Atom-Resolved Studies of the Reaction between H_2S and O on Ni(110)

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(Received 17 September 1992)

The reaction between H_2S and preabsorbed O on Ni(110) has been studied at the atomic level by means of scanning tunneling microscopy (STM). During the reaction, the initially flat $(2 \times 1)O$ structure is replaced by an intermediate rough surface with many small islands and troughs, all covered with a $c(2 \times 2)S$ overlayer. Most surprisingly, this metastable phase converts into the thermodynamically stable $(4 \times 1)S$ reconstructed phase. A new mechanism to activate a surface at the atomic level is suggested.

Scanning tunneling microscopy (STM) has led to unprecedented new structural insight into chemisorption of adsorbates on metal surfaces. Static surface structures as well as snapshots of the dynamics of the chemisorption process, i.e., the nucleation and growth of adsorbate-induced reconstructions, have been recorded in real time and space with atomic resolution [1–4]. These studies suggest that STM has a great potential for studying the reaction between different adsorbates on metal surfaces, i.e., for atom-resolved surface chemistry.

From dynamic STM results, it appears in many cases to be the rule rather than the exception that chemisorption of adsorbates induces a significant restructuring of the metal surfaces, implying that the cost of breaking metal-metal bonds is overcompensated by the energy gained by formation of new metal-adsorbate bonds [2,4]. Thus models for reactions between adsorbates at metal surfaces have to include the coupling to the substrate distortions as a prerequisite for an understanding of important questions such as the following: (i) Does the reaction occur at particularly active sites? (ii) What is the "nucleation and growth mechanism" for the reaction mediated surface structural changes?

In this Letter, we demonstrate how STM can be used as an *in situ* probe to provide unique insight into the mechanisms and the dynamics of surface reactions. The reaction between H_2S and preadsorbed O on the Ni(110) surface has been chosen as a prototype of an adsorbate-adsorbate surface chemical reaction, since reactions between S and O on metal surfaces are important in several catalytical processes [5,6]. The reaction between H_2S and O is followed by studying the surface structural changes at the atomic level during the reaction. It is shown that the initially flat $(2 \times 1)O$ reconstruction, induced by the preadsorbed O, during the reaction is replaced by an intermediate rough surface with many small islands and troughs, all covered with a $c(2 \times 2)S$ overlayer. Most surprisingly, this metastable intermediate phase is transformed into the thermodynamically stable $(4 \times 1)S$ reconstructed phase during continued H_2S exposure at room temperature (RT). The detailed surface morphology turns out to play a crucial role in this transformation since we have previously shown [7] that the

formation of the $(4 \times 1)S$ process is activated and only proceeds at elevated temperatures (≥ 473 K) [7–9]. We will discuss how the present results illustrate a new atomistic view of how metal surfaces can be brought into a highly active chemical state.

The experiments were performed with a fully automated STM [10]. Atomic resolution is obtained on low-corrugated metal surfaces on a routine basis, and STM images can be recorded at a rate of up to three images per second. This dynamic-visualization STM (DVSTM) [2–4] technique makes it possible to follow the time evolution of the surface reactions at the atomic level. The STM images were all acquired in the constant current mode, mainly with positive sample bias voltage (V_t) ranging from 10 mV to 2 V and tunneling current I_t from 0.1 to 2 nA. A comparison to negative-sample-polarity results did not reveal any spectroscopic effects.

We have previously studied in detail the chemisorption of oxygen [2,11] and sulfur [7,9] on Ni(110). Oxygen chemisorbs dissociatively on Ni(110) at RT, and a $(2 \times 1)O$ phase corresponding to an O coverage of $\Theta_O = \frac{1}{2}$ ML (monolayers) develops. From DVSTM studies [11], it has been shown that the (2×1) structure forms via a homogeneous nucleation of low-coordinated -Ni-O- rows along the [001] direction. In Fig. 1(a) is shown a $(2 \times 1)O$ island with an apparent height of ≈ 0.8 Å above the Ni(1×1) terrace. From the registry of the added rows with respect to the underlying (1×1) bulk Ni lattice, we can conclude that the protrusions of the added rows are associated with Ni atoms which are bound together by O atoms chemisorbed in the long-bridge position [12]. The O atoms are not directly visible in the STM topographs at $-2 \leq V_t \leq 2$ V.

At RT, H_2S gas decomposes on Ni(110), leaving chemisorbed S on the surface [13]. As opposed to O, S is at RT chemisorbed in overlayer lattice-gas structures at the unreconstructed Ni(110) surface [7–9]. A $c(2 \times 2)S$ structure is observed at $\Theta_S = \frac{1}{2}$ ML, and from Fig. 1(b) it is seen that individual S atoms, located in the twofold hollow sites, are imaged as protrusions, with a height of ≈ 0.3 Å above the Ni(1×1) terrace [7,9]. On the other hand, if the Ni(110) surface is exposed to sulfur at elevated temperatures (≈ 473 K), we observed an ac-
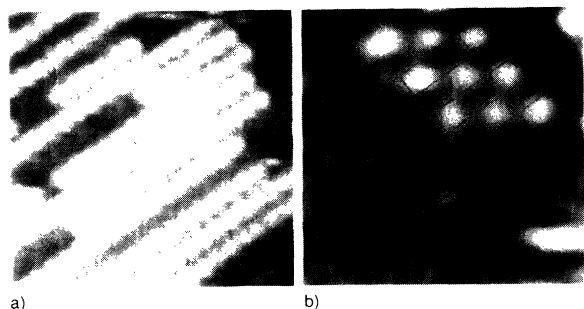
FIG. 1. STM images ($V_t \approx 10$ mV and $I_t = 1-2$ nA) of (a) $(2 \times 1)O$ (63×68 Å^2) and (b) $c(2 \times 2)S$ (31×32 Å^2) islands on Ni(110).

tivated S-induced $(4 \times 1)S$ ($\Theta_S = \frac{3}{4}$ ML [8,13]) reconstruction, the detailed structural model of which is currently under investigation.

The dynamics of the reaction between H_2S and preadsorbed O on Ni(110) was studied by exposing the well-ordered $(2 \times 1)O$ surface [Fig. 2(a)] to H_2S gas ($p \approx 10^{-8}$ mbar) at RT, and STM images were recorded sequentially on the same area. Figures 2(b)–2(f) are snapshots of the surface structure during the reaction after progressively higher H_2S exposures. In the beginning, we observe a random distribution of small irregular black troughs and bright islands next to the troughs [Fig. 2(b)]. The islands and troughs have an apparent height and depth of 0.75 and 0.5 Å, respectively, relative to the $(2 \times 1)O$ terrace. Thus the height difference between the islands and troughs is close to the interlayer distance (1.24 Å) on Ni(110). As the H_2S exposure increases, the characteristic $(2 \times 1)O$ structure gradually disappears, and instead, more troughs and islands are formed [Fig. 2(c)], the average size of which increases only slightly. From a height analysis of STM images over large areas, it can be concluded that the areas of the islands and troughs are identical. Furthermore, it is seen from Fig. 2(c) that both the islands and troughs appear to have a $c(2 \times 2)$ periodicity. Eventually, after an exposure of 20 L of H_2S, the surface appears rough with many small islands and troughs, all exhibiting a $c(2 \times 2)$ structure [Fig. 2(d)]. The average domain size of the islands and troughs is typically smaller than 25×25 Å^2.

For increased H_2S exposure, the small $c(2 \times 2)$ islands suddenly become unstable. They dissolve and, simultaneously, from the islands, one observes [Fig. 2(e)] the growth of low-coordinated rows along the [001] direction; the periodicity along the rows is 1. During the continuous transformation of the islands to the rows, the areas of the $c(2 \times 2)$ troughs gradually decrease, and as more rows are formed, they develop into ordered regions with a periodicity of 4 in the [1$\bar{1}$0] direction. Finally, after a total H_2S exposure to 50 L, all the islands and troughs have disappeared, and the surface ends up locally with a perfectly ordered (4×1) structure, as seen from Fig. 2(f).
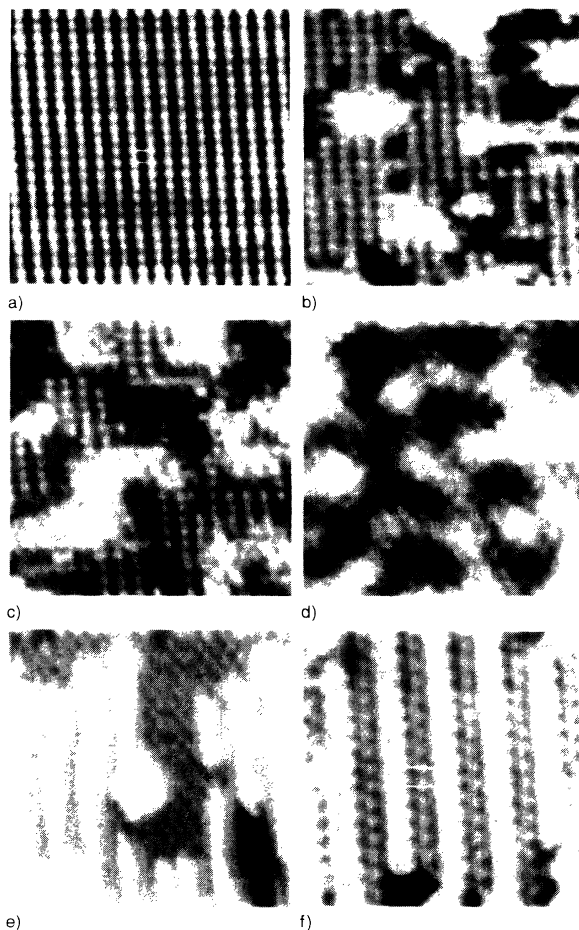

FIG. 2. A series of STM images ($V_t = 10$ mV and $I_t \approx 1-2$ nA) recorded during the reaction, after progressively higher exposure of H_2S. (a) 0 L, (b) 3 L, (c) 8 L, (d) 20 L, (e) 25 L, (f) 35 L. All the images are recorded on an area of 85×91 Å^2 except the last one (f) for which the area is 59×63 Å^2 only.

The $(4 \times 1)S$ structure created at RT contains a certain number of defects, and the average size of the perfect domains is fairly small ($\leq 100 \times 100$ Å^2) which, however, can be increased by postannealing the surface.

How should these reaction-induced surface structural changes be interpreted and understood? It is well documented that H_2S reacts with preadsorbed O on Ni(110) ($\Theta_O = \frac{1}{2}$ ML), resulting in the formation of water which desorbs at RT, leaving chemisorbed S on the surface [13], i.e., $H_2S(g) + O_{ad} \rightarrow H_2O(g)\uparrow + S_{ad}$. The initial phases of the H_2S-O reaction are visualized through the formation of the troughs and islands next to them. When O is removed from the $(2 \times 1)O$ structure the resulting low-coordinated "clean" Ni rows are very unstable. These Ni rows thus relax together and accumulate in small Ni(1×1) islands, leaving Ni(1×1) troughs behind. The fact that the area of the islands and troughs are identical is consistent with a Ni density of $\Theta_{Ni} = \frac{1}{2}$ ML in the

original $(2 \times 1)O$ structure. Sulfur chemisorbs on these $Ni(1 \times 1)$ areas, and $c(2 \times 2)S$ troughs and islands result, as observed in Fig. 2.

This structural identification is confirmed by the STM topograph shown in Fig. 3, where the registry between the $c(2 \times 2)S$ structure on the islands and in the troughs is compared with the registry of the coexisting $(2 \times 1)O$ phase. The grid superimposed on the STM topograph in Fig. 3(a) is derived from the clean (1×1) surface coexisting with the $c(2 \times 2)S$ island in Fig. 1. The corners of the grid thus indicate the positions of the atoms in the underlying $Ni(1 \times 1)$ lattice. It is seen in Fig. 3(a) that in the troughs, the S atoms (the protrusions) of the $c(2 \times 2)$ structure are located in the twofold hollow sites, as are the Ni atoms in the -Ni-O- rows of the (2×1) structure, consistent with our previous findings. The $c(2 \times 2)S$ structure in the troughs and the $(2 \times 1)O$ structure share the same substrate layer. For the islands, it is seen that the protrusions are shifted with half a lattice distance in both the $[1\bar{1}0]$ and the $[001]$ directions, confirming the fact that S on the island, which is one substrate layer higher than the trough, also is chemisorbed in the twofold hollow site. The "island-trough" growth mode is also corroborated by the apparent heights of the different

a)

b)

FIG. 3. (a) An STM image $(43 \times 46 \text{ Å}^2)$ after an exposure of 8 L of H_2S showing the coexistence of three "different" structures, the $(2 \times 1)O$ added rows to the right, and $c(2 \times 2)S$ structures in the troughs and on the islands. The superimposed grid indicates the position of the atoms in the underlying $Ni(1 \times 1)$ lattice. (b) A schematic drawing of the apparent heights of the different structures observed on the islands, in the troughs, and on the terrace.

phases in Fig. 3(a). The height difference between the $c(2 \times 2)$ structures in the troughs and on the islands is 1.25 Å, nearly identical to the interlayer distance on $Ni(110)$. Furthermore, the experimental finding that the $c(2 \times 2)S$ troughs are imaged to be 0.5 Å lower than the $(2 \times 1)O$ terrace, whereas the $c(2 \times 2)S$ island is imaged 0.75 Å higher, confirms the structural identification of the different phases since, as seen from Fig. 1, the apparent height of $c(2 \times 2)S$ and $(2 \times 1)O$ islands above the $Ni(1 \times 1)$ substrate is 0.3 and 0.8 Å, respectively. In Fig. 3(b) is shown a schematic drawing of the apparent heights of the different structures.

During the reaction, the gradual loss of the $(2 \times 1)O$ structure, with $\Theta_O = \frac{1}{2}$ ML, is counterbalanced by the growth of $c(2 \times 2)S$ troughs and islands, with $\Theta_S = \frac{1}{2}$ ML. Since the surface coverage of the intermediate O and S structural phases is identical, and since they cover all the surface area, i.e., no clean $Ni(1 \times 1)$ regions are observed, we can conclude that the H_2S-O reaction is quantitative in the sense that the loss of O adsorbates is equal to the increase in S adsorbates. This has also been confirmed by Auger electron spectroscopy [13].

It is observed that the reaction proceeds through a *homogeneous* nucleation of small $(\leq 30 \times 30 \text{ Å}^2)$ islands and troughs rather than by heterogeneous nucleation at steps and defects. This indicates a very local reaction pathway: Because of the fairly low activation energy for the reaction (11.5 kcal/mol [13]), the impinging H_2S reacts locally with the preadsorbed O, forming water which is desorbed. The Ni in the former $(2 \times 1)O$ structure accumulates locally in the small $Ni(1 \times 1)$ islands and troughs, at which the product S is chemisorbed. The low mobility of the Ni atoms limits the growth of the islands. If the H_2S exposure is stopped at the stage where the entire surface is converted into many small $c(2 \times 2)S$ islands and troughs, and the surface is annealed to 573 K, a flat uniform $c(2 \times 2)$ surface results, indicating that the distribution of islands and troughs at RT does not reflect the thermodynamic equilibrium but rather a kinetically determined metastable state. Further S exposure at RT on this flat and uniform $c(2 \times 2)S$ surface did not lead to the reconstructed $(4 \times 1)S$ structure but rather to a $(3 \times 2)S$ overlayer lattice-gas structure, with $\Theta_S = \frac{2}{3}$ ML [8], explained by a simple compression of the S overlayer along the $[1\bar{1}0]$ direction [7]. As observed previously, the (4×1) sulfur-induced reconstruction evolves from the flat, well annealed $c(2 \times 2)S$ surface *only* after H_2S exposure at elevated temperatures (473 K). In this respect, S differs from other adsorbates such as, e.g., H and O, which at RT both induce a reconstruction of the $Ni(110)$ surface with a long-range mass transport [7,11]. The most probable reason that there exists a high activation energy for S-induced reconstruction of $Ni(110)$ is the fact that the S atom is larger and more sensitive to changes in the surrounding electron density, as compared to, e.g., O and H adsorbates. This results in a larger barrier for penetration into the surface [7].
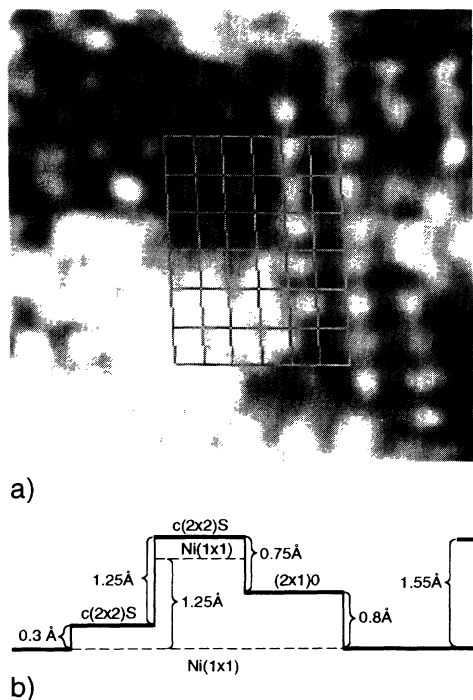
Finally we address the point why the $(4\times1)S$ structure develops at RT from the rough $c(2\times2)S$ structure with all the islands and troughs and not from the flat $Ni(110)$ sulfur-exposed surface. Apparently the detailed surface morphology plays a crucial role in the structural transformation from the $c(2\times2)S$ overlayer structure to the reconstructed $(4\times1)S$ structure. The rough $c(2\times2)S$ surface with many small islands and troughs can be considered as a metastable intermediate surface state which has a higher surface energy than the flat, homogeneous $c(2\times2)S$ surface, and thus the energy barrier for S to react with and/or penetrate into the surface and initiate the surface restructuring is reduced. During the transformation to a thermodynamically stable $(4\times1)S$ state, diffusing Ni atoms removed from the islands react with the S and form the $(4\times1)S$ structure. The energy cost to remove a Ni atom at the periphery of a Ni island is significantly smaller than to pull out a Ni atom from a flat terrace [2,14]. Since finally all the islands and troughs are removed, and a flat, uniform $(4\times1)S$ phase is formed, we can conclude that the Ni density for this phase must be $\Theta_{Ni}=\frac{1}{2}$ ML, an important input parameter when determining the detailed geometrical structure.

Recently, we have also studied the reaction between H_2S and preadsorbed O on $Cu(110)$. The Cu results, which will be published elsewhere, differ from the Ni results in the following ways: For Cu, the reaction is heterogeneous; i.e., defects and step edges act as nucleation sites for the reaction. Furthermore, the $c(2\times2)S$ domains are significantly larger than for the Ni case, typically $\approx 150\times150$ Å^2. The reason is that the diffusivity of Cu is significantly higher than that of Ni [14], and thus the Cu from the (2×1) added rows agglomerates into larger islands onto which S chemisorbs. This implies that for continued H_2S exposure, the Cu does not reconstruct but instead ends up in a $(3\times2)S$ overlayer structure.

In conclusion, we have studied the reaction between H_2S and preadsorbed O on $Ni(110)$ by following the surface structural changes at the atomic level. The heat of chemisorption of O is initially used to "activate" the surface, that is, to break the metal-metal bonds and form the low-coordinated -Ni-O- rows, and the Ni atomic density in the topmost layer is reduced to $\frac{1}{2}$ ML. H_2S reacts very locally with the adsorbed O, water is formed which

desorbs, and a homogeneous nucleation of Ni islands occurs on which S finally chemisorbs. It appears that the detailed morphology of the surface, the many small islands, is of utmost importance in the further reaction-induced structural transformation, and the surface ends up in the S-saturated reconstructed (4×1) phase which otherwise is not accessible at RT. The results suggest how it is possible at the atomic level to activate a surface and thereby open reaction pathways otherwise not accessible. In this way, the results may have important consequences for the field of surface reactivity in general and heterogeneous catalysis in particular.

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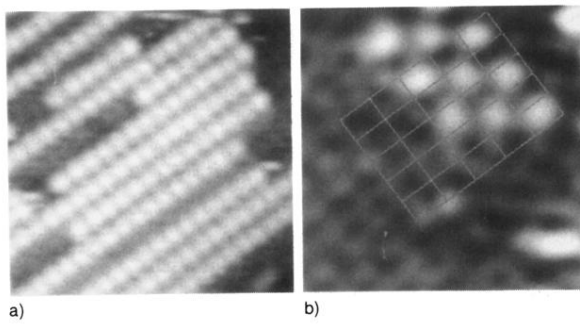[14] J. K. Nørskov, K. W. Jacobsen, P. Stoltze, and L. B. Hansen, Surf. Sci. (to be published).

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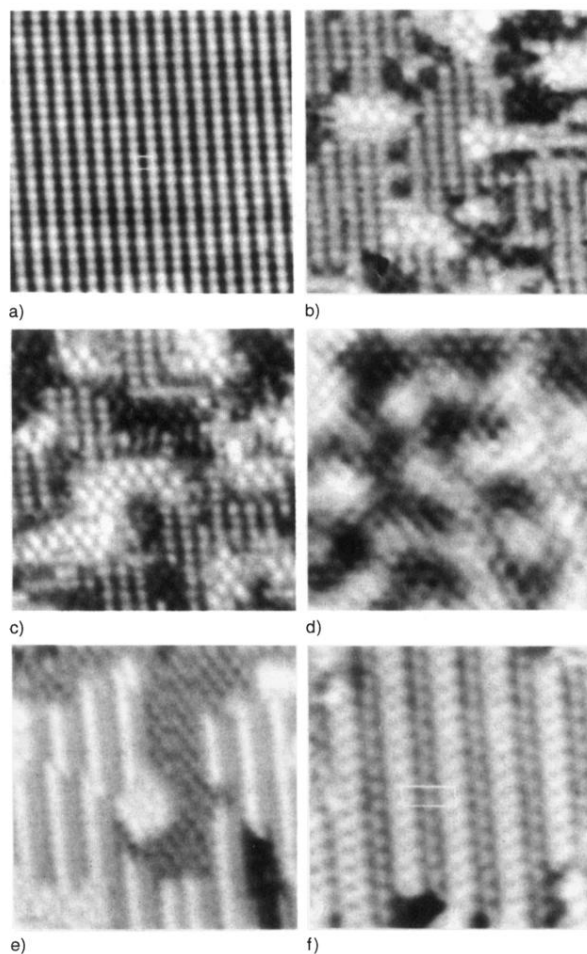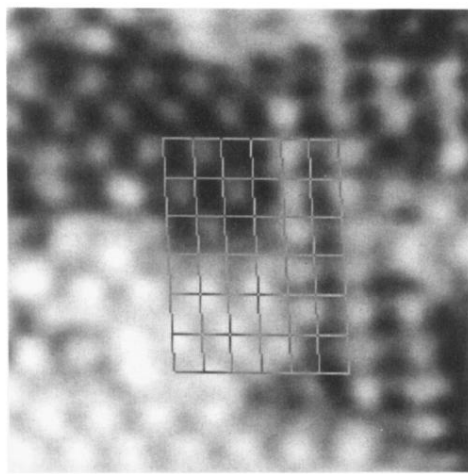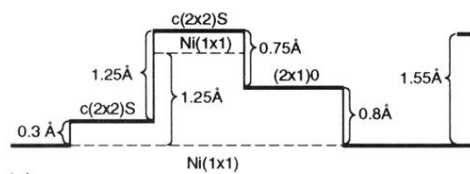
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a)

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