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# Adsorption stages of O on Ru(0001) studied by means of scanning tunnelling microscopy

K Meinel, H Wolter, Ch Ammer, A Beckmann, and H Neddermeyer

Martin-Luther-Universität Halle–Wittenberg, Fachbereich Physik, D-06099 Halle, Germany

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**Abstract.** The adsorption of O on Ru(0001) at a temperature of 400 K is studied in detail by means of scanning tunnelling microscopy (STM). With increasing O coverage, an ordered  $p(2 \times 2)$  structure develops, followed by a  $p(2 \times 1)$  structure. While the  $p(2 \times 2)$  structure grows via island formation, the  $p(2 \times 1)$  structure is abruptly formed by a disorder–order phase transition. After completion of the  $p(2 \times 2)$  structure at a coverage of 0.25 ML, the surface develops a rough structure where the  $(2 \times 2)$  units remain visible but appear with different heights. As the origin of this phenomenon, we propose additional O–O interactions and/or subsurface O due to the increase in O coverage. At coverages between 0.3 monolayer (ML) and 0.35 ML, different preformations of the  $p(2 \times 1)$  structure are observed. First, small fragments of  $p(2 \times 1)$  rows develop, which are randomly distributed over the surface and rotated by  $120^\circ$  with respect to each other. They grow in one dimension and induce a criss-cross arrangement of linear chains of O atoms. Two-dimensional ordering starts via pairing of the  $p(2 \times 1)$  rows. At a critical O coverage slightly below 0.40 ML, suddenly large  $p(2 \times 1)$  domains are formed in three orientations (rotated by  $120^\circ$ ), which coexist with remnants of the  $p(2 \times 2)$  structure. At the saturation coverage of O (0.5 ML), the  $p(2 \times 1)$  domains cover the surface completely.

## 1. Introduction

The adsorption of O on Ru(0001) has been extensively investigated in the past two decades [1–15]. The interest in this system is mainly stimulated by the unique catalytic properties of Ru, the exploitation of which is complicated by O-induced Ru degradation [1]. In addition, O adlayers on Ru(0001) have been frequently used as a model system in studying adsorption, as they are easy to prepare and relatively stable. Almost the whole arsenal of methods of surface analysis have been applied in attempts to understand the O/Ru interaction. The investigations revealed that, above room temperature, O dissociatively adsorbs onto the hexagonal-closed-packed (hcp) Ru(0001) surface possessing hcp-type threefold hollow sites (sites with a Ru atom below, in the second layer) [3]. Initially, a  $p(2 \times 2)$  structure develops, which is completed at a coverage of 0.25 monolayers (ML, relative to the number of surface atoms) [2, 12]. At coverages above 0.37 ML a  $p(2 \times 1)$  domain structure with three domains rotated by  $120^\circ$  to each other is formed by additionally filling the hcp sites; this is completed at the saturation coverage of 0.5 ML attainable in UHV experiments [2, 5, 6, 10, 11].

LEED reveals a fully developed  $(2 \times 2)$  superstructure pattern at coverages above 0.17 ML [2, 10]. The intensity of the superstructure spots displays maxima at the completion of the  $p(2 \times 2)$  and  $p(2 \times 1)$  structures at coverages of 0.25 ML and 0.5 ML, respectively [2]. During the structural transformation, the spot shape remains constant, suggesting the absence of island formation (coexistence of two phases) [14]. Nevertheless, small  $p(2 \times 2)$

O islands have been revealed by scanning tunnelling microscopy (STM) at coverages around 0.1 ML [16]. The structure of the Ru(0001) surface becomes slightly reconstructed during O adsorption [11, 12].

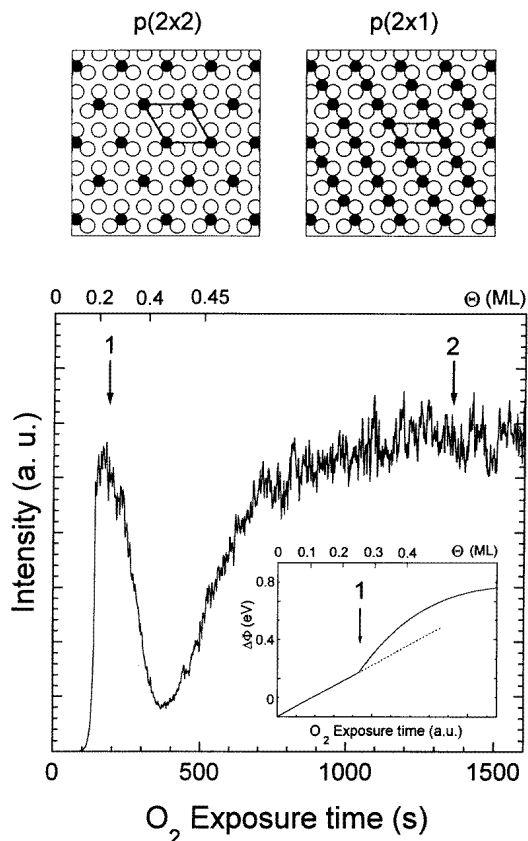
Annealing the O adlayers induces order–disorder phase transitions [14]. At temperatures above 1200 K, O is removed from the surface by desorption and diffusion into the bulk [9]. In addition, the formation of subsurface O has been proposed, starting at temperatures as low as 400 K [7]. On vicinal Ru(0001) substrates with steps parallel to the close-packed atomic rows, LEED experiments revealed special step influences on the O adlayer formation. For the  $p(2 \times 2)$  structure, correlations across the steps have been observed [16]. For the  $p(2 \times 1)$  structure, the discrimination of  $p(2 \times 1)$  domains with  $p(2 \times 1)$  rows parallel to the steps has been found [5]. Furthermore, the formation of double steps has been observed for the saturated  $p(2 \times 1)$  structure after heating the crystal at temperatures around 900 K [17].

Our interest in O adsorption on Ru(0001) results from experiments on the epitaxial growth of Cu films on Ru(0001) [18, 19]. Precovering the Ru(0001) substrate with O causes a drastic change of the Cu film morphology. O floats on top of the growing Cu film, and acts as a surfactant. For O precoverages between 0.2 ML and 0.5 ML, and a substrate temperature around 400 K, a perfect layer-by-layer growth is found. In the present work we analyse the atomic structure of the O adlayers formed at a temperature of 400 K on the Ru(0001) substrate by means of STM at room temperature. In particular, we investigate O coverages between 0.2 ML and 0.5 ML, where the O-induced layer-by-layer growth of Cu was observed. Thus our measurements probe the change of the  $p(2 \times 2)$  to the  $p(2 \times 1)$  O structure. They complete the previous investigations of this structural transition, which to our knowledge were almost exclusively carried out by means of integral methods. The STM investigations were complemented by LEED, which yields, in combination with previous work-function measurements [21], a reliable determination of the O coverage. We show characteristic stages of the superstructure formation, revealing, for the  $p(2 \times 2)$  structure, island growth, and, for the  $p(2 \times 1)$  structure, a spontaneous disorder–order phase transition. After completion of the  $p(2 \times 2)$  structure, a kind of roughening with different height levels is observed, which is probably induced by additional O–O interaction and/or subsurface O distorting the Ru lattice. At coverages between 0.3 ML and 0.35 ML, several preformations of the  $p(2 \times 1)$  structure are revealed. First, fragments of  $p(2 \times 1)$  rows rotated by  $120^\circ$  with respect to each other are developed, which are randomly distributed over the surface. They extend by one-dimensional (1D) growth, inducing a criss-cross arrangement of O atoms. Two-dimensional (2D) ordering starts via pairing of  $p(2 \times 1)$  rows. At a critical coverage slightly below 0.40 ML, large  $p(2 \times 1)$  domains are suddenly formed, which coexist with remnants of the  $p(2 \times 2)$  structure. At the saturation coverage of 0.5 ML, the surface is completely covered by  $p(2 \times 1)$  domains. For our relatively smooth Ru(1000) surface (mean terrace width:  $\sim 100$  nm), no step influences on the O adlayer formation could be observed.

## 2. Experiments

The experiments have been performed in a UHV chamber (base pressure:  $5 \times 10^{-11}$  mbar) equipped with a self-constructed STM, and a commercial system of SPALEED (spot profile analysis of low-energy electron diffraction). The STM operates at room temperature. It consists of a piezoelectric tripod for  $xyz$ -translation of the tip, and a mobile piezoelectric walker for the coarse approach. The tip was electrochemically etched from a W wire. Details of the STM construction have been described elsewhere [22].

The Ru(0001) sample, with a miscut of less than  $0.5^\circ$ , was mounted on a transfer plate made of Mo. It was cleaned *in situ* by cycles of Ar-ion bombardment (energy: 1 keV;



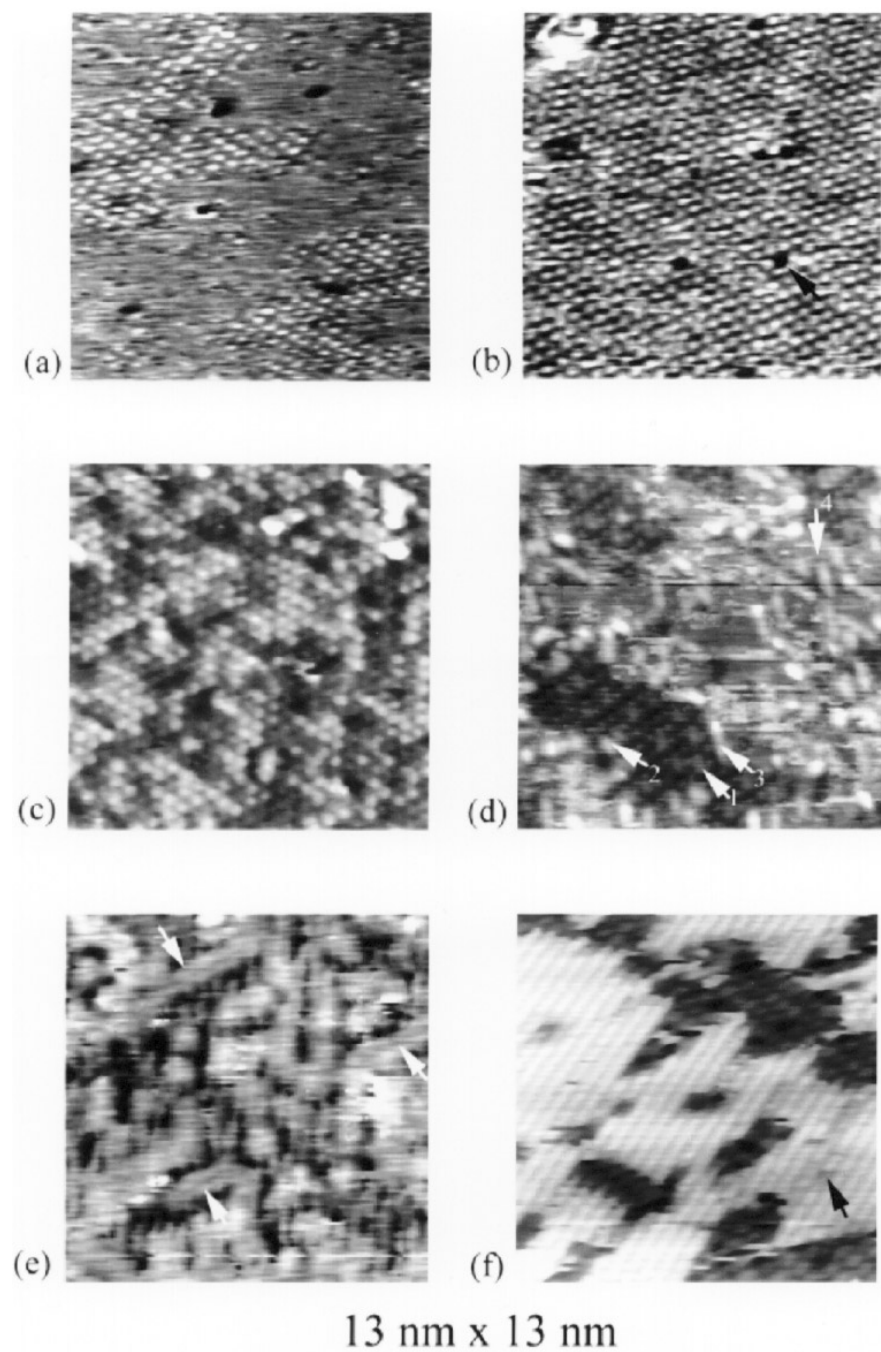
**Figure 1.**  $p(2 \times 2)$  and  $p(2 \times 1)$  superstructures of O on Ru(0001) (shown schematically above) studied in their formation by means of LEED (below). The maxima of the intensity of the (0.5, -0.5) superstructure LEED spot indicate the completion of the  $p(2 \times 2)$  structure (arrow 1) and the  $p(2 \times 1)$  structure (arrow 2), respectively (O pressure:  $2 \times 10^{-9}$  mbar; sample temperature: 400 K; electron energy: 220 eV). The inset shows results obtained from previous work-function measurements [21], which are used to calibrate the O coverage.

current density: typically  $10 \mu\text{A cm}^{-2}$ ), followed by heating to temperatures around 1300 K. After this treatment, we applied cycles of 20 L (Langmuir) ( $1 \text{ L} = 1.33 \times 10^{-6} \text{ mbar s}$ ) O adsorption and desorption by heating the sample to 1600 K, in order to deplete the surface C and S contaminations [20].

The sample heating was performed by means of electron bombardment, and radiative heating from a W filament from the back of the sample. The temperature was determined from the heating parameters, which were initially calibrated by means of a thermocouple. The sample cleanliness was proved by means of LEED and STM. A bright and intense ( $1 \times 1$ ) LEED pattern was always achieved. STM reveals large clean terraces, typically 100 nm in size, separated by monatomic steps. Under stable tip conditions, the STM yields atomic resolution of the Ru(0001) surface.

[t]

The O (purity 0.99998) was dosed via a leak valve with a constant pressure of  $2 \times 10^{-9}$  mbar at a substrate temperature of 400 K. During O exposure, the formation of the O adlayer was followed by SPALEED, which we mainly used as a high-resolution LEED.



**Figure 2.** The dependence on the O coverage of a sequence of STM images revealing characteristic O adsorption structures, at an adsorption temperature of 400 K. (a) 0.2 ML, (b) 0.25 ML (completion of the  $p(2 \times 2)$  structure), (c) 0.3 ML, (d), (e) 0.3 ML–0.35 ML, and (f) 0.39 ML ( $p(2 \times 1)$  structure formation). For explanations, see the text.

We measured the intensity of the (0.5, -0.5) spot of the (2 × 2) superstructure with an electron energy of 220 eV, with the sample oriented perpendicular to the SPALEED axis. The incident beam current was about 1 nA. The SPALEED system works with a LaB<sub>6</sub> cathode. Its efficiency alters in the O atmosphere, which reduces the measured intensity over time. The altering effect was corrected for, by measuring the apparent intensity change of a (2 × 2) spot of an O-saturated O/Ru(0001) sample exposed again to an O atmosphere of  $2 \times 10^{-9}$  mbar.

The STM measurements were performed immediately after O exposure at room temperature. The STM images were taken in the constant-current mode. Typically, we used a sample bias voltage of about -0.6 V, and a sample current of a few nA. The noise level in the z-corrugation was about 0.01 nm. The STM imaging required several hours. Nevertheless, during the STM measurements no further uptake of O from background pressure was observed. For preparing a new O adlayer, the clean Ru(0001) surface was restored by desorbing O by heating the crystal up to a temperature of 1600 K.

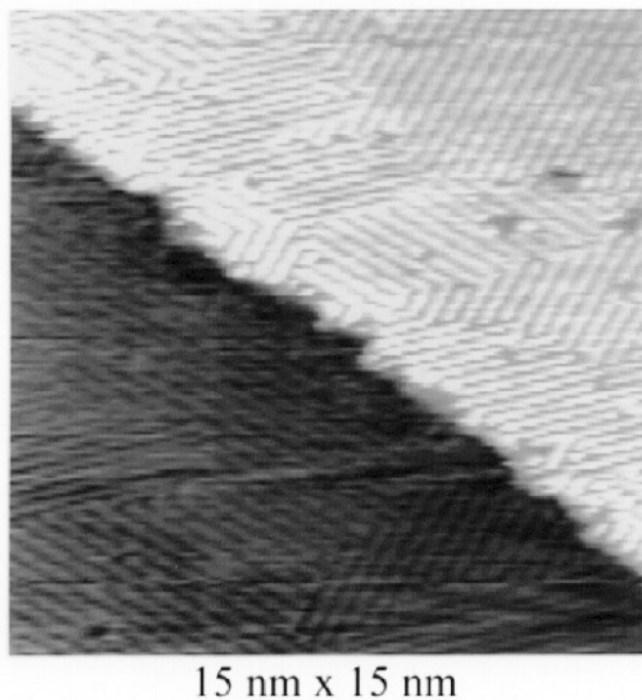
### 3. Results and discussion

The formation of the O adlayer on Ru(0001) is demonstrated in figure 1, where the results of our LEED and previous work-function measurements [21] are combined. The p(2 × 2) and p(2 × 1) structures of the O/Ru(0001) system are shown schematically in figure 1. The two structures yield the same (2 × 2) LEED pattern. The characteristic intensity change of the (0.5, -0.5) superstructure spot measured during O exposure at  $2 \times 10^{-9}$  mbar is shown in the diagram in figure 1. The intensity maxima observed at exposure times of 165 s and of about 1400 s correspond to the completion of the p(2 × 2) structure (arrow 1) and the p(2 × 1) structure (arrow 2), at 0.25 ML and 0.5 ML coverages, respectively [2]. The development of the O coverage can be traced on the top scale of the diagram. The O coverage was deduced from previous work-function measurements (see the inset in figure 1). The work-function change is a direct measure of the O coverage, as revealed from an analysis of Auger electron intensities [9, 20] (see the coverage scale as given at the top). Initially, the work-function change increases linearly with exposure time. At the completion of the p(2 × 2) structure, the slope of the work-function change rises by almost a factor of 3 [2, 20, 21]. Using the first sharp maximum in the LEED spot intensity, and the sharp break in the work-function slope as signatures of the p(2 × 2) completion allows us to correlate the two sets of measurements, as shown in figure 1. The procedure yields a reliable calibration of O coverage versus exposure time. It indicates that the superstructure formation starts at an O coverage of 0.17 ML, proceeding with a constant growth rate, and a sticking coefficient up to about 80% of the saturation coverage of 0.5 ML, which exactly corresponds to previous investigations [10, 13].

The results of the STM investigations are displayed in a series of high-resolution STM images (figures 2 and 3) resolving the dependence on coverage of the atomic structure of the O adlayer. Figure 2(a) shows islands of the p(2 × 2) O structure which develop at a coverage of 0.2 ML. On the islands, hexagonally arranged O atoms are identified; they produce a corrugation of about 0.02 nm. We observe that the p(2 × 2) structure grows via island formation, like in previous STM investigations [15]. The island coverage does not exactly correspond to the exposure. In figure 2(a), it is about 30% smaller than expected. Obviously some of the O atoms migrate as a 2D gas between the islands; this has been directly revealed by STM recently [23]. The identification of the exact position of the O atoms within the p(2 × 2) structure imaged by STM is problematic. In many systems, O atoms appear as depletions, e.g. on Ni(111) [24]. In the case of the O/Ru(0001) system, O

atoms emerge either as depletions or as protrusions, depending on the imaging conditions. In recent investigations of low-temperature adsorption and imaging of O on Ru(0001), we observed  $p(2 \times 2)$  structures with O atoms appearing as depletions [25]. In the present investigation, where we image the O/Ru(0001) structures at room temperature, the O atoms emerge as protrusions. This we conclude from the height of the maxima and minima of the  $p(2 \times 2)$  islands observed at coverages below 0.25 ML. The maxima are measured above the level of the uncovered neighbourhood, and the minima at almost the same level of the uncovered neighbourhood (figure 2(a)). The completed  $p(2 \times 2)$  structure corresponding to an O coverage of 0.25 ML is shown in figure 2(b). Ignoring some point defects (arrow) and a slight distortion caused by temperature drift, a perfect  $p(2 \times 2)$  pattern is revealed.

Slightly increasing the O coverage up to values of about 0.3 ML drastically disturbs the structural perfection. Some of the O-related protrusions appear at a higher level and some at a lower level, therefore leading to a kind of roughening of the  $p(2 \times 2)$  structure. The corrugation of the rough surface structure is about 0.07 nm. It is apparent from the image that the protrusions preferentially form little islands with unique height; the lateral extension of these locally ordered structures is about 4 nm (figure 2(c)). Nevertheless, the  $p(2 \times 2)$  pattern can still be recognized at all height levels. The observed displacements cannot yet be explained. They may be induced by repulsive lateral interactions of the laterally compressed O atoms wrinkling the O adlayer. They could also be induced by vertical distortions of the Ru(0001) substrate. The latter may be caused by O atoms migrating into subsurface sites and therefore distorting the Ru lattice. However, the possible formation of subsurface O as proposed in previous investigations [7] is still a matter of controversy.



**Figure 3.** An STM image of saturated  $p(2 \times 1)$  O/Ru(0001) domains in the vicinity of a monatomic step (adsorption temperature: 400 K).

A further increase of the O coverage to values between 0.3 ML and 0.35 ML locally induces structures which can be considered as transition stages in the development of the  $p(2 \times 1)$  structure. Different  $p(2 \times 1)$  preformations partly coexist on neighbouring terraces, depending on the local O coverage (figures 2(d), 2(e)). As a first indication of the structural transition, we observed the occupation of the  $p(2 \times 1)$  sites between neighbouring  $p(2 \times 2)$  O atoms by individual O atoms (figure 2(d), arrows 1 and 2). This generates small linear fragments of  $p(2 \times 1)$  rows exactly three atoms in length, which are rotated by  $120^\circ$  with respect to each other. The  $p(2 \times 1)$  fragments are randomly distributed over the surface. They can be considered as 1D elements of the  $p(2 \times 1)$  structure. They partly induce a relatively weak contrast, comparable to that of the atoms of the  $p(2 \times 2)$  structure (figure 2(d), arrow 1); they also partly induce a bright contrast with an apparent height of 0.08 nm above that of the  $p(2 \times 2)$  neighbourhood (figure 2(d), arrow 2). In addition, one finds longer (1D) pieces of  $p(2 \times 1)$  rows obviously formed by 1D growth of the former ones, which exclusively display a bright contrast (figure 2(d), arrow 3). However, the individual O atoms of the  $p(2 \times 1)$  rows are not resolved in the STM images. At somewhat greater local O coverage, the images became blurred and noisy. Nevertheless, a criss-cross structure of 1D  $p(2 \times 1)$  pieces is still resolvable (figure 2(d), arrow 4). At larger local O coverage (figure 2(e)), the 1D  $p(2 \times 1)$  pieces are arranged in pairs (see the arrows), indicating the first step of 2D ordering of the  $p(2 \times 1)$  rows. Figure 2(f) shows the O structure observed at a coverage of 0.39 ML. The characteristic stripe pattern of large  $p(2 \times 1)$  domains is suddenly revealed, partly covering whole terraces. The corrugation perpendicular to the  $p(2 \times 1)$  stripes is about 0.02 nm. Initially, the  $p(2 \times 1)$  domains are not complete. They contain some vacancies (figure 2(f), arrow), and coexist with remnants of the  $p(2 \times 2)$  structure, which are visible in a less bright grey tone (corresponding to a deeper level). The origin of the strong contrast between the 2D and 1D  $p(2 \times 1)$  structures, on the one hand (see also figures 2(d), 2(e)), and the  $p(2 \times 2)$  neighbourhood, on the other, is unknown. It corresponds to a corrugation height of about 0.1 nm. However, it certainly does not indicate a real topographic height difference. According to LEED investigations, the O layer is located at almost the same height above the Ru(0001) substrate, independently of the adsorption structure [11, 12]. Hence the contrast is probably induced by electronic effects. The sudden appearance of  $p(2 \times 1)$  domains at O coverages between 0.35 ML and 0.39 ML indicates that they are created by a spontaneous disorder–order phase transition, and not by island growth. This corresponds to previous LEED investigations, which reveal that the  $p(2 \times 1)$  structure is spontaneously induced at a critical coverage of 0.37 ML, without island formation [10, 14]. Figure 3 shows the O structure observed at the saturation coverage of 0.5 ML. The whole surface is covered by completely filled  $p(2 \times 1)$  domains rotated by  $120^\circ$  with respect to each other. No  $p(2 \times 2)$  remnants are observed. The mean size of the  $p(2 \times 1)$  domains is about 10 nm (diameter) on the terraces. The domain size, of course, will change with the adsorption temperature and defect concentration of the substrate.

Finally we have investigated the influence of substrate steps on the O adlayer formation. Unfortunately, for the  $p(2 \times 2)$  structure, the resolution near step edges was insufficient for us to see details of the atomic structure. Therefore we could not analyse whether there are any structural correlations across the steps as reported in the literature [16]. For the  $p(2 \times 1)$  structure, however, the possible influences of step edges could be investigated. This is demonstrated in figure 3, which shows the  $p(2 \times 1)$  domain structure in the vicinity of a step running almost parallel to one of the three  $p(2 \times 1)$  orientations. We observe all three types of  $p(2 \times 1)$  domain on the lower and the upper terrace at the step edge. For vicinal Ru(0001) surfaces it has been found previously that the formation of  $p(2 \times 1)$  domains with  $p(2 \times 1)$  rows parallel to the steps is suppressed [5]. On our well-oriented



Ru(0001) surface with typical terrace widths of 100 nm, this is not the case, even in the close neighbourhood of individual steps. It seems plausible, however, that the effect of domain suppression preferentially occurs on narrow terraces. The same may hold true for the formation of double steps observed after heating an O-saturated vicinal Ru(0001) sample at temperatures around 900 K [17]. After our heating experiments, we occasionally observed relatively small terraces, with widths of about 2 nm. However, we have never found double-layer steps. Obviously, for a highly oriented Ru(0001) surface, the material transport is thermodynamically unfavourable for producing step doubling.

#### 4. Summary

We have investigated the adsorption of O on Ru(0001) at a temperature of 400 K by means of STM. The images reveal a sequence of characteristic stages of  $p(2 \times 2)$  and  $p(2 \times 1)$  O superstructure formation. They were assigned to the O coverage, after calibrating the exposure by means of LEED and previous work-function measurements. At coverages below 0.35 ML, a  $p(2 \times 2)$  structure prevails, which is of perfect order at a coverage of 0.25 ML. Its formation is controlled by island growth. At O coverages around 0.3 ML, a kind of roughening of the  $p(2 \times 2)$  structure is observed, which may be interpreted as an indication of O adlayer wrinkling induced by O–O interaction and/or by deformation of the Ru lattice caused by the penetration of O into the subsurface region. The  $p(2 \times 1)$  structure formation proceeds without island formation, by a spontaneous disorder–order phase transition. Several preformations of the  $p(2 \times 1)$  structure are revealed at O coverages between 0.3 ML and 0.35 ML. Initially small fragments of 1D  $p(2 \times 1)$  rows rotated by  $120^\circ$  with respect to each other are formed, which are randomly distributed over the terraces. They exhibit 1D growth, leading to a criss-cross arrangement of O atoms. 2D ordering starts with pairing of the  $p(2 \times 1)$  rows. At a critical coverage slightly below 0.40 ML, large  $p(2 \times 1)$  domains are formed. Initially, they contain a large number of vacancies, and coexist with remnants of the  $p(2 \times 2)$  structure. At an O saturation coverage of 0.5 ML, the  $p(2 \times 1)$  domains are completed, and cover the entire surface. For our highly oriented Ru(0001) surface (mean terrace width:  $\sim 100$  nm), the experiments neither show influences of steps on the formation of the O superstructures, nor show step doubling by mass transport of Ru atoms.

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