PHYSICAL REVIEW B VOLUME 58, NUMBER 19 15 NOVEMBER 1998-I

Potassium-induced removal of the Ni(100)$(2\times2)p4g$-N reconstruction determined by surface x-ray diffraction

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(Received 6 July 1998)

The ‘‘clock’’ reconstruction of the Ni(100)$(2\times2)p4g$-N system is shown to be removed by potassium adsorption using surface x-ray diffraction measurements. The removal of the reconstruction is discussed in the framework of a simple model of induced surface stresses. [S0163-1829(98)02343-1]

I. INTRODUCTION

The Ni(100) surface undergoes an adsorbate-induced reconstruction when C or N is adsorbed in the fourfold hollow sites of the surface and the coverage of the adsorbate exceeds 0.03 ML.[1] The C or N atoms penetrate into the fourfold site so as to lie almost coplanar with the surface metal layer, and in doing so introduce a large compressive stress.[2] This stress is relieved through an expansion of the hollow sites, which is achieved by tangential movements of the surrounding Ni atoms that result in alternate clockwise and counterclockwise rotations of the Ni atoms with a longer nearest-neighbor distance (see Fig. 1). This substrate distortion turns the otherwise $c(2\times2)$ overlayer structure into an overall $p(2\times2)$ phase with $p4g$ space-group symmetry. This type of ‘‘clock’’ reconstruction has also been observed in a variety of similar systems.[3–5]

Previously, we reported that the low-energy electron diffraction (LEED) pattern for this system changed from $p4g(2\times2)$ to $c(2\times2)$ upon the adsorption of K and postulated that this might be due to the removal of the $p4g$ substrate reconstruction.[6] Here we present surface x-ray diffraction (SXRD) measurements of the Ni(100)$(2\times2)p4g$-N and Ni(100)$c(2\times2)$-(N+K) systems, which provide a quantitative confirmation of this suggestion. The addition of K to the system causes the lifting of the $p4g$ reconstruction and the restoration of a bulklike termination of the metal surface. We discuss this effect and its coverage dependence in terms of the adsorbate-induced surface stresses.[7] Finally, we show that this effect is not specific to the $p4g$-N system.

II. EXPERIMENTAL DETAILS

The measurements were performed in the new INGRID (Instrument for Grazing Incidence Diffraction) endstation on beamline 9.4 of the Daresbury Synchrotron Radiation Source. This chamber allows the use of the five-circle surface x-ray diffractometer with an ultrahigh vacuum (UHV) sample environment. An x-ray wavelength of 0.9 Å was selected with the Si(111) double-crystal monochromator. Ni samples were prepared by repeated sputter and anneal cycles until Auger electron spectroscopy measurements showed no visible contamination and ‘‘sharp’’ (1×1) LEED patterns were obtained. Occasionally, SXRD scans of fractional order or anti-Bragg peaks showed that further sputter/anneal cycles were necessary to remove polishing damage not visible by LEED. The Ni(100)$(2\times2)p4g$-N reconstruction was produced by sputtering the clean Ni(100) crystal in 5×10^{-5} Torr of N_2, at a current of 2 μA and a voltage of 500 V for 10 min. At this stage the $p4g$ reconstruction is visible as a ‘‘fuzzy’’ LEED pattern. An anneal to 600 K for about 5 min then produces a sharper LEED pattern. The potassium was evaporated on to the prepared $p4g$ surface from well-degassed alkali getter sources (SAES, Italy) until the removal of the $p4g$ reconstruction was visible in the LEED

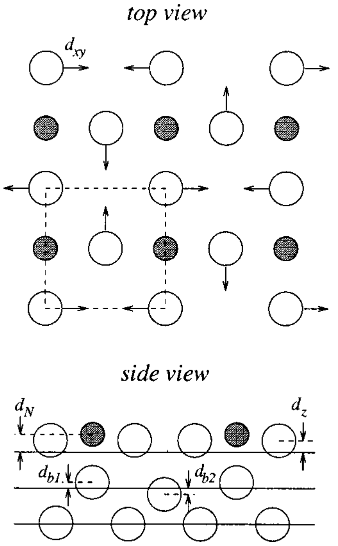

FIG. 1. Top and side views (in a ⟨110⟩ azimuth) of the $(2\times2)p4g$ structure formed by C or N on Ni(100), showing the structural fit parameters used in this work. The adsorbate is represented by the filled circles and the Ni by open circles. The unbroken lines in the side view indicate the z positions of the unreconstructed bulk lattice planes. The square in the top view shows the bulk unit cell.

pattern. While the $p4g$ reconstruction remained stable over days at a base pressure of 2×10^{-10} Torr, the K-dosed surface had to be reprepared each day because of its reactivity.

X-ray diffraction data were taken both in the in-plane geometry (with a low-perpendicular momentum transfer) and along diffraction rods. At each point in reciprocal space a scan was made through the Bragg condition by rotating the sample around its surface normal. The structure factor at each point was then determined by integrating the intensity of the peak and applying angular corrections for the polarization, the Lorentz factor, and the illuminated area.[8] Where possible, data were taken from symmetry equivalent rods and averaged. Although the error in the structure factors produced by the integration process was usually quite low—of the order of 2% (depending on the signal/noise level of each scan)—the reproducibility between symmetry-equivalent rods was found to be of the order of 10%, so that this higher systematic error was used for the structure-factor data sets to allow for imperfections of the alignment matrix and the crystal. Data calculated from structural models were fitted to these structure-factor data sets using a least-squares fit. This was done with the program ROD.[9]

All Miller indices hkl given here refer to the bulk unit cell ($\mathbf{a}_1=[100]_c$, $\mathbf{a}_2=[010]_c$, $\mathbf{a}_3=[001]_c$), which is rotated by 45° with respect to the surface unit cell commonly used in LEED, and which is larger by a factor $\sqrt{2}$. Thus, the missing spots in the $p4g$ LEED pattern are the (0 0.5) in the LEED notation and the (0.5 0.5) in the bulk notation.

III. RESULTS

On both surfaces data were taken along the (11), (22), and (20) diffraction rods and in the in-plane geometry. The comparatively small lattice constant of Ni (3.52 Å) meant that no higher perpendicular momentum transfer than $l=2.5$ could be reached. On the $p4g$-N reconstructed surface two fractional order overlayer rods were measured as well, the (0.5 1.5) and the (0.5 2.5). The rod and in-plane data and the results of the least-squares fit for the Ni(100)$(2\times2)p4g$-N and the Ni(100)$c(2\times2)$-(K+N) systems are shown in Figs. 2 and 3. Also shown for comparison are results for the clean Ni(100)(1×1) surface, which has no lateral relaxation due to its symmetry. It was generally found during fitting that the values for the Debye-Waller temperature factors had only a minimal influence on χ^2, so that temperature factors obtained by fitting had errors of the order of 100%. For this reason the temperature factors for both Ni and N were kept fixed at the value for bulk Ni, 0.37 Å^2.[10]

The results for the Ni(100)(2×2)-$p4g$-N surface are shown in the middle column of Fig. 2. The left-hand column in Fig. 2 shows data for the clean Ni(100) surface (which has no lateral relaxation) for comparison. The structural parameters used in the fit are shown in Fig. 1. Following previous results by Gauthier *et al.* for the Ni(100)$(2\times2)p4g$-C system,[11] a second-layer buckling was introduced, as well as the top-layer in-plane and out-of-plane displacement and the N out-of-plane displacement, a total of five structural fit parameters. There were three further fit parameters, i.e., the scale factor and the occupancies for the top layer Ni and the N. The temperature factors were kept fixed as described above. The data set contained 149 reflections, of which 73 were not symmetry equivalent. The fit achieved a χ^2 of 0.9. The structural parameters found by the fit are shown in Table I. The in-plane displacement d_{xy} obtained here is somewhat shorter than the result of Kilcoyne *et al.*,[12] but d_{xy} is determined by the in-plane data (see Fig. 3), which are particularly sensitive to in-plane displacement. All other parameters fall well within the error bars of the previous results. The rather large percentage error in the N z position reflects the fact that the N is a comparatively weak scatterer so that its contribution to the overall signal is quite weak. The results for the buckling show that the Ni underneath the hollows in which the N is adsorbed follows the upwards relaxation of the top-layer Ni, while the Ni underneath those fourfold hollows into which the top-layer Ni atoms move are displaced downwards. The occupancy found for the top-layer Ni was 0.94 ± 0.05 and for the N 0.85 ± 0.16, again with a large percentage error for the N. The slightly reduced top layer Ni occupancy may be due to defects caused by the sputtering during the preparation of the $p4g$ surface.

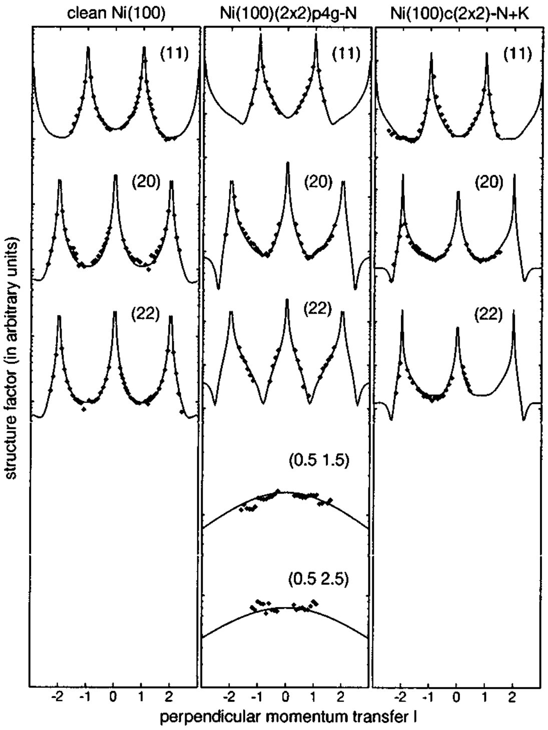

FIG. 2. Structure factor data from the (11), (22), and (20) diffraction rods for clean Ni(100) (left-hand column), the Ni(100)$(2\times2)p4g$-N reconstructed surface (center) showing also two fractional order overlayer rods, and the Ni(100)$c(2\times2)$-(N+K) system (right-hand column). The structure factors are plotted on a logarithmic scale, but not all rods to the same scale.

The changes induced by the transition from the $p4g$-N to the $c(2\times2)$-(K+N) surface previously seen with LEED (Ref. 6) were also observed with SXRD. These include the brightening of the $c(2\times2)$ spots [the (01) and (10) spots in our notation], and the reduction in intensity of the (0.5 1.5) spots.

The diffraction data are less accurate than the previous sets due to the more disordered system and inaccuracies of the instrument alignment matrix. Data taken at large positive l had to be disregarded, and only those at negative l were used for fitting. The data set contained 121 reflections, of

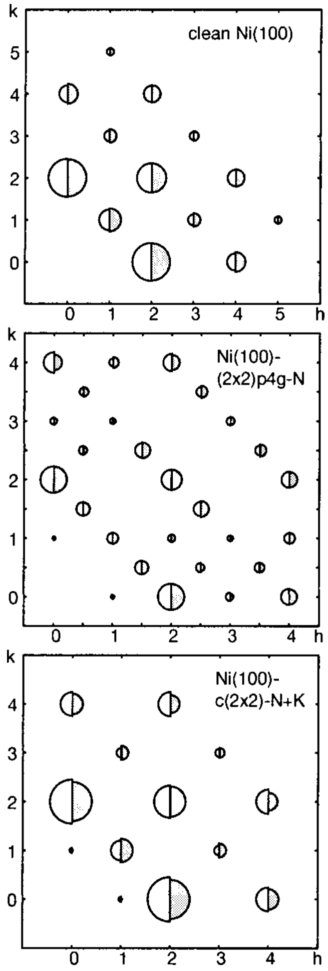

FIG. 3. In-plane data for the clean Ni(100) surface (top), the Ni(100)$(2\times2)p4g$-N surface (center), and the Ni(100)$c(2\times2)$-(N+K) surface (bottom) taken at $l=0.3$. The radius of each circle is proportional to the structure factor; empty semicircles represent data and filled semicircles represent structure factors calculated using the best-fit model.

which 83 were not symmetry equivalent. It was assumed that the K overlayer is disordered and, thus, has no effect on the diffraction peaks. This is supported by the increase in background observed in LEED upon K adsorption.[6] The χ^2 achieved by the fit was 1.0. Figure 2 (right-hand column) shows the diffraction data for the (11), (22), and (20) rods. The overall rod profiles resemble those of the bulk-terminated clean surface.

TABLE I. Structural fit parameters for the Ni(100)$(2\times2)p4g$-N and Ni(100)$c(2\times2)$-(N+K) surfaces. All measurements are in Å. d_N is the height of the N above the top bulk-layer Ni position, d_{xy} is the in-plane top Ni displacement, d_z is the vertical top-layer Ni displacement, and d_{b1} and d_{b2} are the second-layer Ni atom vertical displacements, as shown in Fig. 1.

	Ni(100)$(2\times2)p4g$-N	Ni(100)$c(2\times2)$-(N+K)
d_N	0.20 ± 0.13	1.00 ± 0.7
d_{xy}	0.30 ± 0.01	0.00 ± 0.1
d_z	0.17 ± 0.01	0.16 ± 0.01
d_{b1}	0.11 ± 0.07	0.03 ± 0.03
d_{b2}	-0.07 ± 0.07	0.03 ± 0.03

The same change is shown clearly by the in-plane data, Fig. 3; the surface basically reverts to the bulk-terminated geometry with an expansion of the top layer Ni. The fit parameters used in fitting this surface structure were the top-layer and second-layer Ni z displacements, the occupancy of the N and top-layer Ni atoms, and a scale factor. The structural fit parameters are again shown in Table I. The best fit was obtained with the N atoms moving vertically out of their previous hollow sites, while the top-layer Ni vertical expansion remains unchanged with only a small second-layer expansion. The occupancy of the N atoms was found to be reduced (0.7 ± 0.2), suggesting that the K dosage removes at least part of the adsorbed N, although all structural fit parameters for the N again come with large uncertainties due to the weaker scattering. The top-layer Ni occupancy remained basically unchanged at 0.92 ± 0.03.

IV. DISCUSSION AND CONCLUSIONS

The observed removal of the $p4g$ reconstruction can be discussed in the framework of a simple model of adsorbate-induced surface stresses outlined in Ref. 7. This model asserts that clean metal surfaces are generally under a tensile stress (which in some cases is large enough to cause spontaneous reconstruction). This is a consequence of the redistribution of the d-band bonding charge in the surface layer, which does not have the directionality of covalent bonding. The addition of an electropositive adsorbate such as an alkali adds bonding charge to the metal surface layer, strengthening the interlayer bonds, and, thus, causing tensile (positive) stress. Electronegative adsorbates remove charge, weakening the interlayer bonds and causing compressive (negative) stress. These added stresses can sometimes be large enough to induce a structural change such as a reconstruction. This is the case for the Ni(100)$(2\times2)p4g$-N system where at a critical coverage of N the increased compressive stress is relieved by the formation of the reconstruction.[2]

It should be acknowledged that this simple model does not appear to have universal applicability. Feibelman, for example, has calculated that although O is electronegative and H electropositive, they both appear to cause a compressive stress when adsorbed on Pt(111).[13] Moreover, when potassium atoms are incorporated in the Pt(111) surface to form a surface alloy, a compressive stress is induced[7] [although the incorporation of K into the Pt(111) surface has itself been questioned recently[14]]. Nevertheless, the model provides a framework for the interpretation of the structural changes on this surface, and as there is no evidence that K is adsorbed substitutionally to form a surface alloy in this case, we go on to discuss our results in the context of this model.

The clean Ni(100) surface is under tensile stress.[7] It has been found that the addition of C (which produces the same surface reconstruction as N) causes a large adsorbate-induced compressive stress that increases sharply with coverage until the $p4g$ reconstruction starts to occur at 0.3 ML,[7] where the induced stress levels off and stays fairly constant up to 0.5 ML. Alkali adsorbates, on the other hand, are known to induce a comparatively large tensile stress as discussed above.[7] A stress-induced reconstruction must be caused by a balance of these stresses.

Although absolute values for these surface stresses for the Ni(100)-(N+K) system are not known, estimates can be made from known values for similar systems. The N-induced compressive stress at a coverage of 0.5 ML (as in this experiment) can be estimated to be roughly $-6\,\mathrm{N\,m^{-1}}$ as on the Ni(100)$p4g$-C surface.[7] The onset of the reconstruction occurs at $-4\,\mathrm{N\,m^{-1}}$, so that an additional tensile stress of $2\,\mathrm{N\,m^{-1}}$ would be necessary to lift the $p4g$ reconstruction again. Assuming that the K-induced stress on Ni(100) is similar to that induced by Cs on Ni(111),[7] this would occur at a K coverage of ≈ 0.1 ML, which is indeed close to the coverage at which the LEED pattern is observed to change.[6]

In summary, we have measured the removal of Ni(100)$(2\times2)p4g$-N ''clock'' reconstruction by the coadsorption of K and have proposed an interpretation based on the surface stresses induced by the adsorbates. This demonstrates the feasibility in favorable cases of using selected adsorbates to manipulate surface structure in a controlled manner, using prior knowledge of the expected induced surface stress. The effect demonstrated here is likely to have a wider applicability. We have also observed that the $p4g$ LEED pattern from the Ni(100)$(2\times2)p4g$-C reconstruction is removed by adsorption of potassium. A $c(2\times2)$ LEED pattern is obtained after K adsorption at room temperature. This indicates that a similar structural change is taking place in this system, i.e., the reconstruction is being removed.

ACKNOWLEDGMENTS

This work was supported by EPSRC Grant No. GR/K/23225. The authors would like to thank S. Bennett, C. Muryn, J. M. C. Thornton, and M. Scantlebury for help in the data collection, and the members of the INGRID design and construction team for their assistance in developing the facility.

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