Identification of Step Atoms by High Resolution Core Level Spectroscopy

J. Gustafson,[1,*] M. Borg,[1] A. Mikkelsen,[1] S. Gorovikov,[2] E. Lundgren,[1] and J. N. Andersen[1]

[1]*Department of Synchrotron Radiation Research, Institute of Physics, Lund University, P.O. Box 118, SE-221 00 Lund, Sweden*
[2]*MAX-Lab, Lund University, P.O. Box 118, SE-221 00 Lund, Sweden*
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Vicinal Rh(111) surfaces are studied with high resolution core level photoemission. We demonstrate the possibility to distinguish between the different kinds of surface atoms on these surfaces by virtue of their 3*d* core level binding energies. In particular, the low coordinated step atoms are found to exhibit a clear fingerprint in Rh 3*d* spectra. We demonstrate how this may be used to show that initial oxygen adsorption occurs on the steps and not on the terraces of the vicinal surfaces.

The major influence that steps may have on fundamental processes at surfaces has been recognized for many years. The difference in coordination numbers between atoms at steps and on flat parts of a surface modifies the electronic properties in the vicinity of the steps, thereby permitting processes not possible on flat parts of the surface to occur at the steps. For instance, the importance of steps in modifying inter- and intralayer diffusion [1], nucleation [2], and adsorption, dissociation, and surface diffusion [3–5] has been demonstrated. Whereas a number of studies exist of the effects on various processes caused by steps, previous approaches to study the microscopic origins of these property changes at or close to steps have been limited to scanning tunneling microscopy (STM) [1,3,5], field ion microscopy (FIM) [6], and *ab initio* calculations [2,5,7]. Further, infrared spectroscopy may detect vibrational frequency shifts for adsorbed molecules such as CO adsorbed at steps and other defect sites [8]. However, in this case the information is gained via the adsorbate rather than the substrate yielding different but complementary information. In this Letter we demonstrate how high resolution core level spectroscopy (HRCLS) may utilize the modified electronic structure to provide a clear signature of the lower coordinated atoms present at steps on a vicinal surface. A major advantage of HRCLS is that with the use of high intensity third generation synchrotron radiation sources and efficient detection of the photoelectrons, measurement of a spectrum may be performed in a few minutes or in favorable cases even a few seconds, thereby facilitating studies of processes at steps. Also, vicinal surfaces of most metals are easy to prepare in a form appropriate for HRCLS measurements in contrast to the case of FIM which is limited to refractory metals. Finally, sample preparation and identification and monitoring of, e.g., chemical processes occurring on the surface are significantly helped by the inherent elemental and even chemical sensitivity [9,10] of HRCLS.

In this Letter we report HRCLS results for the vicinal Rh(553) and Rh(151515) surfaces which consist of Rh(111) terraces separated by monatomic steps with the step density being higher on the (553) surface. We dem-

onstrate unambiguously the possibility to distinguish not only surface and bulk Rh atoms, but also the atoms with different coordination numbers at or close by the step. Our findings open up the possibility to, in a straightforward way, study important processes at a step.

The measurements were conducted at beam line I311 at MAX II in Lund, Sweden [11]. The HRCL spectra were recorded at liquid nitrogen temperatures in order to reduce thermal broadenings. The Rh(553) and (151515) crystals were cleaned by cycles of Ar^+ sputtering and annealing to 1200 K, followed by oxygen treatment at temperatures up to 1100 K in order to remove residual C and a short anneal in vacuum up to 1300 K in order to remove adsorbed O. The cleanliness of the surface was checked by monitoring the Rh $3d_{5/2}$, the O 1*s* and the C 1*s* core levels, and the valence band region. Cleaning cycles were continued until no contaminants could be detected. The periodicity of the steps on the surface was inspected by low energy electron diffraction and STM demonstrating the expected periodicity of a (553) and a (151515) surface, respectively.

The atomic arrangement of the Rh(553) surface is shown in Figs. 1(a) (top view) and 1(b) (side view). The steps are separated by five atom wide (111) terraces, and the step itself is a so-called *A*-type step with a (100) microfacet. Three types of atoms with different coordination numbers exist on the surface: 3/5 of the atoms have coordination number 9 and are on the (111) terraces, marked *T* (terrace atoms) in Fig. 1(b), 1/5 have coordination number 7 at the edge of the steps, *S* (step atoms), and the last 1/5 have coordination number 11 underneath the step edges, *U* (underneath atoms). For Rh(151515) the situation is similar, except that the steps now are separated by 15 atoms wide terraces, and thus the ratio between the numbers of *T*, *S*, and *U* atoms is 13:1:1.

In Fig. 1(c) is shown the Rh $3d_{5/2}$ HRCL spectrum from the Rh(553) surface, measured at an emission angle of 45°, as well as a decomposition of the spectrum. We used Doniach-Sunijic line shapes for all components in the decompositions. The Lorentzian and Gaussian contribution was found to be slightly larger in the *S* and *T* components as compared to in the *B* and *U* components.
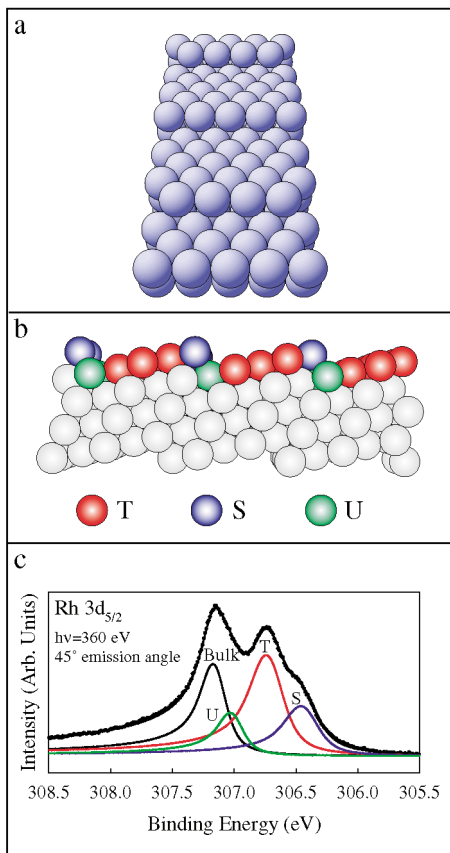
FIG. 1 (color online). Top (a) and side (b) views of the fcc(553) surface with the three differently coordinated surface atoms T (terrace atoms), S (step atoms), and U (underneath atoms) indicated. (c) HRCL spectrum of the Rh $3d_{5/2}$ level from the Rh(553) surface (45° off normal emission), and a decomposition into components from the S, T, U, and bulk atoms.

Here we give a brief description of how the various components may be assigned with further justification presented below. In addition to the bulk peak at just above 307 eV, the raw experimental spectrum clearly contains two additional components at lower binding energies. The component closest to the bulk peak has a binding energy close to that of surface atoms on Rh(111) [12,13] (see also Fig. 3 below), and may therefore be interpreted as due to the terrace atoms, T. The component with the larger shift relative to the bulk peak, visible as a shoulder in Fig. 1(c), is assigned to the low coordinated step atoms, S, as a reduction of the coordination number is expected to cause such an increase of the shift. Use of only these two surface related components is, however, not sufficient in order to achieve consistent decompositions of the spectra at all measured photon energies. An additional component must be included between the terrace and the bulk peaks. This component is interpreted as being due to the almost fully coordinated U atoms underneath the step.

The ratios T:S:U between the integrated intensities of these three components in Fig. 1(c) at first seem incon-

sistent with the values 3:1:1 expected from the number density of these atoms. This is, however, to a large extent an effect of the chosen photon energy and emission angle which both enhance the relative intensity of the S component. In Fig. 2, the integrated intensities of the T, S, and U components at normal emission normalized to the bulk component at each photon energy are shown for photon energies from 360 to 500 eV. This shows a ratio between T and S very close to 3:1, while the U component is slightly smaller than expected. The reduced intensity of the U component could, in addition to errors resulting from this intensity being very difficult to determine precisely due to the U component being between the intense bulk and T components, result from the U atoms being deeper in the surface whereby emission from them will suffer larger attenuation than atoms in the surface layer. This explanation should, as is also the case, result in a smaller deviation with increased photon energy.

The validity of these core level "fingerprints" derived from the (553) surface may be evaluated by comparing Rh $3d_{5/2}$ level spectra from the Rh(553), the Rh(151513), and the Rh(111) surfaces as shown in Fig. 3. As expected, the main features are similar in the three spectra, with one component originating from the bulk atoms and one originating from the terraces, denoted bulk and T, respectively. By comparing the spectra from the Rh(553) and Rh(111), the step related component towards lower binding energy can clearly be seen, confirming our assignment presented above. Turning to the (151513) surface, use of the same components as in the (553) decomposition yields a satisfactory result. The decrease in intensity of the S and U components for the (151513) surface is consistent with the lower step density on this surface. Thus we conclude that the components identified in the Rh(553) spectra provide good fingerprints of the different kinds of atoms present.
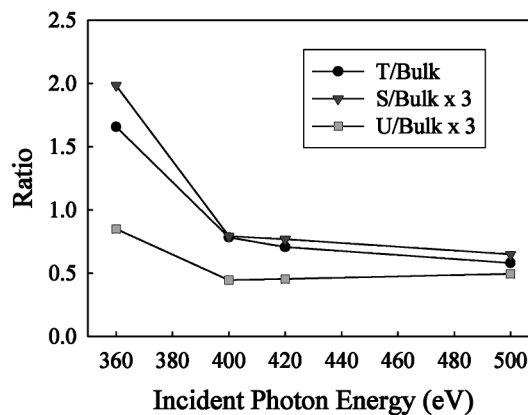

FIG. 2. The area of the T, S, and U components recorded at normal emission, respectively, relative to that of the bulk component in the Rh $3d_{5/2}$ spectrum from the Rh(553) surface. The S and U intensities are multiplied by a factor of 3.
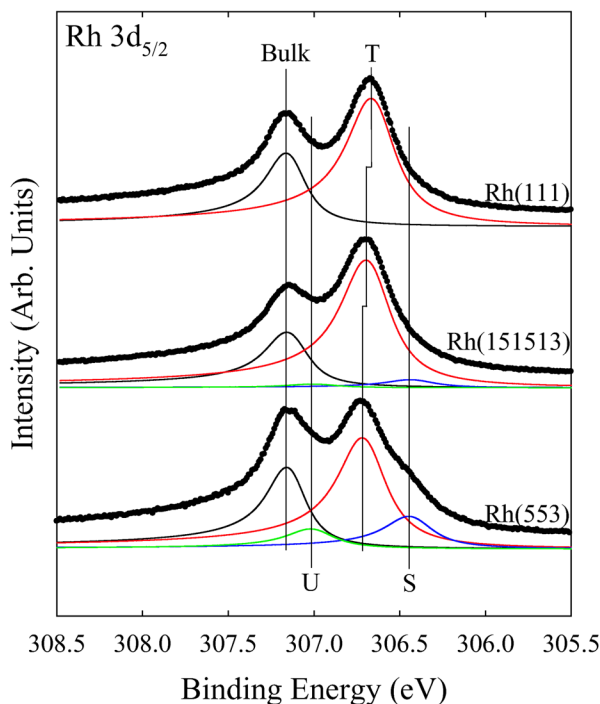
FIG. 3 (color online). The Rh $3d_{5/2}$ core level spectra from the Rh(553) (bottom), the Rh(151513) (middle) and the Rh(111) surface (top), recorded at normal emission. T corresponds to the component originating from the atoms on the (111) terraces, S is from the step atoms and U is from the atoms directly underneath the step.

FIG. 4. The relative binding energy of each component in the Rh $3d_{5/2}$ spectrum from the Rh(553) as well as the T components from the Rh(111) and Rh(151513) surfaces versus the coordination number of the respective atoms. The dashed line is a guide to the eye.

The magnitudes of the binding energy shifts for the S, T, and U components of the Rh(553) surface are also in accord with expectations. Figure 4 shows the binding energy shifts relative to the bulk Rh emission of the various Rh $3d_{5/2}$ components from Rh(553) versus their coordination numbers. As clearly seen, the binding energy shift relative to the bulk component increases almost linearly with the decrease of the coordination number as expected from the so-called partial shift model [14] of core level shifts in metallic systems. In passing we note that the almost perfect linearity shown in Fig. 4 is somewhat coincidental; e.g., the T component differs among the different surfaces. Finally, it may be noticed that under the assumptions that the shifts are dominated by initial state effects as is the case for clean Rh(111) [12,13] and that all levels of the Rh atoms show similar binding energy shifts, the presently measured direction of the $3d$ shift for the S atoms indicates a shift of the $4d$ level towards the Fermi level for these atoms. According to the Hammer-Nørskov model [15,16] such a shift of the $4d$ band in turn indicates an increased reactivity of the step atoms.

As seen from Fig. 3, the binding energy of the T components increases as the step density increases from (111) to (151513) to (553). Thus, the steps affect the binding energy (and thus also the electronic structure) of not only the atoms at the steps, but also of the terrace
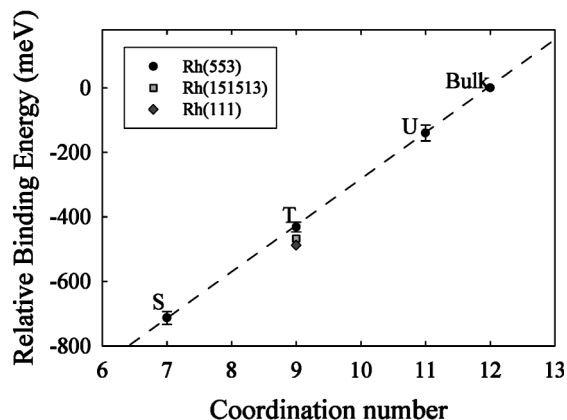
atoms. The detailed reason for this shift is at this time not clear, and we may therefore only speculate. One reason may be differences in the in-plane relaxations on the terrace of the vicinal (553) surface due to a higher tensile stress than on the (151513) and (111) surfaces. Such relaxations, which are known to occur at vicinal surfaces [17], may very well induce small changes of the core level binding energies and should be larger on the (553) surface than on the (151513) surface, qualitatively consistent with our results. Further, recent calculations [18] on Rh(111) have demonstrated that a change of the first interlayer distances of 1% may induce a Rh $3d_{5/2}$ shift of about 60 meV. The *ab initio* calculations necessary for resolving these issues will, however, be very demanding for the present vicinal surfaces due to the large unit cells necessary. Irrespective of the detailed cause, these binding energy shifts and the Hammer-Nørskov model [15,16] indicate that molecules adsorbed on the terraces of the vicinal surfaces may have adsorption energies and reactivities which differ from those found on the Rh(111) surface. Assuming that the $3d$ shifts are reflected by similar $4d$ shifts, the present results indicate a weaker interaction and lower reactivity on the vicinal terraces than on the terraces of the perfect (111) surface.

As an illustration of the potential of this method, we have briefly studied the initial adsorption of oxygen on the Rh(553) surface. Figure 5 shows the Rh $3d_{5/2}$ spectrum obtained from the surface exposed to 0.2 L (0.06 ML) [1 L = 10^{-6} torr sec, ML = number of Rh atoms in the Rh(111) surface] of oxygen at a temperature of 320 K. When comparing this spectrum to that of the clean Rh(553) surface [see Fig. 1(c)], it is immediately clear that most of the S component disappears, indicating that most of the S atoms are influenced by adsorbed oxygen atoms after an oxygen exposure of only 0.2 L. As we find for Rh(111) that an exposure of about 1.2 L (0.25 ML) is
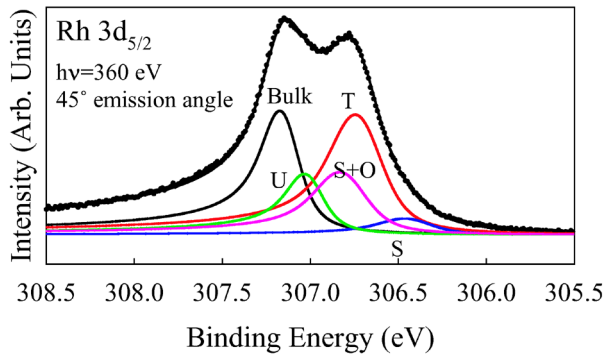
FIG. 5 (color online). HRCL spectrum of the Rh $3d_{5/2}$ level from the Rh(553) surface after an oxygen exposure of 0.2 L (45° off normal emission, 0.06 ML). A decomposition into S, T, U, bulk, and oxygen induced ($S + O$; see text) components is included.

needed in order to form the (2×2)-1O structure, this shows in a very direct way that in the initial stage of oxygen adsorption, the oxygen atoms adsorb at the steps as opposed to on the terraces of the Rh(553) surface. In order to derive more detailed information on the adsorption site of the oxygen atoms, a decomposition is needed. This is a difficult task as the oxygen induced Rh components are expected to have binding energies between the T and the B peaks making it difficult to obtain a unique decomposition. However, a good decomposition may be obtained, as shown in Fig. 5, by introducing a new component (denoted $S + O$) between the T and U components and leaving the T, S, and U components unchanged in binding energy. Relative to the clean S atoms, the shift of this component is about +370 meV, i.e., almost equal to the shift induced by the bonding of one oxygen atom to a Rh atom on the Rh(111) surface [13]. The intensity of the $S + O$ component is roughly equal to the reduction in intensity of the S component upon oxygen adsorption. Based on these two observations we interpret the $S + O$ component as due to S atoms which each bond to one adsorbed oxygen atom. We also find that the intensity of the T component is reduced slightly upon oxygen adsorption. Assuming a similar oxygen induced shift as found for the S component or for the Rh(111) surface [13], the intensity removed from the T component should reappear so close to the U peak that it cannot be resolved. The strong reduction of the S component and the smaller reduction of the T component is consistent with oxygen atoms occupying every second of the threefold hollow sites formed by two S atoms and one T atom along the upper side of the step. We therefore suggest that this is the arrangement of the oxygen atoms at the steps.

In conclusion, we have shown that the emission from step atoms on a vicinal surface may be resolved in HRCLS. The magnitude of the binding energy shift with respect to the bulk atoms depends almost linearly on the coordination number of the atoms. These results hold promise for future dynamical investigations of important processes at steps. We have, as an example of the capabilities of the method, shown that oxygen initially adsorbs on the step edges before filling the terraces.

*Electronic address: Johan.Gustafson@sljus.lu.se

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