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J. F. van der Veen
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The Structure of Surfaces II

Proceedings of the 2nd International Conference on the Structure of Surfaces (ICSOS II), Amsterdam, The Netherlands, June 22–25, 1987

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Preface

This book collects together selected papers presented at the Second International Conference on the Structure of Surfaces (ICSOS-II). The conference was held at the Royal Tropical Institute in Amsterdam, The Netherlands, June 22–25, 1987. It was held in part to celebrate the 25th anniversary of the NEVAC (Netherlands Vacuum Society). The International Organizing Committee members were:

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The ICSOS meetings serve to assess the status of surface structure determination and the relationship between surface or interface structures and physical or chemical properties of interest. The papers in this book cover: theoretical and experimental structural techniques; structural aspects of metal and semiconductor surfaces, including relaxations and reconstructions, as well as adsorbates and epitaxial layers; phase transitions in two dimensions, roughening and surface melting; defects, disorder and surface morphology.

Amsterdam, Berkeley
October 1987

J.F. van der Veen
M.A. Van Hove

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Particular thanks go to all the individuals who contributed much to the well-being of both the conference and the proceedings, especially Louise Roos, Jan Verhoeven, Dorine Heynert and the members of the Local Organizing Committee: F.H.P.M. Habraken, A.G.J. van Oostrom, G.A. Sawatzky, and W.F. van der Weg. An important element was of course the contribution from the International Advisory Committee members: D. Aberdam, J.C. Bertolini, M. Cardona, G. Comsa, L.C. Feldman, F. Garcia Moliner, D.R. Hamann, D. Haneman, A.A. Lucas, T.E. Madey, K. Müller, S. Nakamura, A.G. Naumovetz, P.R. Norton, G. Rovida, W.E. Spicer, A.G.J. van Oostrom, and R.F. Willis.

Contents

Relaxation and Reconstruction on Ni(110) and Pd(110) Induced by Adsorbed Hydrogen

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The influence of adsorbed hydrogen on the structure of the surface regions of Ni (110) and Pd (110) was derived from dynamical LEED I / V-analyses of the clean, (2x1) H covered and (1x2) "row pairing" reconstructed surfaces as reported in earlier publications (see references). In this article the resulting modification of the oscillatory contraction / relaxation of the topmost interlayer spacings of the clean surfaces is discussed in terms of the electrostatic forces acting between these layers. The extension of the reconstruction into deeper layers is related to the relief of lattice strain which is shown to be a general phenomenon for reconstructed surfaces.

The three-dimensional structure of solids results from a delicate balance of different interactions and represents the minimum in free enthalpy integrated over all of these interactions. The truncation of the bulk at the surface causes the cessation of part of these interactions in the surface region which subsequently also necessitates a structural rearrangement of that region in order to again achieve the most stable configuration. This can lead either to a collective (vertical) motion of entire layers, i.e. a change in interlayer spacing (relaxation) or to nonuniform vertical and/or lateral displacements of atoms in the topmost layer(s) (reconstruction) [1]. The latter also results in a larger unit cell at the surface. Clearly also the presence of an adsorbate can likewise affect these interactions and thus also the resulting substrate structure.

Such effects were investigated in a systematic study of the structure of the clean and hydrogen covered Ni(110)- and Pd(110)-surfaces. Both of these surfaces exhibit ordered superstructures upon hydrogen adsorption at T<180K, namely a (2x1) structure at a coverage of Θ=1.0 and a (1x2) structure at Θ=1.5 monolayers [2,3]. The structural arrangement of the substrate atoms for the clean and adsorbate covered surfaces - and of the adsorbate atoms in the case of the (2x1) structure - was determined by analysis of Low Energy Electron Diffraction (LEED) intensities [4-8]. Mechanistic details on the formation and stability especially of the high coverage (1x2) structure were reported in a foregoing paper [9].

The sample preparation followed standard recipes, further details thereupon and on the experimental setup are given elsewhere [3]. Surface cleanliness was controlled by means of Auger Electron Spectroscopy (AES), work function ($\Delta\phi$) measurements and Thermal Desorption Spectroscopy (TDS) upon hydrogen adsorption.

On both surfaces exposure to hydrogen at T<180K leads to the appearance of extra beams of a (2x1) structure in the LEED pattern which reach their maximum intensity at Θ=1.0 monolayer exhibiting ~1 order of magnitude less intensity than the integral order beams. In contrast to Pd(110), where this structure forms from low coverages on, i.e. by an island growth mode, on Ni(110) a series of ordered structures precedes the (2x1) [1,2]. All of them are proposed to exhibit zig-zag chains of H atoms along the close packed rows of Ni atoms in [1$\bar{1}$0] direction as a common structural element [2]. Upon further hydrogen adsorption these extra beams decay and instead beams of a (1x2) structure emerge and grow in intensity. At a coverage of 1.5 monolayers the (2x1) related beams have completely disappeared and those of the (1x2) have reached their maximum intensity comparable to that of the integer order beams. The disordered ("streaked") (1x2) structures formed on either surface at T>200K, which are distinctly different in their structural and mechanistic properties from the low temperature (1x2) structure [9,10], and the population of subsurface sites at Θ>1.5 on Pd(110) even at 120K [11] are not subject of this article.

The I/V-analysis was based on dynamical LEED calculations. The data base for the different analyses is summarized in Table 1. Further details on the calculations, structural and nonstructural parameters can be found elsewhere [5,6,8,9]. In good agreement with previous studies [4,7] for the clean (1$\bar{1}$0) surfaces of Ni and Pd (Fig. 1a) an oscillatory contraction/relaxation is found for the topmost interlayer spacings [5,8], which fits well into a common trend of a variety of fcc (110) surfaces (Table 2). Other examples include Cu, Ag, Al and Rh [14-18]. In all of these cases the distortion decays rapidly for going to deeper layers. Contraction of the order of 5-10% in the first interlayer spacing are followed by an expansion of 2-5% in the subsequent one. Distortions in the third interlayer spacing are already that small that in most cases they are within the incertainty of the results. Apparently there is also a tendency to smaller effects in 4th row elements as compared to 3rd row ones.

Table 1. Data base for LEED I/V-analyses of clean and H_{ad} covered (110) faces of Ni and Pd and reliability factors R_{ZJ} and R_P of the resulting optimum structures

	normal incidence			off-normal incidence				Ref.
	No. integral order beams	No. fractional order beams	Energy-range [eV]	No. integral order beams	No. fractional order beams	Energy-range [eV]	R_{ZJ}, R_P	
Ni(110) clean	10	-	40-390	-	-	-	0.04, 0.20	[5]
Ni(110)-(2x1)H	3	3	40-180	0	5	40-180	0.17, 0.27	[5]
Ni(110)-(1x2)H	6	5	40-220	-	-	-	0.15, 0.38	[6]
Pd(110) clean	7	-	40-240	9	-	40-240	0.14, 0.22	[8]
Pd(110)-(2x1)H	3	1	40-180	13	5	40-180	0.17, 0.23/ 0.19, 0.37	[8]
Pd(110)-(1x2)H	5	3	40-220	-	-	-	0.22, 0.50	[9]

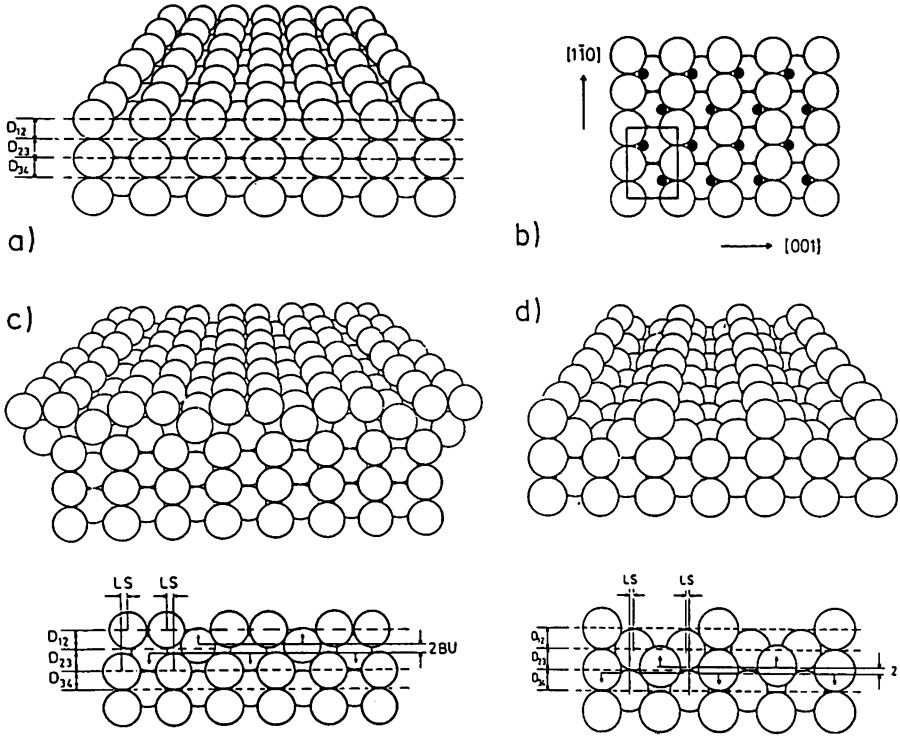

Fig. 1. Perspective view and structural parameters of the clean (1x1) (a) and the (1x2) "row-pairing" (c) and "missing row" (d) reconstructed fcc(110) surfaces and top view of the (2x1)H structure (b).

These effects can be understood on the basis of electrostatic forces. There is a net transfer of electron density from the top of the WIGNER SEITZ cells of the surface atoms towards their (lateral) perimeter, i.e. a net flow of charge from the ridges into the troughs in [110] direction [20,21]. Quantum mechanical forces acting on an atomic nucleus can simply be described by the classical electrostatic forces resulting from the relaxed electron charge distribution [20]. The depletion of negative charge on the ridges consequently leads to an inward motion of the atoms in the topmost layer.

HO and BOHNEN have extended this description. In their picture layers which consist of a lattice of positive and negative point charges representing the ion cores and the electron density in between are stapled on top of each other [21]. The vertical forces between these layers are determined by their vertical stacking sequence. For a fcc(110) surface this can be shown to result in an inward motion of the topmost layer (contraction) and an outward motion of the second layer (expansion) while in the bulk these forces cancel because of symmetry reasons.

The rapid decay of the distortion amplitudes in deeper layers and the generally smaller effects in 4th row elements (larger unit cell) can be

Table 2. Oscillatory contraction/relaxation of the topmost three interlayers spacings D_{12} , D_{23} and D_{34} for clean and adsorbate covered metal surfaces

Surface	ΔD_{12}[%]	ΔD_{23}[%]	ΔD_{34}[%]	Ref.
Ni(110)	-8.4 ± 1.5	+ 3.1 ± 1.5	-	[4]
	-8.5 ± 1.5	+ 3.5 ± 1.5	+ 1.0 ± 1.5	[5]
Ni(110) + (2x1)H	-4.5 ± 1.5	+ 5.0 ± 1.5	0.0 ± 1.5	[5]
Ni(110) + c(2x2)S	+ 10.2	-3.2	-	[13]
Cu(110)	-8.2 ± 0.6	+ 2.5 ± 0.8	-0.9	[14]
Cu(110) + "(1x1)"	-0.8	+ 2.8	-	[15]
Pd(110)	-6.0 ± 2.0	+ 1.0 ± 2.0	-	[7]
	-6.0 ± 1.5	+ 1.0 ± 1.5	0.0 ± 1.5	[8]
Pd(110) + (2x1)H	-2.2 ± 1.5	+ 2.9 ± 1.5	0.0 ± 1.5	[8]
Ag(110)	-5.7	+ 2.2	-	[16]
Al(110)	-8.6	+ 5.0	-1.6 ± 1.2	[17]
Rh(110)	-7.0 ± 1.0	+ 2.0 ± 1.0	-	[18]
Rh(110) + (1x1)H	-2.0 ± 1.0		-	[18]
Ni(111)	0	0	-	[19]
Ni(111) + (2x2)H	0	0	-	[19]
Fe(110)	0	0	-	[12]
Fe(110) + (2x1)H	0	0	-	[12]
Fe(110) + (3x1)H	0	0	-	[12]

attributed to the distance dependent decrease in electrostatic forces. The same holds for the much smaller effects on close packed surfaces (=larger interlayer spacings) [12,19]. A more realistic description of the lattice distortions would refer to the variations in atom-atom distance instead of those in interlayer spacing. Especially on the more open surfaces the former quantitiy is much smaller in numbers than the latter one (e.g. <3% instead of 8.5% for Ni(110)).

For both surfaces the unreconstructed phase is most stable. Earlier reports in the literature on a structural transition at 220K on Pd(110) [22] could not be confirmed, despite of extensive experiments no indication of any structural transition was found between 100K and 500K. The stability of the clean surfaces is also evident from the high temperatures for the roughening transition for Ni(110) [23]. In the case of several 5^{th} row elements in contrast the symmetry break at the surface causes a (1x2) "missing row" reconstruction of the (110) surfaces [24-26], which is generally attributed to the more delocalized character of the 5d electrons and their consequently stronger participation in the metallic bond [27,28].

The presence of the adlayer on the hydrogen covered surfaces - in the (2x1) structure at Θ = 1.0 - has a sizable effect on the distortions of the interlayer spacings. Most notably the contraction of the topmost interlayer

spacing is reduced by ~40%. The next deeper spacing is hardly affected reflecting the rather local character of the metal-hydrogen bond. The adsorbate thus tends to partially offset the effect of the surface cut. This again can be understood in terms of electrostatic forces as described above. That description would also propose much weaker adsorbate effects on close packed surfaces, in good agreement with experimental results (Table 2). Even a change in sign of those distortions, as observed for S/Ni(110) [13] appears plausible for strongly interacting systems.

Also in the (2x1) hydrogen covered surfaces the substrate remains unreconstructed, the superstructure is created solely by the ordered adlayer (Fig.1b). This does not completely rule out any H induced distortions of the local adsorption complex, it just limits their amount to below the limits of detectability in the LEED analysis (~±0.03Å). The adsorption site - the quasi-threefold site aside the short bridge in [1$\bar{1}$0] direction - and the adsorption geometry and also the zig-zag arrangement of H_{ad} atoms within the (2x1) structure are identical on both surfaces. There are, however, subtle differences in the (indirect) adsorbate-adsorbate interactions mediated through the metal. The sequence of lattice gas structures on Ni(110) arises from repulsive interactions in [001] direction between adatoms on nearest neighbor and on next-nearest neighbor close packed Ni-rows in [1$\bar{1}$0] direction, while the island growth of the (2x1) on Pd(110) is indicative of attractive interactions between neighbored zig-zag rows. These interactions are, however, of the order of tenths of a kcal/mole, as compared to typically 65 kcal/mole for a metal-hydrogen bond. Even small changes in the metal-substrate interactions thus can tip the sign of these indirect interactions.

For both metals the (1x2) structure at Θ =1.5 monolayers was attributed to a reconstruction of the substrate rather than to an ordered adsorbate overlayer because of the relatively strong intensity of the extra beams [3]. From the excellent agreement even in smaller features especially for Ni our LEED analysis indeed unambiguously decided in favor of a reconstruction of the "row pairing" type in both cases, caused by a lateral displacement of neighbored rows of metal atoms in [001] direction as shown in Fig.1c [6]. While this assignment agrees with recent ion scattering results [10,29] and He diffraction experiments [2,11] it is in conflict with results of other studies favoring a "missing row" type geometry [30]. Furtheron our structure analysis gave clear evidence of a vertical distortion also in the second layer, i.e. the reconstruction extends deeper into the bulk than just affecting the topmost layer [6]. This in fact turned out as a critical refinement of our analysis, which only allowed to clearly distinguish between both types of reconstructions [6]. From the structural parameters of both of these structures in Table 3 it is evident that again the lattice distortions are less pronounced for the case of Pd(110) than those in the corresponding structure on Ni(110). The general relaxation pattern, however, given by the alternating vertical displacements within the second layer and the changes in interlayer spacings, remains the same. An EELS study of the phonon dispersion on the Ni(110)-(1x2)H structure renders further support not only for the type of reconstruction but also to the specific relaxation pattern of the metal atoms [31].

The continuation of the reconstruction into deeper layers of the surface region reflects the tendency of the system to minimize distortions in the metal-metal coordination and bond length for a given configuration of the surface layer itself. Instead of an abrupt change between first and second layer the lattice strain is gradually relieved over several layers. This would predict also a lateral distortion in the third layer followed by a

Table 3. Structural parameters (± 1.5 %) of the (1x2) reconstructed surfaces

Ni(110)-(1x2)H	Pd(110)-(1x2)H
D_{12} = 1.27 Å	D_{12} = 1.37 Å
D_{23} = 1.31 Å	D_{23} = 1.47 Å
D_{34} = 1.25 Å	D_{34} = 1.37 Å
BU = 0.25 Å	BU = 0.15 Å
LS = 0.30 Å	LS = 0.20 Å

slight buckling in the fourth layer. These latter modifications were neglected so far since their amount should rapidly decay as compared to the topmost layers and because of the reduced contribution of deeper layers to the LEED intensity. But further LEED calculations shall be performed to test this.

Recent LEED I/V analyses likewise revealed deeper layer distortions in the (1x2) "missing row" reconstructions of the clean (110) surfaces of Au [24], Ir[25] and Pt[26]. In these cases there is a strong inward motion of the ridge atoms, which can also be understood in terms of the above electrostatic description and which is partly offset by a lateral motion of the second layer and downward motion of the atoms directly underneath in the third layer (Fig.1d). Similar behavior was also predicted from a recent "embedded atom" calculation of the clean (1x2) reconstructed Ir(110) surface [28]. Also in these structures the deeper layer atoms thus make way in order to gradually relieve the strain introduced by the topmost atoms.

In summary results of a LEED structure analysis of the clean and hydrogen covered (110) surfaces of Ni and Pd were used to elucidate the effect of the adsorbate on the structure of the underlying substrate. The modification of the oscillatory contraction/relaxation of the clean surface in the (2x1)H structures and the (multilayer) "row pairing" reconstructions in the (1x2)H structures are discussed in comparison with corresponding structures of clean surfaces. It is shown that the former can be understood in terms of electrostatic forces, while the reconstruction of deeper layers too is identified as a general feature, which serves to minimize the lattice strain imposed by the structure of the topmost atoms.

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