Adsorbate-induced reconstruction of O and S on Ni(100): a local model

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Abstract. The p(2×2) as well as the c(2×2) structures of sulphur and oxygen on Ni(100) at coverages of $\theta = 0.25$ and $\theta = 0.5$, respectively, were investigated with high precision LEED structure analyses. A uniform expansion of the topmost nickel layer with an underlying buckling reconstruction of the second layer was found in all cases. The total amplitude of adsorbate-induced changes of the substrate is roughly proportional to coverage and depends on the chemical species adsorbed. However, the geometry of the local adsorption cluster (adsorbate plus nearest neighbour atoms in the first and second substrate layers) is almost coverage-independent for both oxygen and sulphur. Nickel atom positions more distant from the adsorbate atom tend to be near that of the clean surface.

These results indicate that a model of local reconstruction may be the key for an understanding of the observed structures: the adatom creates a local reconstruction which is largely independent of coverage but depends on the reactivity of the adsorbed chemical species. Additionally, we show that this simple model provides a possible explanation of the experimental observation that—in contrast to the well-ordered oxygen p(2×2)-structure at $\theta = 0.25$—the adsorption of sulphur at the same coverage leads to a streaky p(2×2) LEED pattern, indicating partial disorder.

1. Introduction

In the early days of surface science the prevailing picture of adsorption on low indexed surfaces was simple: the adsorbate atoms were assumed to sit in a more or less ordered formation on a basically unchanged substrate retaining the structure of the uncovered surface.

The application of new as well as more sophisticated techniques of surface structure determination has dismantled this primitive assumption by contradicting the rigidity of the underlying substrate. Depending on the chemical properties of substrate and adsorbate a substantial restructuring of the adjacent metal atoms is induced in many cases.

There are some very obvious cases like the Ni(100)2×2–C p4g clock reconstruction [1,2] where superstructure spots generated by the substrate show up in the diffraction

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pattern, in addition to those of the adsorbate layer. But even for a densely packed surface with a 'simple' diffraction pattern like Ni(111)2×2–O a substantial lateral and vertical reconstruction of the topmost nickel layer has been detected [3–5].

Thus the observation of a substrate-induced reconstruction has become an important feature in most surface structure determinations. But there is still more to learn from the improved structure sensitivity: *the comparison of chemically similar elements* adsorbed at a sequence of coverages on the same substrate may be useful to hint at the adsorption mechanisms involved.

In this paper we present a compilation of the results of our high precision LEED structure analyses of oxygen and sulphur adsorbed on the same Ni(100) crystal, which enables us to set up a useful local model of the induced substrate changes leading to a consistent understanding of the different adsorbate geometries and ordering behaviour.

2. The adsorbate system: O and S on Ni(100)

The clean Ni(100) surface is well-known to be unreconstructed and to show only a slight contraction of about 1% of the topmost interlayer spacing as compared with the bulk value of 1.7604 Å [6].

The adsorbates oxygen and sulphur belong to the same group of the periodic table, suggesting a roughly similar chemistry, but different reactivity. Therefore the substrate changes induced by adsorption can be expected to be of the same type but with different magnitudes.

In the LEED experiment for both elements similar superstructures can be observed on the Ni(100) substrate, a p(2×2) structure at a coverage of $\theta = 0.25$ and a c(2×2) structure at $\theta = 0.5$. A full record of our experimental procedure can be found in the literature [6–10].

Whereas both c(2×2)-structures and the p(2×2)–O are well ordered as judged from the sharp diffraction spots in the LEED pattern, a fully ordered p(2×2)–S structure could not be observed under any of our experimental conditions (see [9]). Although there has been an argument on this point in the past [11–13] we conclude that the streaks observed in $0\bar{1}1$ and $01\bar{1}$ directions hint at partial disorder in the adsorbate layer.

This observation is difficult to interpret, especially under the assumption of an inert substrate. The corresponding interaction between the adsorbate atoms must be of a sophisticated nature as simple sterical reasons can be ruled out. This is due to both elements forming a well-ordered c(2×2) structure at twice the coverage as compared with the p(2×2) case. The precise adsorbate geometries as determined with LEED give rise to a possible simple explanation for this difference, as will be shown later.

3. The structure analyses

Although the full description of LEED measurements and calculations can be found in the literature [6–10] some important points according to the precision of the analyses will be summarized here.

All experimental IV-spectra were measured under the best possible conditions regarding the cleanliness of the crystal and the optimum formation of order of the

adsorbate layer. The IV-spectra were recorded for normal primary beam incidence using a fast computer-controlled TV measurement system [14–17]. The calculations in the energy range from 50 to 350 eV used the full dynamical LEED theory (standard programmes from [18]). This ensured a large overlap between experimental and theoretical data (at least 1330 eV) for the comparison with the Pendry R-factor [19].
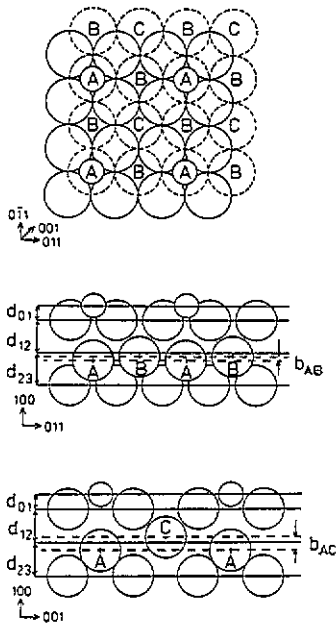

Figure 1. Structural model for the LEED analyses of p(2×2)–O and –S on Ni(100). The adsorption sites denoted C are additonally occupied for the c(2×2)-structures.

The parameters for the structural models shown in figure 1 included the three topmost interlayer spacings d_{01}, d_{12} and d_{23}. Depending on the structure—p(2×2) or c(2×2)—two or one buckling parameters, b_{AB} and b_{AC}, modelled a reconstruction of the second substrate layer. All parameters were varied independently within reasonable limits.

At this point it appears logical to ask whether the reconstruction is a necessary part of the structural models. The answer can be given easily from a comparison between the corresponding IV-spectra. Figure 2 shows the results of calculations for the $(\frac{1}{2} \frac{1}{2})$-beam of the p(2×2)–O structure against the experimental curve. Clearly the reconstruction improves the fit considerably as the reproduction of peak positions as well as the intensity level is poor for the unreconstructed model. This is also reflected in a vast improvement of the R-factor from 0.75 to 0.31 in this case.

Table 1 summarizes the results of the structure analyses together with the respective R-factors for all structures, whereby the error bars are evaluated according to [19]. It should be kept in mind, however, that the resulting uncertainty of the results may be overestimated by a simplification underlying the error definition: as many small and overlapping peaks are present in both measured and calculated IV-spectra (cf figure 2), the amount of structure-sensitive information available is considerably larger than estimated in the original derivation of [19], where intensity spectra are assumed to be exclusively composed of well separated Lorentzian peaks instead.
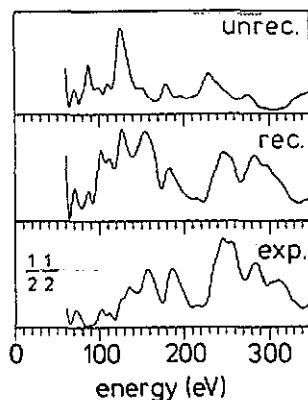
Figure 2. Comparison of experimental (expt.) and calculated IV-spectra of the $(\frac{1}{2}\ \frac{1}{2})$ spot of Ni(100) p(2×2)–O taken at the best fit geometry with (rec.) and *without (unrec.) reconstruction of the second substrate layer.*

Table 1. Results of the structure analyses of O and S on Ni(100). The corresponding structural parameters are displayed in figure 1.

Structure	Oxygen		Sulphur	
	p(2×2) [7]	c(2×2) [6]	p(2×2) [9]	c(2×2) [8]
d_{01}(Å)	0.80 ± 0.05	0.77 ± 0.04	1.25 ± 0.03	1.30 ± 0.02
d_{12}(Å)	1.80 ± 0.02	1.86 ± 0.02	1.77 ± 0.02	1.79 ± 0.02
d_{23}(Å)	1.75 ± 0.02	1.76 ± 0.02	1.76 ± 0.03	1.74 ± 0.02
b_{AB}(Å)	0.04 ± 0.04	0.035 ± 0.02	0.07 ± 0.05	0.01 ± 0.03
b_{AC}(Å)	0.10 ± 0.07	—	0.07 ± 0.05	—
R_{Pendry}	0.24	0.28	0.21	0.25

4. The local model

How do the results of the structure analyses fit into a consistent picture of the adsorption process? To answer this question it is useful to consider the *changes* of the substrate from the clean surface instead of the isolated values. Figure 3 shows the structural parameters in an overview, whereby the two or three inequivalent atoms in the second substrate layer are denoted with letters A, B and C according to figure 1. Atoms A and C are equivalent in the c(2×2) case, as both are located below adsorbate-occupied sites.

It is no surprise that the adsorbate heights differ largely for oxygen and sulphur as their number of electrons differ and consequently their bond length to the substrate. With increasing coverage an unexpected difference shows up between both elements: whereas the oxygen height decreases from 0.80 Å to 0.77 Å for coverages of $\theta = 0.25$ and $\theta = 0.5$ respectively, the sulphur atom is shifted from 1.25 Å to 1.30 Å at the same time. If the adsorbate atoms are mainly bound to the top substrate layer, there is no reason why both elements should behave differently.

A closer look to figure 3 reveals that there may be another decisive parameter for the adsorbate height instead of the topmost layer spacing. The distance between the adsorbate atom and the second substrate layer atom A directly below turns out to be independent within the error bars: the respective values for the p(2×2)- and
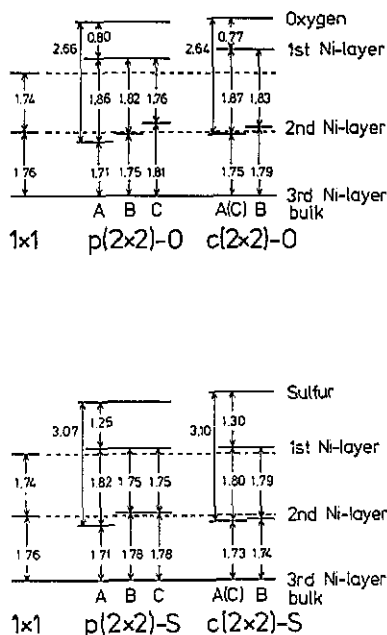
Figure 3. Comparison of the results of the structure analyses as compared with those of the clean Ni(100) surface. The second layer substrate atoms are named A, B and C according to figure 1.

c(2×2)-structures are 2.66 Å and 2.64 Å for oxygen, and 3.07 Å and 3.10 Å for sulphur. This observation is also in agreement with total energy calculations for the c(2×2)-structures indicating the formation of some type of bonding between the adsorbate and the nearest atom in the second substrate layer [20,21].

The overall change of the first nickel layer spacing is in line with the expectations, as there is an expansion growing linearly with increasing adsorbate coverage (see table 1). Compared with the clean surface the resulting upward shifts of the topmost nickel atoms are larger in the case of the chemically more reactive oxygen with 0.07 Å for the p(2×2)-structures and 0.12 Å for the c(2×2)-structures, whereas the values with sulphur are only 0.03 Å for both structures. The latter agreement is caused by a 0.02 Å downward shift of the centre of mass of the second substrate layer for the c(2×2)-structure, which compensates the increase of the first layer expansion in comparison to the p(2×2)-structure (0.03 Å → 0.05 Å). For all other structures the average distance of the second nickel layer to the bulk resembles the value of the clean surface.

The adsorbate-induced buckling is strongly correlated to the results above, as the local displacements turn out to be determining the global relaxation values. Looking at the local relaxation, which is defined as the distance between the second layer substrate atom and the topmost layer, again a coverage-independent value is found for the atoms A (see figure 1), i.e. 1.86 Å and 1.87 Å for oxygen, and the smaller values of 1.82 Å and 1.80 Å in the case of sulphur at coverages of $\theta = 0.25$ and $\theta = 0.50$, respectively.

With increasing lateral distance from the occupied sites the influence of the adsorbate atoms on the second substrate layer weakens and therefore the reconstructive downward shift is decreasing. In the case of the p(2×2) structures the local relaxation

of the atoms B is reduced to 1.82 Å for oxygen and to 1.75 Å for sulphur. The latter value already agrees very well with the relaxation of 1.74 Å observed for the clean Ni(100) surface. In the p(2×2) case the influence of sulphur adsorption therefore seems to cease at the second layer atoms that are not directly below the occupied adsorption sites. This is not true in the c(2×2) case, where corresponding values of 1.82 Å (O) and 1.79 Å (S) indicate a significant displacement for all atoms. But it must be kept in mind that increasing coverages mean a higher density of adsorbate atoms which in turn tends to reduce the amount of reconstruction. In the limit of a hypothetical 1×1 adsorbate structure a reconstruction is not possible for symmetry reasons. The values observed are in line with this expectation, as the buckling amplitudes are reduced drastically with increasing coverage.

Consequently the local relaxation of atoms C, which are the atoms furthest from the adsorbate in the p(2×2) structures, can be expected to be the least influenced by the adsorbate. In fact, the local relaxations of 1.76 Å for oxygen and 1.75 Å for sulphur both agree very well with the relaxation value of 1.74 Å for the clean surface.

In conclusion the local model of adsorption can be summarized: independently from the coverage the sequence of structures is dominated by an atomic cluster formed by the adsorbate atom and its nearest neighbour nickel atoms in the first and second nickel layer. The geometry of this cluster is coverage-independent and can be characterized by two parameters, the bond length between adsorbate and adjacent second-layer nickel atom, d_A, and the local relaxation, d_S. Due to the different chemical properties these parameters (table 2) are different for both elements, whereby d_S characterizes the amount of substrate modification. Due to the different chemical reactivities, the latter one is smaller for sulphur as compared with oxygen.

Table 2. The parameters of the local model.

	Oxygen	Sulphur
d_A (Å)	2.65 ± 0.06	3.09 ± 0.06
d_S (Å)	1.87 ± 0.03	1.82 ± 0.03

The global relaxation of the topmost substrate layer is determined by two factors: the height of the centre of mass of the second substrate layer with respect to the bulk remains constant; and the displacement of the atoms not within the cluster depends on the chemical reactivity and density of the adsorbate layer. Thus for low coverages, i.e. the p(2×2) structures, the furthest atoms C of the second substrate layers show local relaxations in agreement with those of the clean surface, whereas the nearer atoms B are lowered differently for both elements, resulting in a global relaxation between 1.74 Å and d_S. For higher coverages, the buckling amplitudes tend to decrease due to the increased adsorbate density. Consequently both c(2×2) structures show smaller buckling amplitudes bringing the global relaxation to a value near d_S.

5. The disordered p(2×2)-S structure

The local model of adsorption is able to provide a consistent explanation of the different ordering of sulphur and oxygen at the coverage $\theta = 0.25$. As discussed above, the main difference between both adsorbate structures is the range of influence of the

reconstructive changes in the second nickel layer. Whereas the atoms B (figure 1) are significantly shifted down by oxygen adsorption, they are not influenced by the adjacent sulphur cluster.

The possible implications on the ordering process are obvious: assuming the nearest and next-nearest adsorption sites to remain unoccupied due to some kind of repulsive interaction, it may be energetically favourable for a neighboured oxygen atom to occupy the p(2×2) site, as part of the lowering of atoms in the surrounding of the cluster has already been done by the first atom. No such kind of interaction exists for the sulphur atoms, as all possible sites are equivalent in the light of missing second-layer modifications. Assuming all other interactions beyond the range of next-nearest neighbour sites to be negligible sulphur could order in a p(2×2)-pattern as well as a c(4×2)-pattern.

The results of a Monte Carlo simulation of adsorbates on a square lattice can be taken as a guideline for this latter case [22]. Under the assumption of repulsive nearest and next-nearest neighbour interactions microdomains of p(2×2) and c(4×2) structures coexist in a disordered pattern at low temperatures. The disorder was caused by a statistical sequence of double speed atom rows with or without a shift of a single lattice vector in between. The streaks observed in the experimental LEED pattern are compatible with this type of disorder. Additonally a metastable p(2×2) structure could be formed in the simulations at coverage $\theta = 0.25$ by slowly cooling down, whereby the domain walls had still c(4×2)-structure.

In conclusion, we find that the local model derived from carefully performed structure analyses not only describes the structural features in a consistent way, but also can give an idea about the type of interaction that may be responsible for the different ordering processes of both p(2×2) structures.

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