Fig. 2(a) consisting of 44 Cu atoms and presumably a similar number of O atoms, decreases to 38 Cu atoms in Fig. 2(b), the 16 atoms in Fig. 2(c), and has disappeared entirely in Fig. 2(d). These images are representative of others taken in this study, and show that the (2×1) islands appear to shrink in an anisotropic fashion: They diminish in length in the [001] direction. We infer from this that the conversion of methanol to methoxy occurs via the removal of oxygen from the ends of the (2×1)O islands. This behavior is considerably different than that recently reported for the reaction of H_2S on a Ni(110)-(2×1)O surface, where $c(2\times2)$ sulphur islands were observed to nucleate randomly across the surface [14].

We repeated these experiments using increased oxygen doses. This was found to lead to a decrease in the amount of methanol that would adsorb onto the surface, consistent with molecular beam studies [5]. On these surfaces, the amount of oxygen present was too high to be completely reacted away and long islands of the (2×1)O reconstruction still remained on the surface. Between the islands, methoxy-induced structures were present as were observed in Figs. 1 and 2.

We discovered during this phase of the experiment that if we simply waited long enough for the sample to warm to room temperature, we could observe the gradual disappearance of the methoxy-induced structures from the surface. Since methoxy desorbs by decomposing into formaldehyde and hydrogen [1,3–6], we believe that we are observing one of if not the final stage of formaldehyde synthesis from methanol: the breakup of the methoxy is-

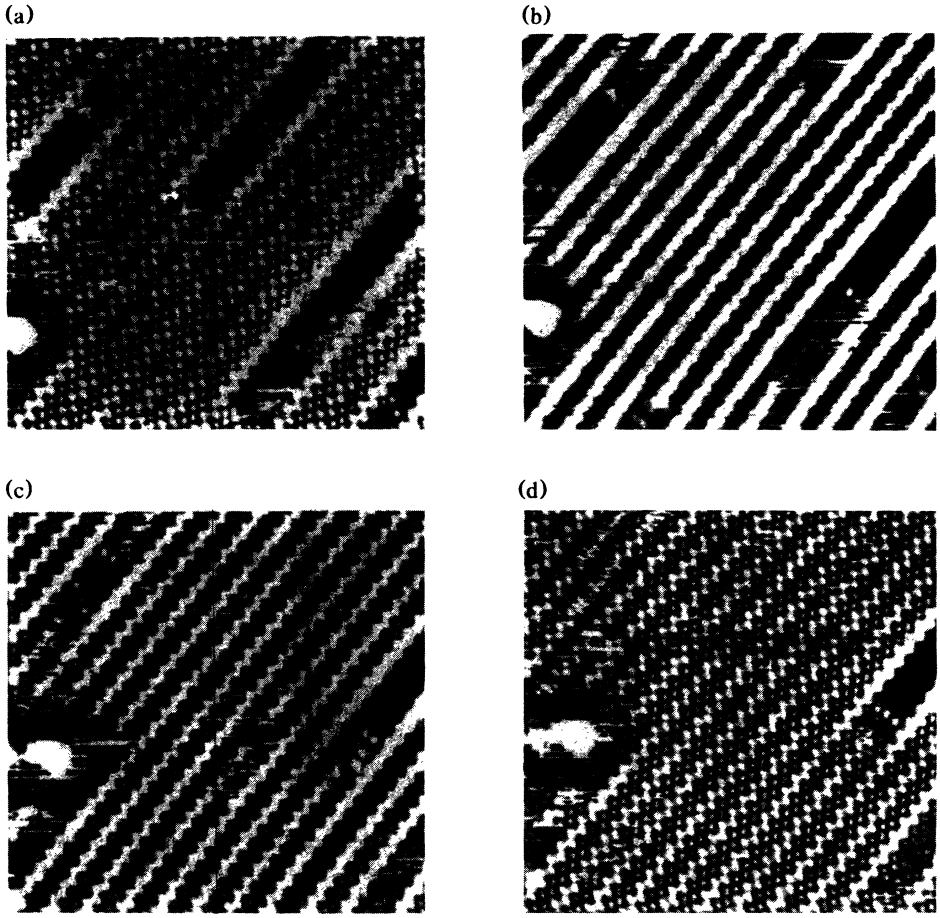

FIG. 2. (a)–(d) Four 200 Å ×200 Å images taken sequentially of the same area of the surface. These images show the (2×1) Cu-O islands being reacted away. Cu-O islands shrink in the [001] direction. (a) $V=-0.5$ V, $I=1.0$ nA; (b) $V=2.0$ V, $I=1.0$ nA; (c) $V=1.0$ V, $I=1.0$ nA; and (d) $V=0.5$ V, $I=1$ nA.

lands. To further explore this, we repeated these experiments using deuterated methanol (D_3COD) and observed the formation of the same methoxy-induced structures but not their disappearance, consistent with the 30 K higher decomposition temperature of D_3CO on Cu(110) [5].

The disappearance of methoxy islands depended quite critically on their size. In Fig. 3, two isolated "zigzag chains" present in (a) have disappeared in (b) and a third has diminished in length. We found this behavior to be typical; isolated zigzag chains were the first to disappear and often could be observed shrinking in the [001] direction. Wider islands could be observed to disappear next, and in general, we found that, under these conditions, the wider the island, the longer it remained on the surface. As islands disappeared, we could observe the island length shrinking in the [001] direction, but we never observed a diminishing of island width. Figures 3(c)–3(e) show the disappearance of a large island containing over 130 (5×2) unit cells. Methoxy-related features disappear from the island edge close to the base of a nearby step while the interior of the island remains intact. As this island disappears, the base of the step grows outward. In STM studies of the Cu(110)-(2×1)O system, the removal of Cu atoms from step edges as (2×1) islands were formed on the terraces was considered conclusive evidence that the (2×1) reconstruction involved added-row Cu atoms [11,12]. Here, the addition of Cu atoms to step bases upon the breakup of methoxy islands must be viewed as being conclusive evidence that the (5×2) methoxy-induced structure is an actual surface reconstruction involving added Cu atoms. We have measured the ratio of areas covered by the methoxy island and areas added to step edges upon desorption and conclude that the (5×2) methoxy reconstruction involves at least 0.4 of added Cu atoms. We note in Figs. 3(c)–3(e) that as the methoxy island disappears, no change occurs in the nearby (2×1)O islands suggesting that no oxygen is incorporated in the (5×2) areas.

To summarize, we have used scanning tunneling microscopy to follow the reaction pathway corresponding to the synthesis of formaldehyde on oxygen-predosed Cu(110) surfaces. Images show the shrinking of (2×1)O island edges in the [001] direction and the evolution of a methoxy-induced (5×1) reconstruction that incorporates added Cu atoms. Sequential STM images show the disappearance of these methoxy-related structures as the sample warms, this was found to depend critically on is-

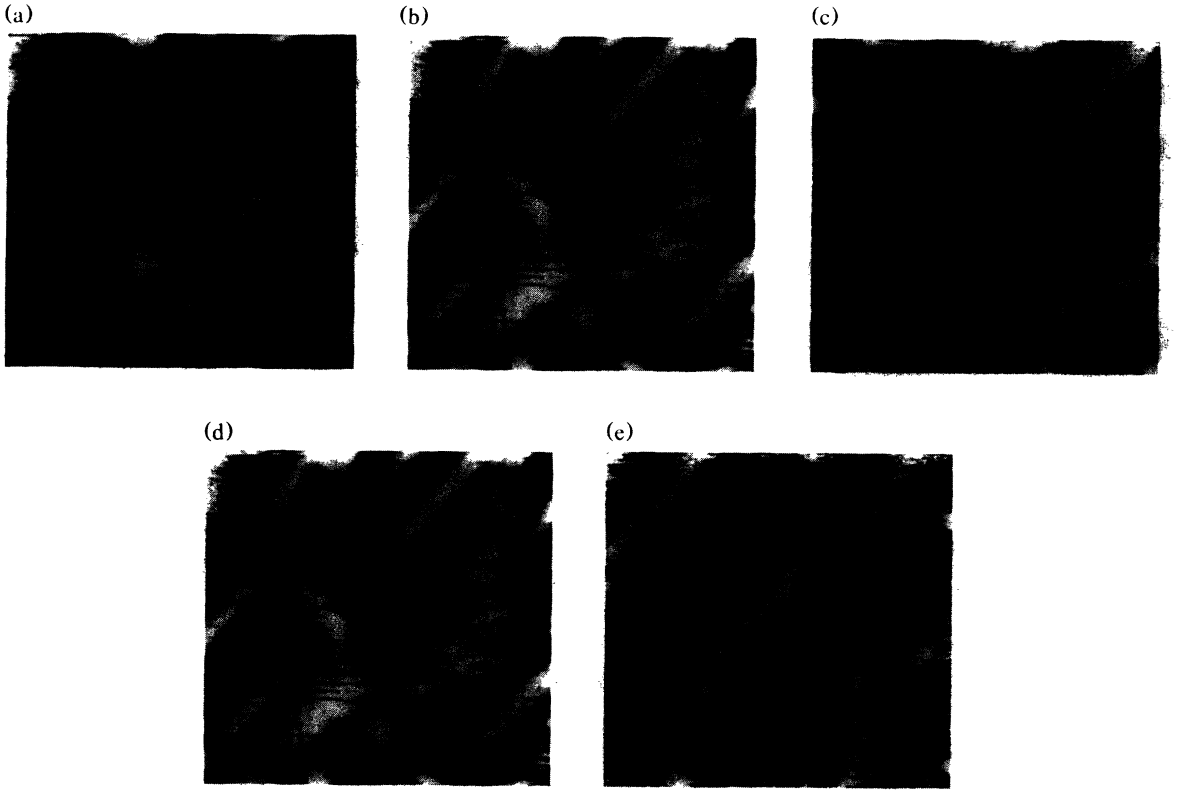

FIG. 3. STM images showing methoxy islands disappearing as the sample warms to room temperature. (a) and (b) show small isolated "zigzag" chains disappearing first; tick marks indicate chains that are present in the 200 Å×200 Å area in (a) but have either completely disappeared in (b) or significantly shrunk. (c)–(e) are sequential images of a larger area (300 Å×300 Å) showing the disappearance of an island containing over 130 (5×2) unit cells. This results in both a shrinking of the island in the [001] direction and the subsequent addition of Cu atoms to the base of a nearby step; tick marks show the advance of the step ($V=-2.5$ V, $I=1$ nA).

land size, with smaller islands disappearing from the surface first. The breakup of the islands appears to occur from the island edges resulting in a shrinking of island length in the [001] direction and the release of incorporated Cu atoms.

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*Present address: Physics Department, University of Warwick, Coventry CV4 7AL, United Kingdom.
†Also at Chemistry Department, University of Reading, Whiteknights Park, P.O. Box 224, Reading RG6 2AD, United Kingdom.

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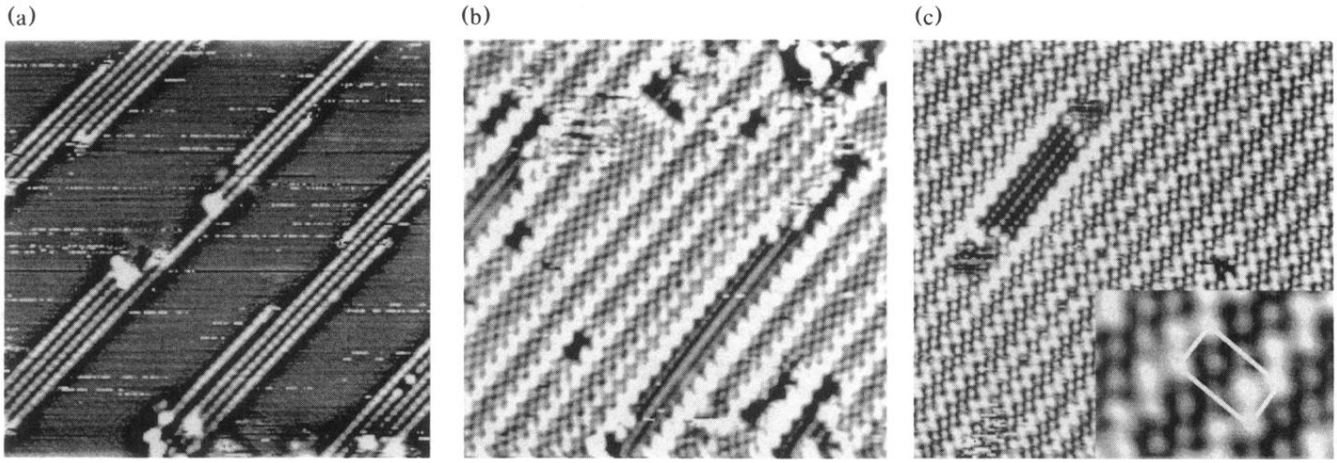

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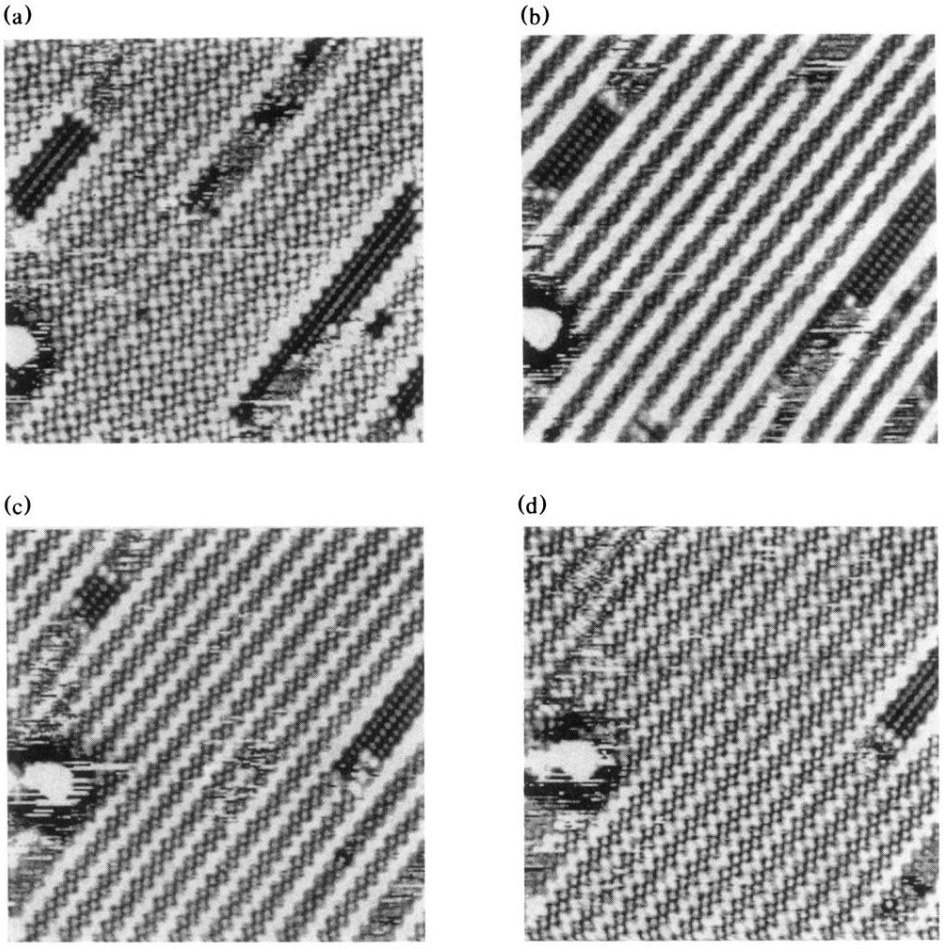

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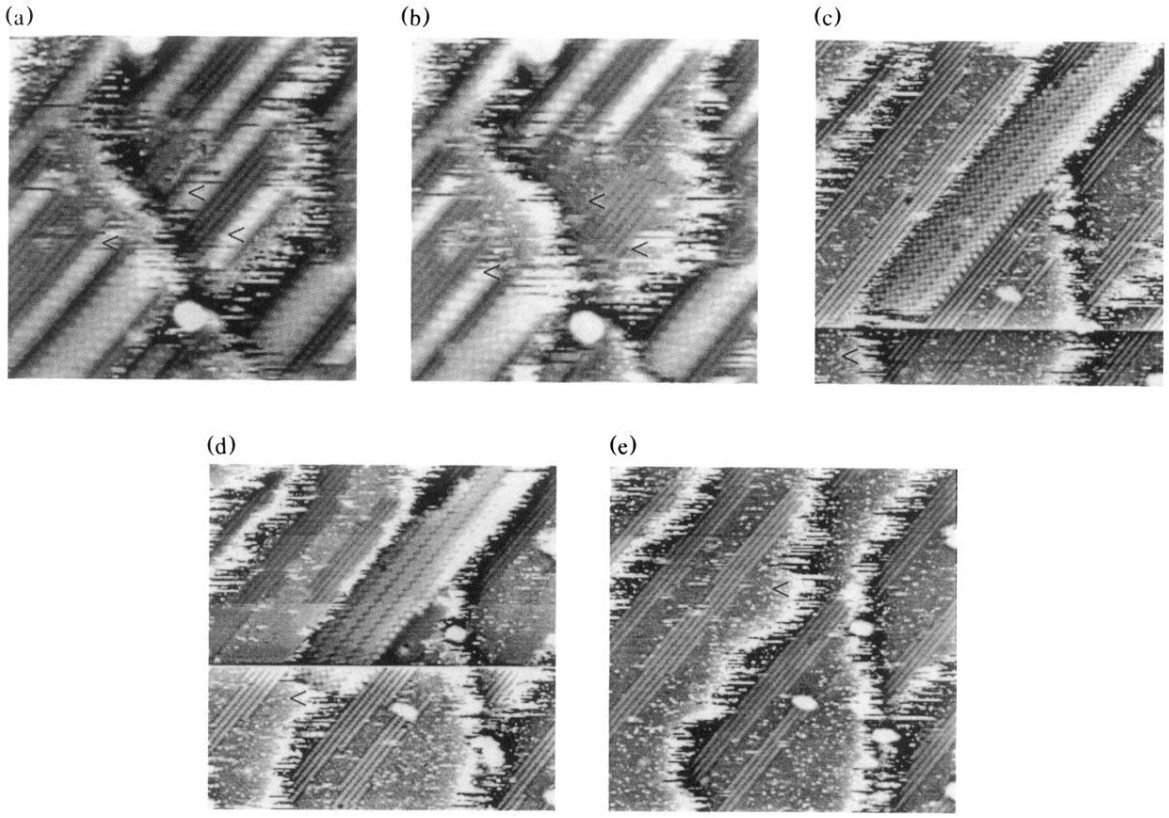

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