Structural parameters of Pd(110) and Pt(110)-(1 × 2) in the temperature range 300–900 K studied by low-energy ion scattering

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Abstract

Pd(110) and Pt(110)(1 × 2) are studied by low-energy ion scattering using two scattering modes, i.e. surface blocking and NICISS (neutral impact collision ion-scattering spectrometry). The data give information on the surface structure and vibrations of surface atoms in the temperature range 300–900 K. The Pd(110) surface shows roughening at 550 K. There is no evidence for an anomaly of the surface thermal vibrations. The average thermal vibrational amplitudes of the surface atoms are determined for the $[1\bar{1}0]$ and $[1\bar{1}2]$ directions, and correspond to Debye temperatures of 149 and 100 K, respectively. The results are compared with the respective values for Pt(110). © 1997 Elsevier Science B.V.

Keywords: Low energy ion scattering (LEIS); Palladium; Platinum; Surface structure

1. Introduction

The clean Pd(110) surface is not among the "famous" fcc (110) surfaces such as Au, Pt and Ir. The surface is "bulk-terminated", and no surface reconstruction occurs. The accepted structural data are regular lattice sites for the toplayer atoms and a 0.12 ± 0.03 Å contraction of the first-layer spacing [1], i.e. there is a small reduction of the interplanar distance of the two outermost planes of $\Delta d_{12}/d_{12} = 0.08$. The Pd single-crystal surfaces have attracted great interest in chemisorption studies, of which only few will be mentioned here. The major subject of these studies is the interaction with hydrogen on Pd(110) [2] or on Pd(100) [3].

Here we present experimental results obtained by ion scattering methods for Pd(110). The data analysis gives values for the surface Debye temperatures, the interlayer spacing between the first and second layers, and evidence for a roughening of 550 K. Previously, an order–disorder transition was reported to occur at 250 K on Pd(110) [4], but this was not confirmed in He diffraction experiments [5]. In some instances the Pd(110) data are compared with corresponding Pt(110) results.

2. Experimental

For the experiments we used a UHV system which is described in detail elsewhere [6]. It is an ion-scattering apparatus equipped with a plasma discharge ion source, a magnet for mass analysis of the ion beam, and beam-defining apertures. The

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ion beam was pulsed for the analysis, i.e. a low-current ion beam was used. For sputter cleaning of the crystal surface, Ar and Ne 500 eV ion beams below 1 μA were used at grazing incidence. The crystal was mounted on a two-axis goniometer, allowing control of the angle of incidence ψ (relative to the surface plane) and of the azimuthal angle ϕ. An LEED system served for inspection of the crystal structure; in the case of Pd(110), it showed a (1 × 1) pattern. An electrostatic analyser was available to check surface cleanliness with primary He or Ne ion beams, i.e. operating in the plain ISS mode [7]. Long heating times at higher temperatures cause sulfur segregation on the surface. For structure analysis, we use the TOF (time-of-flight) system consisting of a drift tube and a channel-plate detector. The TOF system was mounted at a fixed laboratory scattering angle of $\Theta = 165°$. We apply two modes of ion scattering for structure analysis: (i) surface blocking, in which the angle of incidence ψ and the ion energy are fixed and the azimuthal angle ϕ is varied, and (ii) NICISS (neutral impact collision ion-scattering spectrometry), in which the azimuthal angle ϕ and the ion energy are fixed and the angle of incidence ψ is varied. The surface normal, (110), lies in the plane of scattering in all the experiments described here. The effect on which these techniques are based is the shadow cone formed behind an atom exposed to a parallel beam of ions [7]. The evaluation of the NICISS results is based on a two-atom scattering model [8]. The actual scattering angle of $\Theta = 165°$ is taken into account in the two-atom scattering model. We use a ZBL (Ziegler–Biersack–Littmark) potential. For the calculation of the thermal mean-square displacements of the surface atoms, the validity of the Debye model is assumed.

3. Results

The first set of data (Fig. 1) shows blocking patterns of the Pd(110) surface at different temperatures. The energy of the Ne ions used was 2.08 keV. Each point in the plots represents a full scattered-ion spectrum measured by TOF. The

minima are marked by the crystallographic directions. The structure is qualitatively comparable to patterns observed from other non-reconstructed fcc (110) surfaces [7,9]. Of interest is the change of, for example, the [1$\bar{1}$0] minimum with temperature. The valley narrows and the minimum yield increases (Fig. 2). In bulk channeling experiments the minimum yield is usually called χ_{min}. Here it is also a useful experimental parameter to observe structural changes. With low-energy ions and surface channeling we found good correlations with roughening transitions. The surfaces of Au(110), Ir(110) and Pb(110) show an increase of the minimum yield at 650, 1.050 and 400 K, respectively [8,10–13]. These surfaces show roughening transitions at the respective temperatures [14,15]. For comparison, we show the behaviour of the minimum yield of the [1$\bar{1}$0] valley of Pt(110)-(1 × 2), where the (1 × 2)↔(1 × 1) phase transition at about 950 K is well separated from the roughening transition at 1.050 K [16,17]. The Pt(110) data show no evidence for roughening in the temperature range accessible in our experiment [18].

The second set of experimental data are "polar" plots (Fig. 3). The points represent measured TOF energy spectra. The lines were calculated using a two-atom scattering model [8]. The agreement between the calculation and the experiment is excellent within the ψ range of interest for both the [1$\bar{1}$0] and [1$\bar{1}$2] directions. The fit includes the mean-square thermal amplitudes of the surface atoms using the Debye model. The corresponding Debye temperatures are $\theta_\perp[1\bar{1}0] = 149$ K and $\theta_\perp[1\bar{1}2] = 100$ K, respectively. $\theta_\perp$ ("perpendicular") is used because NICISS is most sensitive to the perpendicular component of the thermal displacement of the surface atoms [7]. In the experiment along the [1$\bar{1}$0] surface chains the shadow cone is "calibrated" at a distance of 2.74 Å, the atomic distance in the close-packed chains.

From the position of the second peak in Fig. 3b (i.e. the polar plots for the [1$\bar{1}$2] direction), the distance between the first and second layer is evaluated. The first critical angle at $\psi_{crit} = 16°$ gives a calibration of the shadow cone at 4.77 Å, the atomic distance of the [1$\bar{1}$2] surface chains. The second critical angle at $\psi_{crit} = 48°$ is due to the shadows cast from the top-layer atoms on the
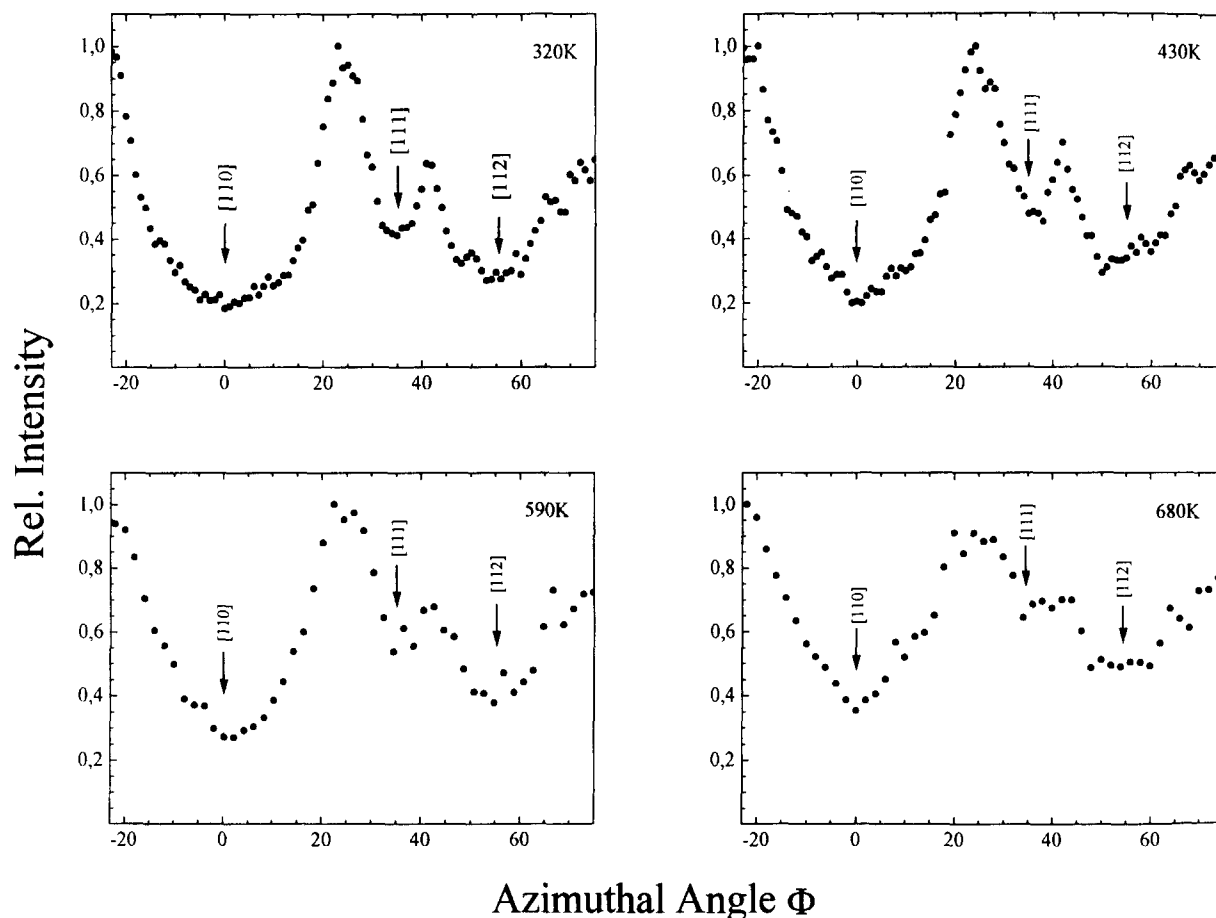
Fig. 1. Azimuthal dependence of the neutral particle scattering yield for Ne (2.08 keV) incident on Pd(100). The glancing angle of incidence is $\psi = 10°$, the scattering angle is $\Theta = 165°$. The surface crystallographic directions are marked by $[hkl]$.

second-layer atoms. Since there is no reconstruction other than planar relaxation, the second-layer atoms sit half-way between the top-layer atoms. The shadow cone has a parabolic shape [7]. So, with two calibration points, the shadow cone can be estimated. The estimate of the interlayer distance is then a simple geometrical problem. This distance is reduced as compared to the bulk planar distance (Fig. 4). The roughening transition at 550 K is not evident in the interplanar distance. For comparison, we show the relaxation value of the Pt(110) surface for a somewhat larger temperature range (Fig. 4b). Here the $(1 \times 2) \leftrightarrow (1 \times 1)$ surface phase transition at $T = 960 \pm 30$ K has no signature in the interplanar distance.

4. Discussion

The structural data reported here are within the range of values reported previously. The interplanar distance between the first and second layer for Pd(110) is reduced by $\Delta d_{12} = -0.3 \pm 0.1$ Å compared to the bulk value, somewhat higher than the "standard" value of $\Delta d_{12} = -0.12 \pm 0.03$ Å [1]. There is a theoretical value for the contraction of $\Delta d_{12} = 0.15$ Å [19]. This estimate is based on the embedded atom model (EAM). This theoretical model has been proved to be successful in many applications. In the case of Pt(110)-(1 × 2) we find $\Delta d_{12} = -0.5 \pm 0.1$ Å, as compared to the values given in Table 1.
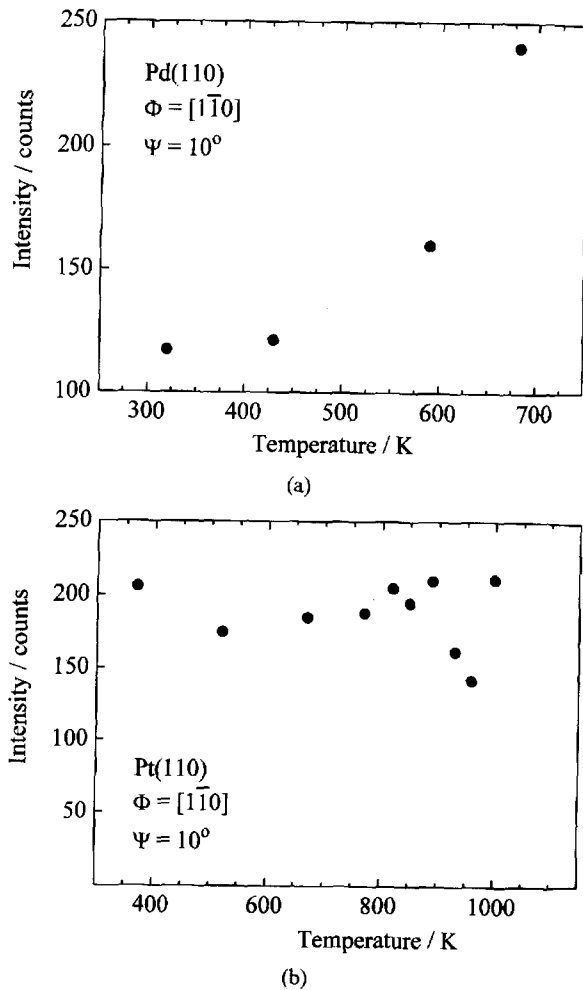
Fig. 2. (a) The minimum intensity of the [1$\bar{1}$0] surface half channel for 2.08 keV Ne scattered from Pd(100) under an angle of incidence of $\psi = 10°$ and a scattering angle of 165°. (b) As (a), but for Pt(100)-(1 × 2).

For both surfaces the NICISS data are about a factor of 2 higher than some previous results. The agreement is better with the more recent data obtained by RHEED [16,17] and XPD (X-ray photoelectron diffraction) [24]. It is possible that the older data are too low. The temperature dependence of Δd_{12} agrees with previous findings for Au(110) and Ir(110); for Pt(110) there is also no significant change when going across the order–disorder transition at 960 K. The surface Debye temperature for Pd(110) found in the literature is $\theta_\perp(110) = 191$ K [25]. Our value is slightly lower,
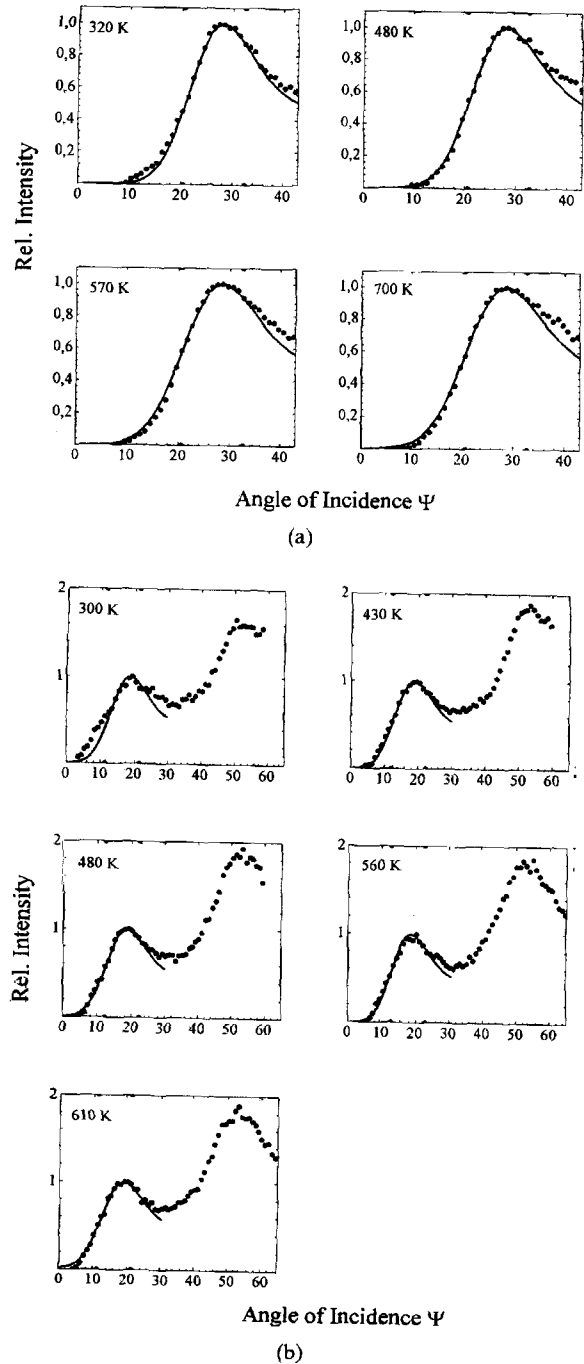

Fig. 3. (a) Polar intensity variation of 2.08 keV Ne scattering from Pd(100) along the [1$\bar{1}$0] direction for different temperatures. The scattering angle is 165°. The lines were calculated using a two-atom scattering model, and points are experimental values. The fit range (20–32°) is marked. (b) As (a), but for the [1$\bar{1}$2] direction. The fit range is 11–21°.

Pd(110)

Relaxation $\Delta x / x$

0,4

0,3

0,2

0,1

300   400   500   600

Temperature / K

(a)

Pt(110)

Relaxation $\Delta x / x$

0,5

0,4

0,3

0,2

0,1

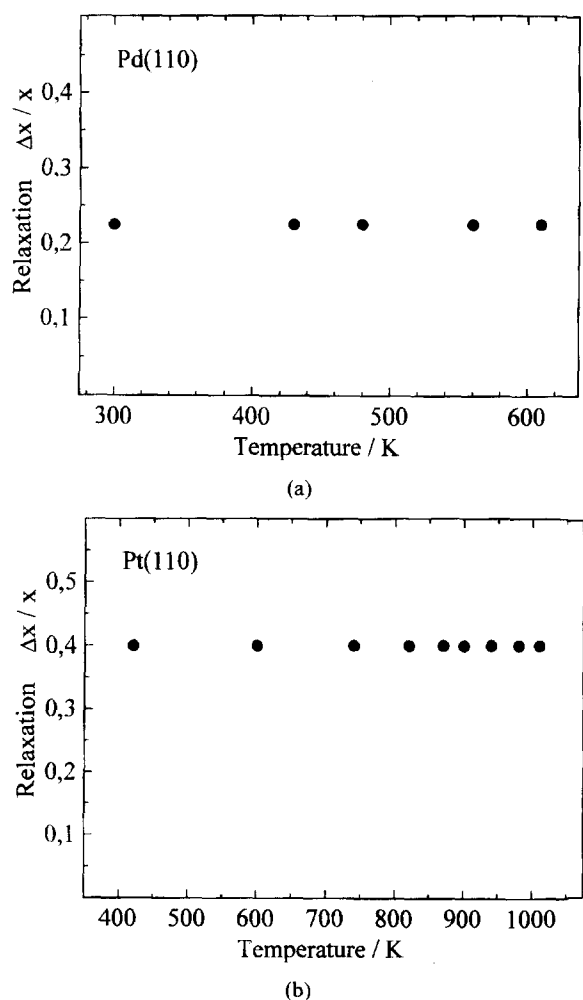400   500   600   700   800   900   1000

Temperature / K

(b)

Fig. 4. (a) Relaxation of the interplanar distance of Pd(100) between the first and second layer with respect to the bulk value. (b) Relaxation of the interplanar distance of Pt(110)-(1 × 2).

a trend also observed in other cases [10–14]. The deviation may reflect the fact that the relaxations and the Debye temperatures are related, i.e. if relaxations are neglected in theoretical calcula-

tions, the Debye temperatures tend to be higher, as pointed out by Jackson [25]. Since in the NICISS experiment, $\theta_\perp$ and Δd_{12}, the Debye temperature and the relaxation, are evaluated independently, the results are consistent. We find a rather large relaxation compared to some previous results, but in agreement with the physics, we find lower $\theta_\perp$ values. There is a recent compilation of θ_D data for a number of single-crystal surfaces [26], but the Pd(110) surface is not included. For the Pd(100) surface a value of 0.57 θ_{bulk} is given, corresponding to $\theta_{surface}(100) = 156$ K. In the case of Pt(110)-(1 × 2) we find two experimental values: $\theta(110) = 140$ K [22] and $\theta(110) = 107$ K [27]. The first value is based on medium-energy ion scattering (MEIS), while the second is based on LEED. In the RHEED evaluation [16,17], the "standard" procedure or "rule of thumb" [26] is accepted, i.e. $\theta_{surface} \approx \theta_{bulk}/\sqrt{2}$. This estimate yields $\theta_{surface} = 166$ K for Pt. Our experimental value is $\Theta_\perp(110) = 112$ K for Pt(110)-(1 × 2). Other values are not reported for the surfaces in question. We note that "there are major inconsistencies in the reported ratio of the surface to bulk Debye temperature" [26]. In the case of the NICISS experiments, the evaluation of θ_D is rather model-independent [7]. The agreement with the Debye model is self-evident, because in all cases we find a linear increase of the mean-square thermal displacements $\langle (\Delta Z^2) \rangle$ with increasing temperature [8,10–13,18].

A new finding is the Pd(110) roughening at 550 ± 20 K. This is the first time we have reported a roughening measured by an ion beam technique not supported by other experimental evidence or theoretical predictions. The estimation of the roughening temperature is based on a comparison with the results from Au(110) [13]. In the case of Au(110), the first evidence of a change of the

Table 1
Relaxation of the interplanar distance of Pt(110)-(1 × 2)

	Method						
	NICISS	RHEED	LEED	LEED	MEIS	XRD	XPD
Δd_{12}	-0.5 ± 0.1	-0.34 ± 0.04	-0.26	-0.28	-0.22	-0.27	-0.42
Ref.	This work	[16,17]	[20]	[21]	[22]	[23]	[24]

surface structure with temperature is "seen" about 120 K below the roughening temperature evaluated from diffraction experiments [15]. In the Pd(110) case (Fig. 2a), we find by this "rule of thumb" the roughening temperature to be at about 550 K. At present no calculations or simulations have been performed to prove these ion-scattering data.

Acknowledgements

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