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Preparation and thermal stability of the clean metastable Pt(100)-(1 × 1) surface: a thermal energy helium scattering study

K. Kuhnke [a,*], K. Kern [a], G. Comsa [b]

[a] *Institut de Physique Expérimentale, EPFL, CH-1015 Lausanne, Switzerland*
[b] *IGV, KFA-Forschungszentrum Jülich, D-52425 Jülich, Germany*

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Abstract

A titration method to prepare the *clean* metastable Pt(100)-(1 × 1) surface employing thermal energy helium scattering is demonstrated. In contrast to earlier recipes it achieves a significantly reduced residual hydrogen coverage below 1%. The clean surface begins to reconstruct at significantly lower temperatures than a surface covered with only a few percent of hydrogen. The surface is highly reactive and under conventional UHV conditions (10^{-8} Pa hydrogen residual pressure) the hydrogen coverage increases by 1% every seven minutes.

Keywords: Atom–solid scattering and diffraction – elastic; Hydrogen; Low index single crystal surfaces; Nitrogen oxides; Platinum; Surface chemical reaction; Surface relaxation and reconstruction; Surface structure, morphology, roughness, and topography

1. Introduction

The phenomenon of surface reconstruction is not yet completely understood although an exhaustive number of theoretical and experimental studies have focused on this rather complex problem. If for a given crystal plane the reconstructed surface represents the equilibrium state, the unreconstructed metastable surface possesses the inherent tendency to reconstruct. Their study may therefore assess the driving force of reconstruction more directly than measurements on reconstructed surfaces can [1]. Indications of the reason for reconstruction of a given surface may for example be found in the characteristics of the surface phonons (mechanical instability) and of the electronic states of the metastable non-reconstructed surface. For such type of investigation it is thus important to prepare a metastable surface with a low defect concentration – specifically with the lowest possible adsorbate coverage. For the unreconstructed Pt(100) surface different preparations have been proposed which, however, leave a significant amount of hydrogen chemisorbed on the surface so that the physical behavior of the surface may differ substantially from the behavior of a perfectly clean one.

The clean Pt(100) surface is known to undergo an irreversible reconstruction which results in a hexagonal close-packed top-layer. Two well-ordered reconstruction phases, one metastable and one stable phase, are known for Pt(100). Both have been characterized by LEED [2], and He diffraction [3]. The reconstructed phases have a compressed top layer in which

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[*] Corresponding author.

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the atom density is 20% higher than in a bulk layer perpendicular to the (100) direction. The metastable phase called Pt(100)-hex is obtained by annealing a sputtered surface between 900 and 1100 K. A helium diffraction scan of this phase is dominated by 1/5th order diffraction peaks as is shown in Fig. 1 top. The stable phase, Pt(100)-hex-rot, is obtained by annealing at or above 1300 K. A detailed X-ray study of this phase [4] shows that upon cooling down from near melting temperature the top-layer atom rows rotate with respect to the substrate up to an angle of 7° which is the value of the stable room temperature phase.

The unreconstructed Pt(100)-(1 × 1) cannot be prepared by annealing of a sputtered surface but must be prepared via chemisorption of adsorbates on one of the reconstructed phases. NO [5,6] and CO [6] are adsorbates which completely lift the reconstruction near room temperature. In order to obtain a clean unreconstructed surface the adsorbate has to be removed in a second step without initiating reconstruction [5,7]. Due to the reduction of the atom density in the top layer during the lifting of the reconstruction, adislands which cover 20% of the surface are created. The island size was found to increase with the temperature at which the reconstruction is lifted [8] resulting in an average island distance of 110 Å for the preparation at 300 K presented in this paper (see figure caption of Fig. 1 bottom).

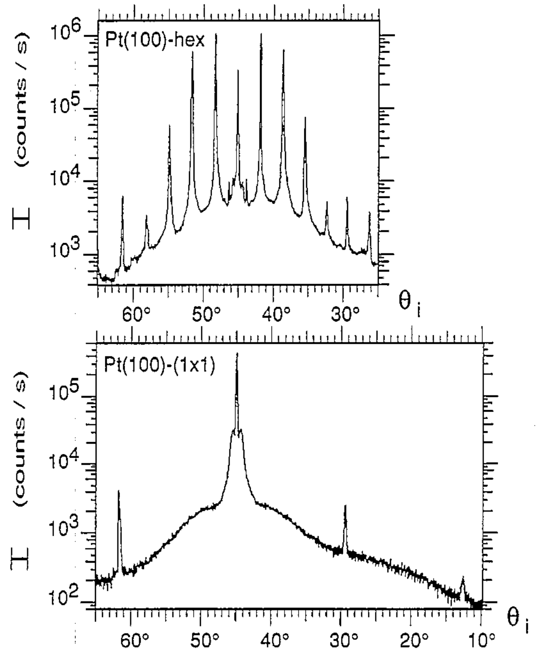

Fig. 1. Top: Helium diffraction scan from the reconstructed Pt(100)-hex phase along the crystallographic ⟨100⟩ direction which is dominated by 1/5 order diffraction peaks (see also Ref. [3]). The He kinetic energy is 17 meV. Total scattering angle 90°. Note the logarithmic intensity scale. Bottom: Diffraction scan from clean Pt(100)-(1 × 1) prepared by the titration method proposed in this paper. The peaks correspond to the (10), (00) i.e. specular, (−1 0) and (−2 0) diffraction peaks of the unreconstructed phase in the ⟨100⟩ direction. The He kinetic energy of 17 meV corresponds almost to an anti-phase scattering condition with respect to the Pt islands. The two broad structures close to the specular peak are entirely elastic features. They are ascribed to the diffraction from the Pt islands with an average island distance of 110 Å.

In this paper we introduce a preparational method which results in a much lower residual adsorbate coverage than previous preparations based on the recipe [5] by Bonzel et al. In this recipe the NO saturated unreconstructed surface is heated to 440 K to desorb and decompose the NO except for a small oxygen coverage which is needed to stabilize the unreconstructed structure at this temperature. After cooling to slightly above room temperature the oxygen is removed by hydrogen dosing. The resulting hydrogen coverage is reduced by subsequent heating, a procedure which is, however, critical as a too high temperature will result in an onset of the reconstruction. After heating residual hydrogen coverages of 5% to 10% are left on the surface [6].

In the *titration* method introduced in this paper the hydrogen dosing is stopped exactly when all oxygen has been reacted off. Thus no surplus hydrogen is adsorbed and no subsequent heating is necessary. The hydrogen coverage can be kept below 1% by virtue of the extreme coverage sensitivity of the specular helium scattering which is used as a monitor. In principle, similar although less sensitive control may be achieved by Auger monitoring of oxygen coverage, work function measurements or other methods.

This paper is organized as follows: In Section 2 we introduce the experimental set-up and sketch the method of specular thermal energy He scattering which is exploited in this investigation as a monitor of adsorbate coverage. The preparational procedure is developed in Section 3 and the residual coverage of the cleaned surface is discussed. Section 4 focuses on the influence of chemisorbed hydrogen on the onset of surface reconstruction.

2. Experimental

The He scattering apparatus used for the investigation is described in detail elsewhere [9]. In brief, we use a helium atom beam from a Fenn type nozzle with kinetic energies adjustable between 17 and 70 meV. Improved detection [10] of the scattered He atoms is by ionization followed by mass selection. The total scattering angle is variable but was fixed to $\theta_i + \theta_f = 90°$ for the experiments described here with a total angular resolution of $\Delta \theta_i = 0.15°$. The experiments were performed on a platinum single crystal cut and polished for a (100) surface orientation. After extensive cleaning over several weeks the surface was found to exhibit terrace widths of a well annealed reconstructed phase larger than 800 Å [9].

Thermal energy helium beam diffraction yields structural information on the surface layer in reciprocal space. Thermal helium atoms are a non-destructive surface probe as the atoms are reflected from the repulsive potential already several Å above the surface atoms. The variation of reflection distance on a periodic surface represents a phase grid for the incident He wave which results in a He diffraction pattern. The diffraction patterns thus reflect the surface periodicity. A perfectly flat surface (like the one of a jellium) will result in the observation of only the zeroth diffraction order, the specular peak. Close-packed unreconstructed metal surfaces exhibit almost negligible corrugation compared to typical He beam wavelengths and thus behave similar to flat surfaces. Unordered adsorbates on such a surface will locally scatter the He atoms diffusely. As a result, intensity is removed from the specular peak. It was found experimentally that the scattering cross section of adsorbates like CO and Xe on this type of surface is much larger than the geometrical diameter of the molecule [11]. The analysis of specular reflection measurements achieves in these cases a sensitivity for adsorbate coverage changes of the order of 10^{-4} to 10^{-3} of a monolayer. Generally, most types of defects on a surface, like e.g. adatoms and steps, contribute to diffuse scattering. For certain systems like hydrogen adsorbed on closed packed metal surfaces a completed monolayer exhibits again a high reflectivity whereas vacancies in such a layer act as diffuse scatterers [11].

3. Preparation of the clean Pt(100)-(1 × 1)

3.1. Analysis of the conventional preparation

NO adsorbs on the reconstructed Pt(100) surface at room temperature and directly lifts the reconstruction under easily accessible and reproducible conditions. When the reconstruction is lifted at a high enough temperature, the adisland density stays low. The preparation of the so-called "almost clean" unreconstructed surface employing NO adsorption was developed by Bonzel et al. [5]. Norton et al. quantified the adsorbate coverage by nuclear microanalysis (NMA) for a surface which was prepared following a slightly modified recipe [6]. The proce-

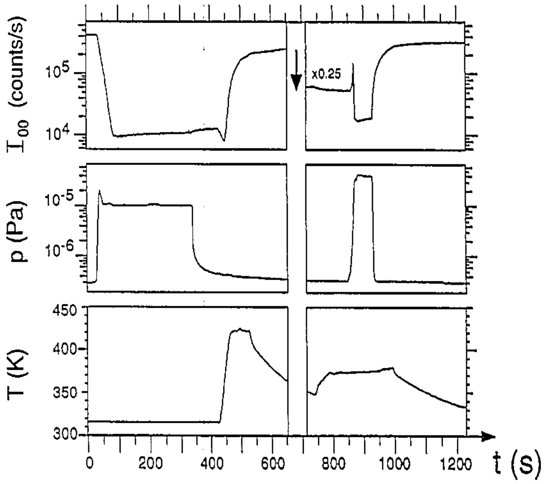

Fig. 2. Preparation of the unreconstructed surface according to the preparational variant of Norton et al. (see text) monitored by helium specular atom scattering ($E_{He} = 70$ meV). Specular reflected He intensity, pressure in the sample chamber measured by an ionization gauge, and sample temperature were recorded every 2 s. Note the logarithmic scales for He reflectivity and pressure. The data were taken in two sets: in the left part NO gas is dosed followed by heating of the sample. In the right part dosing of H_2 at slightly elevated temperature is shown; for H_2 the pressure reading has to be multiplied by a factor 2.5. The residual pressure due to the helium beam is 3×10^{-7} Pa. Between the two data sets the sensitivity of the He detector was reduced to 25% of the initial value.

dure is as follows: At room temperature the reconstructed Pt(100) surface is exposed to NO from the gas phase. After dosing 10^{-2} Pa s of NO on a room temperature surface the reconstruction is lifted and a c(2 × 4) NO superstructure is present on a Pt(100)-(1 × 1) substrate. Annealing of the NO covered surface at temperatures around 443 K for 30 to 60 s leads to a decomposition of the adsorbed NO. The surface is then partially covered by oxygen only. The surface periodicity as observed in low energy electron diffraction (LEED) is (1 × 1) indicating that the surface remains unreconstructed. After cooling to 273 K, the oxygen coverage is removed by slowly heating to 373 K in a 10^{-4} Pa H_2 atmosphere. This procedure leaves a significant hydrogen coverage on the surface. By annealing for 50 s between 373 and 383 K, the adsorbate coverage can be reduced to less than 10^{14} hydrogen atoms per cm^2, i.e. 5%–10% of a hydrogen monolayer with no detectable traces of oxygen [6].

Fig. 2 shows the simultaneous behavior of the specular He intensity, the pressure in the sample chamber and the sample temperature during a preparation following the above recipe. The three values, counting rate, pressure, and temperature are recorded once in two seconds. During the measurement, the data acquisition was interrupted for 1 min ($t = 650$ s to $t = 710$ s) while the efficiency of the He detector was reduced to 25% of the initial value.

The measurement begins with the well ordered reconstructed Pt(100)-hex phase. Upon dosing NO the specular intensity drops rapidly. This observation is indicative of the formation of a diffusely scattering NO adlayer. From a detailed measurement in Fig. 3a we find that with 5×10^{-4} Pa · s of NO the He reflectivity has reached a minimum and decreases no further. We conclude that the NO saturation coverage has been reached and the NO dosing might well be stopped at this point. In the He diffraction pattern of this surface, there are no superstructure peaks in ⟨100⟩ direction indicating that the reconstruction has been lifted. The essentially linear decrease in the semi-logarithmic plot is compatible with a random type adsorption on the surface. If we identify the observed saturation with the saturation coverage of $\Theta_{NO}(T = 300\ \mathrm{K}) \approx 0.5$ [5,12] we obtain a sticking coefficient of $S \approx 0.5$ and estimate the diffuse cross section of NO on Pt(100) for specular He scattering to be $\Sigma \approx 60$ Å^2. The value is reasonable. It corresponds to half the value of the cross section measured for CO/Pt(111) [13] which is a comparable system.

Pumping off the NO in the experiment in Fig. 2, the specular intensity increases slightly. This intensity change can be ascribed to a reduction of NO coverage but is to a small degree also due to He–NO gas phase scattering. After the NO pressure becomes negligible, the surface temperature is increased to

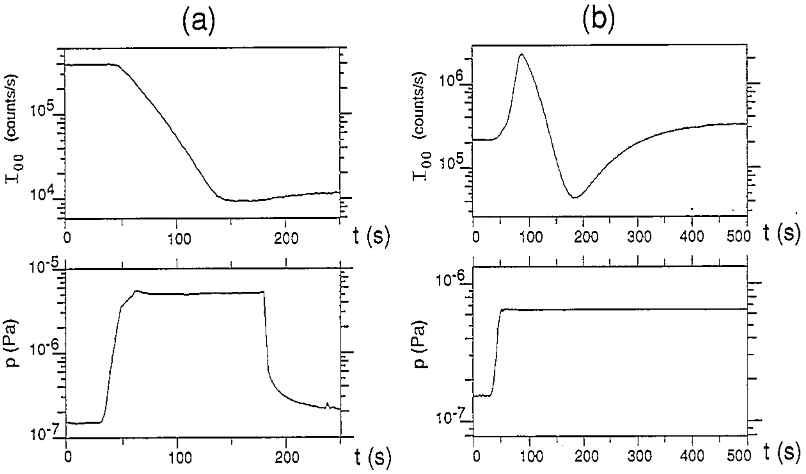

Fig. 3. Specular reflected He intensity (top) of a 17 meV beam as a function of time during sample preparation. The pressure in the sample chamber is shown below. The residual pressure of 1.5×10^{-7} Pa is due to the helium beam. (a) Dosing of NO gas at 300 K on a well ordered Pt(100)-hex surface. (b) Dosing of H_2 gas at 320 K on an oxygen covered (1 × 1) surface which was generated by NO adsorption followed by heating to 420 K. The pressure reading has to be multiplied by a factor of 2.5 for H_2.

420 K. As a result, the He specular intensity increases which reflects the desorption of NO molecules as was already described by Bonzel et al. [5]. The drop just after the beginning of the heating is probably due to the Debye–Waller effect corresponding to the very low Debye temperature of the adsorbed NO layer. After reducing the temperature again and stabilizing it at about 375 K we dose H_2. In the literature, dosing is started at temperatures as low as 275 K, but no reason for the necessity to cool down that far is given. We found no difference to a preparation including this cooling. Upon hydrogen exposure, the He reflectivity exhibits a peak followed by a drop-off. The peak is in fact too sharp to be properly reproduced in Fig. 2. Under the given experimental conditions the reflectivity changes are on a time scale which is much shorter than the averaging time of the specular intensity (1 s). More sensitive measurements were thus undertaken at a reduced hydrogen pressure. Such a measurement is shown in Fig. 3b. It reveals a delayed and gradually accelerating rise of intensity, then a decrease to a lower level than the initial one followed by a slow increase which levels off at a medium intensity value. From a comparison with hydrogen adsorption measurements on Pt(111) we can understand the last two stages as an increasing hydrogen coverage which decreases the reflectivity for small coverages followed by the formation of a better reflecting hydrogen adlayer once a certain coverage has been attained [11]. The low final reflectivity compared to the one of the clean surface indicates that only a partial hydrogen adlayer is formed at room temperature [14]. Having thus identified the formation of a hydrogen layer in the later stages, we still have to account for the initial rapid rise of the reflectivity. From the mechanisms which lead to intensity changes in specular He reflectivity it is only an overall reduction of adsorbate concentration on the terraces which can give rise to this drastic increase in reflectivity. This is in agreement with the description given by Bonzel et al. [5] according to which adsorbed oxygen reacts with hydrogen and desorbs. When a larger amount of adsorbed oxygen is present on the surface either due to a shorter annealing time or due to annealing at lower temperatures a significantly higher hydrogen dose is necessary to reach the sharp maximum in the specular He signal. This behavior suggests that the observed process can be regarded as a titration. The accelerated rise of the He specular signal indicates a reduced sticking coefficient of hydrogen (or a reduced reaction rate) in the presence of adsorbed oxygen. The hydrogen sticking coefficient increases as more and more oxygen is removed from the surface which in turn increases the rate of hydrogen adsorption. This autocatalytic mechanism well explains the continuously increasing slope.

3.2. Titration method

In the preparation in Fig. 2, we obviously passed the point of lowest coverage in the sharp peak and obtain (at $t \approx 900$ s) a medium reflectivity which is due to a significant hydrogen coverage. When the hydrogen has been pumped off the gas phase and the surface is kept at 375 K for 1 min the hydrogen partially desorbs, which is recognized from the continuous increase in specular reflectivity. We determined the final reflectivity obtainable by the preparation following the recipe of Norton et al. to be 3.5×10^5 counts/s (at 0.5 mA detector emission current) after cooling to 330 K (Fig. 2).

The peak of the He specular intensity in Fig. 3b gives the opportunity to observe the exact moment when all oxygen has been removed and additional

Table 1
Recipe to prepare the clean Pt(100)-(1 × 1) using the He specular reflectivity as a monitor

Action	Temperature (K)	Time	Stop condition: specular intensity..
Dosing of NO at 10^{-6} Pa	300	~ 100 s	..stops decreasing
Heating sample	420	5 to 15 min	none
Dosing of H_2 at 10^{-6} Pa; with increasing reaction rate: gradual reduction of H_2 pressure to 10^{-7} Pa	$\leqslant 340$	several minutes	..reaches sharp maximum

hydrogen has not yet adsorbed. We can thus dose H_2 at much lower pressure (5×10^{-7} Pa) and continuously reduce the hydrogen pressure when the reflectivity maximum is approached. In this way the dosage can be terminated exactly at maximum reflectivity. This modified preparation will be referred to as *titration method* (see Table 1) because we titrate quantitatively (in fact remove) the adsorbed oxygen by hydrogen dosage. This preparation carried out under identical conditions as the recorded measurement (Fig. 2) results in a final reflectivity of 6.3×10^5 counts/s (0.5 mA detector emission current).

The preparation by titration method thus yields a surface with almost doubled specular He reflectivity which results from a substantially reduced hydrogen coverage. Knowing that the upper limit of hydrogen coverage given for the preparation by Norton et al. [6] is $\theta = 0.1$ and assuming that after the titration procedure essentially no adsorbates are present on the surface one can estimate the cross section Σ of a single hydrogen atom on Pt(100) from

$$I_{\text{spec}}(\theta) = I_{\text{spec}}(0)(1-\theta)^{(\Sigma/A)}, \qquad (1)$$

where $I_{\text{spec}}(0)$ and $I_{\text{spec}}(\theta)$ are the reflectivity of the clean surface and the surface with hydrogen coverage θ, respectively. $A = 7.70$ Å^2 is the area of the surface unit cell.

As we determined $I_{\text{spec}}(0) = 6.3 \times 10^5$ counts/s and $I_{\text{spec}}(\theta = 0.1) = 4.5 \times 10^5$ counts/s one obtains $\Sigma = 43$ Å^2 for hydrogen on Pt(100). This value is larger than the cross section of a single H atom adsorbed on Pt(111), which is $\Sigma = 24$ Å^2 (for a He energy of 63 meV) [11]. If the titration preparation would lead to a non-zero coverage an initial coverage larger than $\theta = 0.1$ or a cross section even larger than $\Sigma = 43$ Å^2 would have to be assumed. This strongly suggests that the titration preparation in fact results in a hydrogen terrace coverage below 1%. However, it cannot be excluded that a small amount of adsorbates "hides in the shadow" of the steps at the adisland perimeters which already act as diffuse scatterers for the He beam. The substantial reduction of adsorbate coverage with respect to earlier preparational procedures is reflected also in the lowered temperature of the onset of reconstruction which will be discussed in Section 4.

After the preparation by titration we observe a substantial decay of the specular intensity. While the ordered reconstructed phases of Pt(100) show no significant decrease of specular intensity in the UHV within an hour, the decrease of reflectivity of the clean unreconstructed surface was observed to be about 1% in 10 s at 300 K surface temperature and a residual pressure reading of 3×10^{-8} Pa (with the He beam contribution of 3×10^{-7} Pa having been subtracted). Assuming that the background gas consists essentially of hydrogen (ionization gauge correction factor 2.5) and making use of the cross section for diffuse He scattering determined above (43 Å^2) a rough estimate of the sticking coefficient of 0.3 for H_2 adsorption on the clean unreconstructed surface is obtained. An increase of $\Delta\theta_H = 1\%$ occurs already within about 7 min at 1×10^{-8} Pa H_2 pressure. It follows that the ultimate limit for the cleanliness of the unreconstructed Pt(100) surface is determined by adsorption from the residual gas which depends on the background pressure and the time necessary to accomplish a given measurement. For a typical measuring time of five minutes a preparation which leaves even less adsorbates on the surface than the titration method would not be meaningful unless the background pressure can be reduced significantly below 10^{-8} Pa [15].

The titration method can moreover be employed in a complementary procedure to the titration by hydrogen: When hydrogen adsorbing from the residual gas has reduced the surface reflectivity, cleanliness can be restored by dosing small amount of NO. In this way the reflectivity of the clean surface can almost be regained. There is, however, a small residual loss which increases monotonously when the procedure is repeated several times. This loss may be due to the fact that at room temperature products of the NO + H_2 reaction (especially NH_3 and intermediate reaction species) do not readily desorb [16] whereas in the proper preparation all nitrogen is desorbed in a heating process before the hydrogen titration. A contribution to the residual intensity loss will also be adsorption of molecules from the residual gas which can not be desorbed, neither by dosing hydrogen nor by dosing NO.

4. Investigation of the thermal stability of the unreconstructed phase

One question discussed in the literature concerning the metastable Pt(100)-(1 × 1) surface is whether

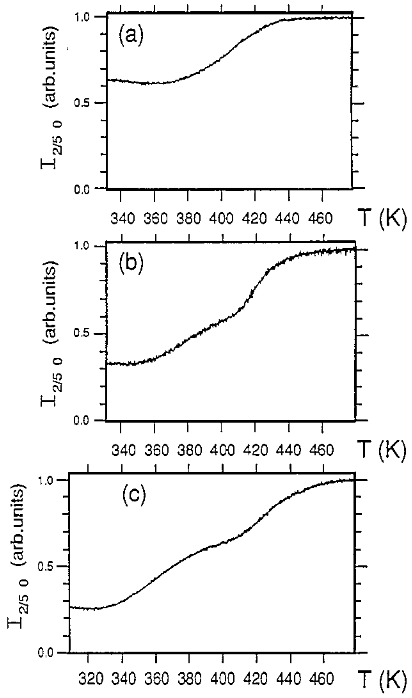

Fig. 4. He intensity during a temperature ramp of 0.06 K/s for differently prepared surfaces at the position of the 2/5 order diffraction peak. The intensities are normalized to the respective intensity at 480 K. The He beam energy is 70 meV. (a) Pt(100)-(1 × 1) surface prepared by the titration method, (b) "almost clean" Pt(100)-(1 × 1) surface immediately after the preparation shown in Fig. 2, (c) Pt(100)-(1 × 1) surface prepared by the titration method, then saturated with hydrogen at 300 K.

this phase exists only when it is stabilized by chemisorbates or whether the phase could exist also without adsorbates [7,17]. In the above sections we have shown that an unreconstructed (1 × 1) surface stays intact even though the adsorbate coverage passes through a state of very low (probably < 1%) adsorbate coverage during hydrogen titration. This strongly indicates that, although chemisorption is needed to prepare the surface, the removal of the adsorbate does not necessarily lead to the onset of reconstruction. In this section we will study some aspects of structural stability by determining the temperature of the onset of reconstruction.

Fig. 4 shows a study of the intensity at the position of the 2/5 order He diffraction peak for differently prepared surfaces. In the graphs of Figs. 4a and 4b the temperature ramp has been started immediately after the preparation of the unreconstructed surface by the titration method and the procedure of Norton et al. [6], respectively. In Fig. 4c the surface prepared by the titration method has been saturated with hydrogen at 300 K before the ramp was started. The increase of intensity with temperature may be attributed to two processes: hydrogen desorption and initiation of surface reconstruction. The recorded He intensity consists of three contributions: an elastically scattered background from unreconstructed surface areas, the 2/5 order diffraction intensity from reconstructed surface areas and an inelastic background. We used the rather small heating rate of 0.06 K/s in order to reduce the influence of kinetic effects while keeping the adsorption still negligible. The observed rise in intensity in Fig. 4 occurs between 350 and 460 K. Above 460 K and below 350 K there is almost no intensity change with temperature. The increase in the background due to the Debye–Waller effect is much smaller than the changes in counting rate observed within this temperature interval of about 100 K [18].

Qualitatively the intensity increase in Figs. 4b and 4c proceeds in two steps (two shoulders) while in Fig. 4a it occurs in only one step. From diffraction scans we find in all three cases that at 460 K a pronounced 2/5 order diffraction peak is present. The shoulder at higher temperature (leading from an intensity of 0.65 to 1.0) which is present in all three cases is therefore ascribed to the reconstruction. The shoulder in the $I(T)$ curves at lower temperature (in the intensity range 0.30 to 0.65) is related to the adsorbed hydrogen. This is evident as the latter shoulder is completely absent for a clean surface (Fig. 4a), while it is most pronounced for the hydrogen saturated surface (Fig. 4c). The shoulder is of an intermediate size in Fig. 4b and begins only at 350 K, in agreement with the fact that the hydrogen coverage was already reduced by heating to 375 K for 1 min (see Fig. 2).

The reason why hydrogen desorption leads to an increase in diffuse intensity in the first shoulder has not been identified. The shoulder is – like the specular reflectivity – sensitive even to H coverages of less than 10%. Most likely, the measuring position is close enough to the Lorentzian specular peak to profit from its rise due to the increase in reflectivity more than it looses in diffuse scattering contribution from the reduction of adsorbate coverage. Another

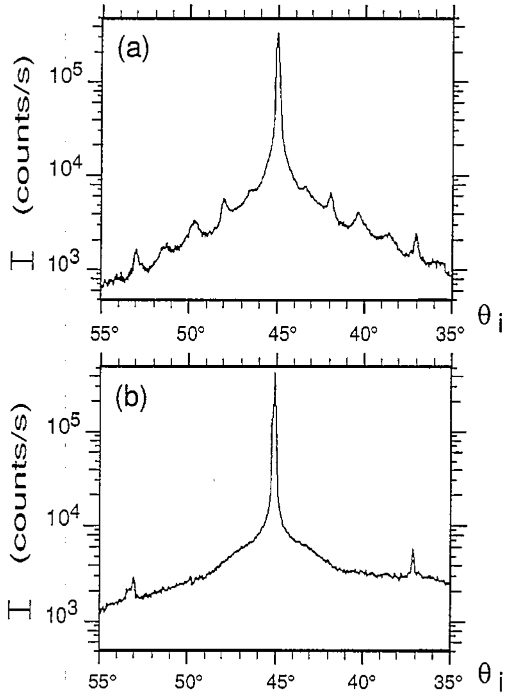

Fig. 5. He diffraction patterns at 390 K surface temperature. Total scattering angle $\Theta_i + \Theta_f = 90°$, He beam energy 70 meV. The central peak at $\Theta_i = 45°$ is the specular peak. The peaks at $\Theta_i = 53°$ and $\Theta_i = 37°$ correspond to the (10) and the (-10) diffraction peaks of the unreconstructed surface structure. The measuring time for each scan is 15 min. (a) Pt(100)-(1×1) surface prepared by the titration method, then heated to 390 K. (b) Pt(100)-(1×1) surface prepared by the titration method, then saturated with hydrogen at about 300 K and heated to 390 K.

possible explanation is an adsorbate induced change in cross section for inelastic processes. A third reason may be an increased diffuse scattering due to an increased defect concentration on the terraces which may occur just before the beginning reconstruction.

Fig. 5 demonstrates most strikingly the effect of the presence of hydrogen on the onset of reconstruction. Both diffraction scans were recorded at 390 K. For the measurement shown in Fig. 5b the surface was initially saturated with hydrogen at room temperature. No sign of ordered surface reconstruction is found at 390 K. The scan in Fig. 5a was obtained for a surface initially prepared by the titration method. Here, in contrast, we find roughly 4% [19] of the surface to be reconstructed. The time to perform each diffraction scan is 15 min. Thus, the fact that both diffraction patterns in Fig. 5 are symmetric indicates that the surface structures are quasi-equilibrated and are not subjected to changes on this time scale. This observation proves that a very small residual hydrogen coverage stabilizes the (1 × 1) phase up to more than $T = 390$ K. This stabilization occurs for the hydrogen saturated preparation and for the preparation of the "almost clean" surface.

We conclude that the practically clean Pt(100)-(1 × 1) surface prepared by titration is stable only up to 370 K (indicated by the onset of the intensity rise in Fig. 4a) while a hydrogen coverage – once present – irreversibly extends the stability up to 400 K. Thus, the appearance of a weak reconstruction pattern at or below 390 K can be regarded as an indicator of surface cleanliness as demonstrated in Fig. 5a.

5. Conclusion

We have employed thermal energy He atom scattering to monitor the preparation of the well ordered Pt(100)-(1 × 1) surface. We established a titration method monitored by specular He scattering which allows the controlled preparation of adsorbate-free Pt(100)-(1 × 1) terraces ($\theta < 1\%$). The surface thus prepared shows no traces of reconstruction.

The ordered unreconstructed surface is very reactive compared to the ordered reconstructed phases. Under typical UHV conditions (1×10^{-8} Pa) contamination of a freshly prepared surface occurs within a few minutes as the hydrogen coverage increases by approximately 1% every seven minutes. However, controlled dosing of a small amount of NO gas around 300 K restores surface cleanliness.

The clean Pt(100)-(1 × 1) surface was found to reconstruct already at 370 K while the presence of even less than 10% of a monolayer of hydrogen extends the stability range of the unreconstructed surface to 400 K.

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[13] $\Sigma \approx 120$ Å^2 for a He beam energy of 63 meV at $\theta_i = 40°$; see Ref. [11].

[14] The fact that no full hydrogen coverage is present at 300 K under saturation conditions is not surprising since the saturation at 120 K corresponds to full coverage (1.28×10^{15} atoms/cm^2) [17] and hydrogen thermal desorption spectra, e.g. in B. Pennemann et al. Surf. Sci. 249 (1991) 35, exhibit several desorption states already below room temperature.

[15] We might call the surface preparation proposed in this paper "practically clean" in contrast to the "almost clean" preparation by Bonzel et al. and Norton et al. [5,6] because the proposed preparation leads to a surface cleanliness which cannot be improved under typical UHV conditions for practical reasons.

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[18] For a surface Debye temperature of $T_D = 231$ K a temperature increase of 100 K corresponds to an intensity reduction of 8.4%. The surface Debye temperature for Pt(111) was determined to be $T_D = 231$ K by B. Poelsema et al., Surf. Sci. 117 (1982) 60. The values $T_D = 221$ K and $T_D = 234$ K have been determined for the reconstructed Pt(100)-hex and Pt(100)-hex-R phase respectively [9]. The value for the unreconstructed surface may be slightly different but has not been measured.

[19] It can be estimated that about 4% of the surface area is reconstructed by comparison of the integrated 2/5 order intensity in Fig. 5a (3.0×10^3 counts/s above background, 0.4° fwhm) with the diffraction pattern of a well annealed Pt(100)-hex phase at the same beam energy and detection efficiency (1.8×10^5 counts/s above background, 0.17° fwhm).