

Nucleation and growth of a H-induced reconstruction of Ni(110)

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The dynamics of the hydrogen-induced reconstruction of Ni(110) at room temperature has been studied by scanning tunneling microscopy. The nucleation and growth of the "streaky" (1×2) H phase reveal that the reconstruction is very local in nature and evolves as a combined added and missing-row model with -Ni-H- chains growing preferentially along the $[1\bar{1}0]$ direction. The hydrogen chemisorption induces a substantial mass transport, which explains why the restructuring is an activated process.

It is well known that for adsorbates that interact strongly with the substrate, such as oxygen, carbon, and nitrogen, the chemisorption is often accompanied by a restructuring of the surface, which completely changes the bonding at the surface and creates new ordered structures with a significantly altered atomic density in the topmost layers.¹ For an adsorbate such as hydrogen for which the interaction with the metal is so weak that it desorbs around room temperature (RT), the energy cost to break a nearest-neighbor metal bond is higher than the energy gained by chemisorption of hydrogen on a restructured rather than on a virgin metal surface.² Thus hydrogen will often either chemisorb in lattice-gas structures on the undistorted metal surface or induce a reconstruction for which the energy cost in breaking the metal bonds is shared in a collective fashion between a sizable fraction of a monolayer of hydrogen adsorbates. The latter scheme often results in reconstructions with no long-range mass transport as for the row-pairing model.³ However, in the present Rapid Communication it is shown unequivocally that hydrogen adsorption indeed does induce a reconstruction of the Ni(110) surface where metal atoms are moved around over several unit cells.

We have used scanning tunneling microscopy (STM) to study in real space and time the dynamics, i.e., the nucleation and the growth of the "streaky" (1×2) hydrogen phase on Ni(110), with elongated half-order low-energy electron-diffraction (LEED) spots, indicating a long and short coherence length along the $[1\bar{1}0]$ direction and the $[001]$ directions, respectively. There has been a long-standing controversy concerning the structure of this (1×2) phase, and the driving force for its formation is still under vigorous dispute⁴⁻¹⁴ although the structure has been studied since the early days of modern surface science.¹⁵ We show unequivocally that the reconstruction evolves as a combined added- and missing-row model in which added rows of -Ni-H- atoms grow preferentially along the $[1\bar{1}0]$ direction, i.e., a long-range mass transport is *directly* observed. Furthermore, the results reveal unambiguously that the reconstruction is of a very local nature. Single hydrogen atoms can "pull" Ni atoms out into new highly anisotropic -Ni-H- chainlike structures. Based on the present results for the H/Ni chemisorption system, a simple coherent picture evolves which is felt to be of general importance for a detailed understanding of

the interaction between chemisorbed atoms and metal surfaces.

The experiments were performed with a fully automated STM described elsewhere.¹⁶ The images shown below, recorded in the constant-current mode, are typically obtained in ≈ 3 sec. The fast scanning allows consecutive images to be stored and later replayed in the form of STM movies,¹⁶ thereby visualizing structural changes during hydrogen adsorption. The bias voltage (V_t) is applied to the sample with the tip at virtual ground, and normally electrons tunnel from filled tip states to empty sample states. The Ni(110) crystal was cleaned by repeated Ne sputtering and annealing and oxidation-reduction cycles until a perfect, impurity-free (1×1) surface was obtained, as observed by LEED, Auger, and STM. The (1×2) phase was produced by exposure to hydrogen of < 5 L ($1 \text{ L} = 10^{-6}$ Torrsec) at RT.

Figure 1(a) shows an STM image of the Ni(110) surface prior to hydrogen exposure. As seen, the individual Ni atoms are indeed resolved on this (1×1) surface, and the corrugations along and perpendicular to the close-packed rows are ≈ 0.04 and ≈ 0.08 Å, respectively.¹⁷

The formation of isolated chains, added rows, of atoms directed along the close-packed direction is initiated when the surface is exposed to hydrogen at RT for an exposure ≤ 0.1 L. The chains appear at a height of ≈ 0.3 Å above the surface, and they are located midway between the close-packed rows of the (1×1) surface [Fig. 1(b)]. As will be discussed below, the chains are interpreted as added -Ni-H- rows directed along the $[1\bar{1}0]$ direction. From Figs. 1(b) and 1(c), we conclude that the periodicity of the protrusions along the chains is 2.5 ± 0.1 Å, equal to the interatomic distance along the $[1\bar{1}0]$ direction, and the protrusions of the chains are situated midway between the $[001]$ rows of the bare (1×1) surface. Associating the protrusions with Ni atoms, the chains are thus consistent with a fcc stacking sequence. The hydrogen atoms, which bind to the Ni atoms, are, however, not observed in the STM topographs in the V_t range from -3 to $+3$ V.

In the following, we will address the important issue of the growth mode of the reconstructed phase. The dynamics of the reconstruction was studied by recording consecutive images during the inlet of hydrogen at RT, and Figs. 2 and 3 are snapshots from such STM movies. It appears from our studies that the nucleation and growth of

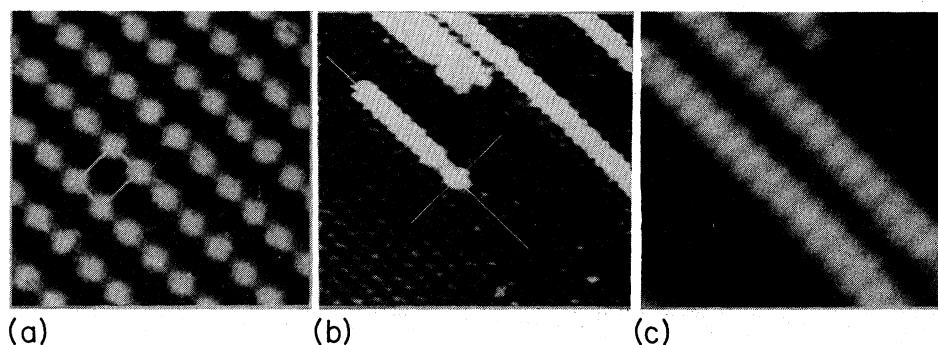


FIG. 1. (a) Atomically resolved STM topograph ($21 \times 21 \text{ \AA}^2$) of a bare (1×1) Ni(110) surface ($V_t = 0.08 \text{ V}$ and $I_t = 0.70 \text{ nA}$); the corrugation along the $[1\bar{1}0]$ and $[001]$ directions are 0.04 and 0.08 \AA , respectively. (b) STM topograph ($71 \times 75 \text{ \AA}^2$) showing the registry of the added rows with respect to the (1×1) Ni surface ($V_t = 0.004 \text{ V}$ and $I_t = 3.01 \text{ nA}$). (c) Atomically resolved STM topograph ($31 \times 32 \text{ \AA}^2$) of two added rows. The periodicity along the $[1\bar{1}0]$ direction is 2.5 \AA ($V_t = 0.002 \text{ V}$ and $I_t = 2.90 \text{ nA}$). The apparent height of an added row is $\approx 0.3 \text{ \AA}$.

the $ST(1 \times 2)$ phase depend on whether it is occurring on large, flat terraces or close to monatomic steps. On terraces far away from steps, we observe that the reconstruction develops through the removal of Ni atoms, as missing rows (black patches), in the $[1\bar{1}0]$ direction and nucleation of these Ni atoms into added rows (white chains) directed in the same direction *on* the terrace. From Fig. 2, we see how the missing and/or removed Ni rows and added -Ni-H- rows are initially randomly distributed in the $[001]$ direction, but at later times, when the hydrogen coverage has increased, the missing and/or added rows appear to be spaced with a preferred spacing of $7.2 \pm 0.1 \text{ \AA}$, i.e., twice the $[001]$ lattice spacing, consistent with the observation of a streaky (1×2) LEED pattern.¹⁸ Scanning a large area and following the growth to hydrogen saturation, the total area of the patches is found to be equal to the total area of the added rows,¹⁹ from which we immediately can determine the Ni density in the $ST(1 \times 2)$ structure to be 0.5 ML (monolayers).

In contrast to this, the growth mode close to a step edge is illustrated in Fig. 3 where a fairly large area of $\approx 520 \times 520 \text{ \AA}^2$ [Fig. 3(a)] was scanned. In the consecutive images 3(b) to 3(d) we zoom in on the region in Fig. 3(a) close to the edge. In this region it is observed that Ni atoms are removed by creating missing Ni rows, directed along the $[1\bar{1}0]$ direction, into the upper terrace from the

step edge. These removed Ni atoms diffuse out on the terrace where they react with the impinging hydrogen atoms and nucleate into (1×2) chains and/or islands. These added rows grow highly anisotropically along the close-packed direction, and in the region in Fig. 3(d), close to the step edge, we observe a perfect (1×2) structure, while there is still a (1×1) structure on the upper terrace in Fig. 3(d). The fact that a perfect (1×2) structure is observed in certain areas, whereas on the terrace [Fig. 3(a)] next to this ordered area, missing and added rows are randomly distributed, is again consistent with the streaky (1×2) LEED pattern.

We can thus conclude that the reconstruction proceeds as a combined added- and missing-row growth mode with a considerable long-range mass transport. It is seen that not only do the added -Ni-H- rows on the terraces locally have a (1×2) structure, but the same holds for the missing rows created either by "digging" into the step edge or down on the flat terrace. The growth mode is clearly inconsistent with both a pairing-row model,^{6,7} for which no long-range mass transport occurs, and with a conventional missing-row model where one would observe a buildup of Ni at the step edge; we observe just the opposite.

From the present dynamical STM studies, we can, furthermore, conclude that the reconstruction is of very local nature. Single hydrogen atoms are indeed able to

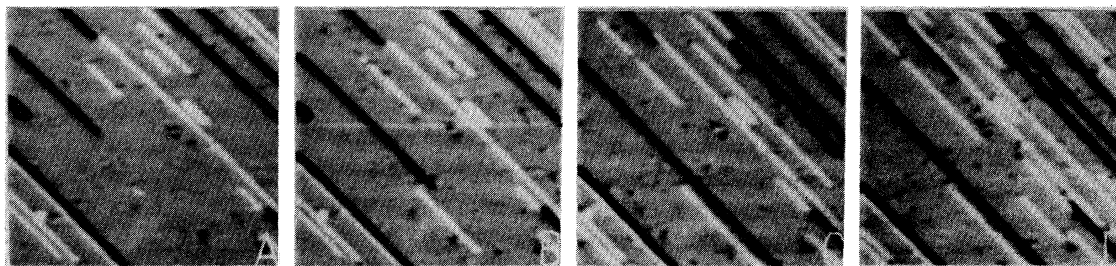


FIG. 2. Four snapshots from a STM movie during hydrogen exposure over a region of $306 \times 321 \text{ \AA}^2$ ($V_t = 0.08 \text{ V}$ and $I_t = 0.67 \text{ nA}$), showing the dynamical growth of the $ST(1 \times 2)$ phase. The black and white rows in the $[1\bar{1}0]$ direction are missing and added rows, respectively.

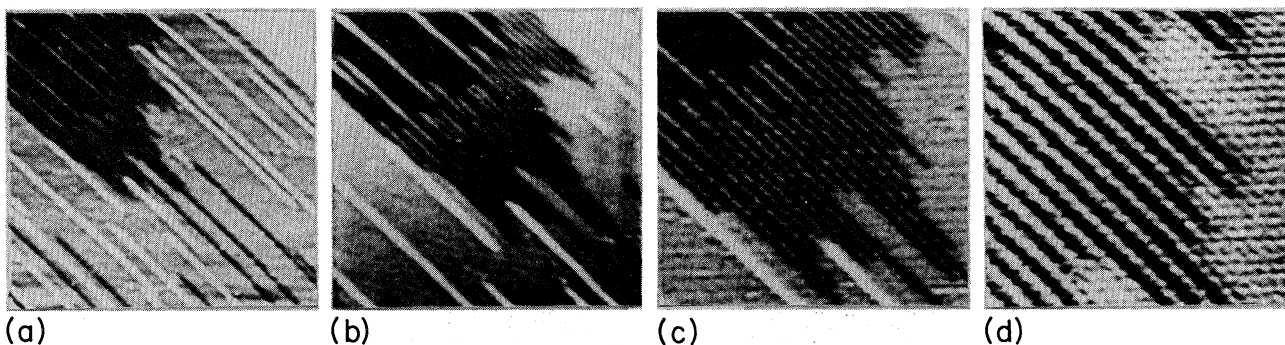


FIG. 3. Series of STM topographs ($V_t=0.005$ V and $I_t=2.4$ nA) close to a step edge. (a) is of a region of $(510 \times 535 \text{ \AA}^2)$, and in the consecutive images, we zoom in on the region in (a) close to the step edge, and the regions of (b) to (d) are $(306 \times 321 \text{ \AA}^2)$, $(204 \times 214 \text{ \AA}^2)$, $(102 \times 107 \text{ \AA}^2)$, respectively.

“pull out” Ni atoms from the surface, and these Ni atoms combine into the -Ni-H- chains. This strongly opposes a view often stated in the literature, viz. that the reconstruction is restricted to well-ordered structures where a sizable fraction of a monolayer of adsorbates can act to distort the surface in a collective fashion.

When scanning in a hydrogen atmosphere ($p > 10^{-8}$ mbar) at RT, the density of added and missing rows in the $[1\bar{1}0]$ direction became very high, with perfect (1×2) reconstructed areas of several hundred Angstrom. When the hydrogen was pumped away ($p < 10^{-10}$ mbar), the density of added and missing rows slowly decreased due to thermal desorption of hydrogen from the β_2 state.¹⁰ The picture after 1–2 hours at RT was typically terraces of $\text{Ni}(1 \times 1)$, with a few missing and added rows in the $[1\bar{1}0]$ direction randomly spread in the $[001]$ direction. This is in accord with the observation that the streaks in the LEED pattern disappeared when the hydrogen partial pressure was reduced. When the H coverage is increased, the streaky diffraction pattern returned, and by additional H exposure, the streaks coalesced into fractional-order spots, i.e., a nearly perfect (1×2) reconstruction. This implies that the transition from (1×1) to the $\text{ST}(1 \times 2)$ is reversible and activated since the reconstruction only occurs at elevated temperatures ($T \geq 220$ K).

Based on the present results, a simple coherent picture evolves which explains the previously published data on this system. Chemisorption of H on $\text{Ni}(110)$ at low temperatures (LT) ($T \leq 220$ K) leads to the formation of four different lattice-gas structures, the final one being a (2×1) structure at $\theta_{\text{H}}=1$ monolayer (ML).^{4,17} For continued H exposure this structure converts into a (1×2) hydrogen-induced reconstruction which is completed at $\theta_{\text{H}}=1.5$ ML.^{3,4,10,17} However, all the LT phases are metastable and suffer an *irreversible* transition at higher temperatures to the $\text{ST}(1 \times 2)$ hydrogen phase^{4,9–12} which, as discussed above, also can be produced by RT hydrogen exposure. A recent dynamical LEED analysis showed that the $\text{LT}(1 \times 2)$ phase is reconstructed in a pairing-row configuration, i.e., a merely *displacive* reconstruction.³ Hence the $\text{ST}(1 \times 2)$ phase *does not* evolve directly from the $\text{LT}(1 \times 2)$ phase as a small rearrangement of the Ni and H atoms. Rather, the transformation between the two structures upon heating involves a long-

range mass transport. During the phase transformation, in which 0.5 ML of H is desorbed, the surface may momentarily pass through the virgin (1×1) phase,¹⁰ and rapidly proceeds to a $\text{ST}(1 \times 2)$ by a hydrogen-assisted long-range mass transport of the Ni atoms, resulting in the nucleation of the added -Ni-H- rows. It is this mass transport which explains why the phase transformation from the LT to the streaky phase is irreversible.¹⁰ Once the $\text{ST}(1 \times 2)$ phase is formed, there is no way to regenerate the sharp $\text{LT}(1 \times 2)$ structure or the lattice gas phases by cooling in hydrogen gas to below 220 K. Cooling simply freezes the added -Ni-H- rows, consistent with the observation that the LEED pattern slightly improves intensity-wise. Only after an anneal, where the added rows dissolve and Ni atoms diffuse and regenerate the (1×1) structure, can the LT ordered phases be regenerated by hydrogen exposure at cryogenic temperatures. The previously reported activation energy of 25 kJ/mol (Ref. 11) for the transformation from the LT phases to the $\text{ST}(1 \times 2)$ at $T \geq 220$ K is thus associated with the *directly* imaged long-range mass transport. The observed removal and nucleation of diffusing Ni atoms is the rate-determining step in the reconstruction.¹²

Concerning a detailed atomic model for the $\text{ST}(1 \times 2)$ phase, the STM data show that the Ni atoms locally form a $p(1 \times 2)$ added-row structure, with $\theta_{\text{Ni}}=0.5$ ML, associating the Ni atoms with the protrusions of the chains. The hydrogen atoms, which bind to the Ni atoms, are not directly observed in the STM topographs, but both predictions, based on the effective-medium theory,²⁰ and EELS (Ref. 5) measurements, suggest a threefold coordinated site at the inclined rudimentary (111) face of the added row.

Previously, a number of models have been proposed for the “streaky” (1×2) phase such as a mixture of undistorted (1×2) and distorted (2×1) patches,⁵ a “paired row”-like model,^{6,7} a missing-row-type model,^{4,12} and a model where pairs of Ni atoms are statistically formed out of phase in the $[001]$ direction.¹⁰ Recently Kuk, Silvermann, and Nguyen¹⁴ concluded that the structure locally was a (5×2) reconstruction formed by a combination of row-pairing and -missing $[001]$ rows, i.e., the top-layer Ni atoms were paired along the $[001]$ direction by a 0.5 \AA lateral displacement, and every fifth $[001]$ row was missing.

From the present STM results we have seen no evidence at all for a (5×2) structure, and the observation of perfect, intense integer-order LEED spots in the $[1\bar{1}0]$ direction and streaks in the $[001]$ direction appears inconsistent with a (5×2) structure.

In conclusion, we have unambiguously shown the hydrogen-induced restructuring of the Ni(110) surface into the streaky (1×2) phase proceeds by a combined added- and missing-row growth with a substantial long-

range mass transport. This directly explains why the transformation to the streaky phase is an activated process.

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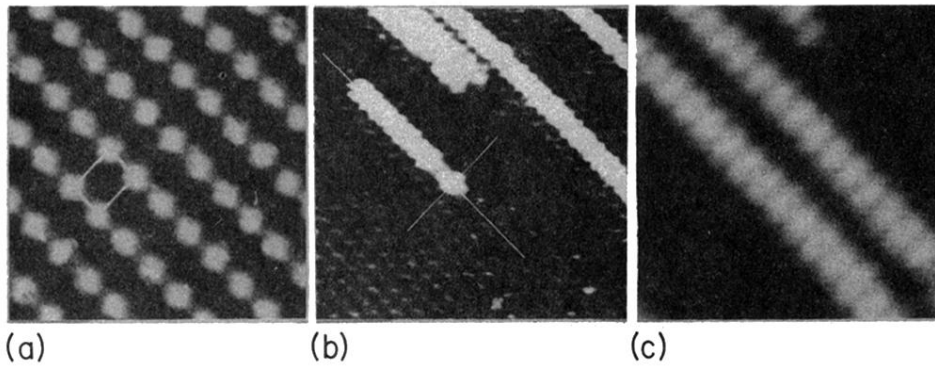


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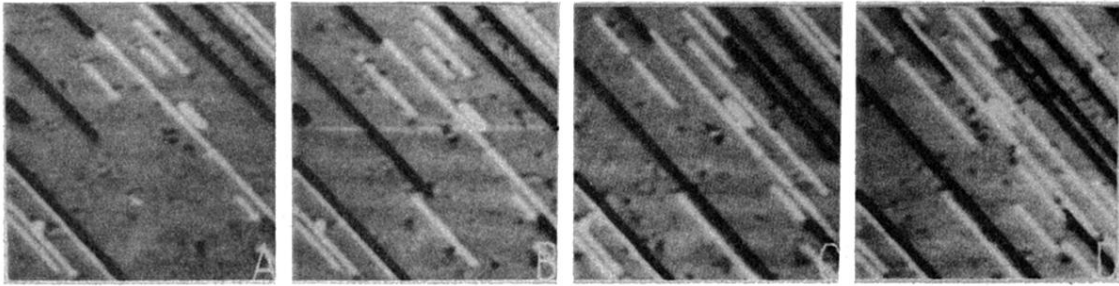


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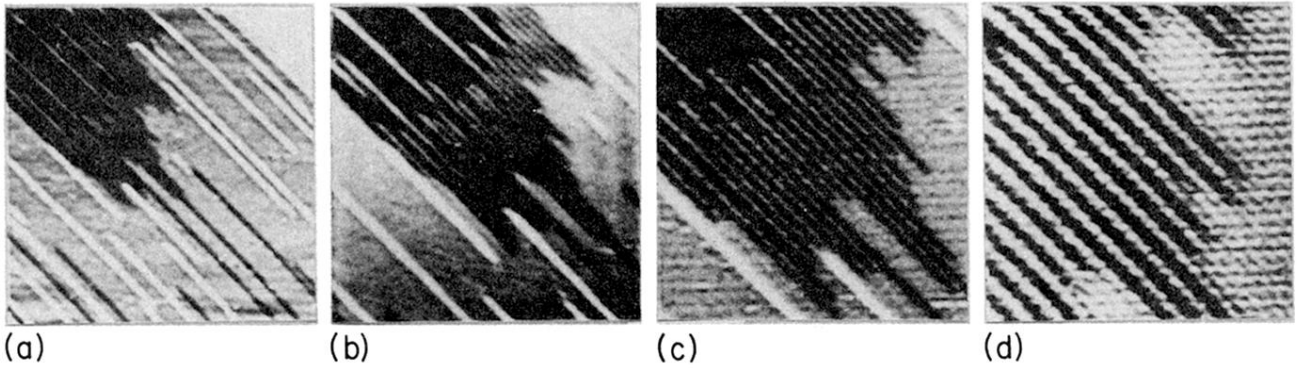


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