Non-local Effects on Oxygen-Induced Surface Core Level Shifts of Re(0001)

E. Miniussi,^{†,⊥} E. R. Hernández,[§] M. Pozzo,[∥] A. Baraldi,^{*,†,⊥} E. Vesselli,^{†,⊥} G. Comelli,^{†,⊥} S. Lizzit,[#] and D Alfe^{||,&}

[†]Physics Department and CENMAT, University of Trieste, Via Valerio 2, I-34127 Trieste, Italy

[‡]Laboratorio TASC IOM-CNR, S.S. 14 Km 163.5, I-34149 Trieste, Italy

[§]Instituto de Ciencia de Materiales de Madrid (ICMM-CSIC), Campus de Cantoblanco, 28049 Madrid, Spain

Department of Earth Sciences, Department of Physics and Astronomy, TYC@UCL, and London Centre for Nanotechnology, University College London, Gower Street, London WC1E 6BT, United Kingdom

¹IOM-CNR, Laboratorio TASC, S.S. 14 Km 163.5, I-34149 Trieste, Italy

[#]Sincrotrone Trieste S.C.p.A., S.S. 14 Km 163.5, 34149 Trieste, Italy

[&]IOM-CNR, DEMOCRITOS National Simulation Centre, I-34100 Trieste, Italy

ABSTRACT: The electronic structure of clean and oxygencovered Re(0001) was investigated by combining high energy resolution core level photoelectron spectroscopy and density functional theory. For the clean surface, we detect two distinct Re $4f_{7/2}$ components shifted by 95 meV, which we ascribe to photoemission from the bulk and the top layer of the crystal. Oxygen adsorption at room temperature leads to the appearance of new core level components, which we associate to non-equivalent Re atoms from the topmost layer. In addition to the linear relationship between oxygen-induced



core level shifts and number of O-Re bonds, we find that the binding energy shift also depends on the number of oxygen atoms at second and third nearest neighbor positions. This non-local effect is discussed in terms of 5d band center shift and of charge transfer between the metallic substrate and the O atoms.

INTRODUCTION

The electronic and structural changes ensuing from the break of the three-dimensional symmetry of a crystal at the surface are spectroscopically reflected in a different binding energy (BE) of the core electrons of bulk and surface atoms, whose energy separation is termed the surface core level shift (SCLS).¹ SCLS measurements have often been employed to obtain information about the local-scale evolution of the electronic structure of adsorbate systems during physical/chemical processes of interest. This owes to the fact that, although core levels are spatially confined to the region surrounding the atomic nucleus, and thus do not participate directly in chemical bonds, they are sensitive to the charge redistribution induced, e.g., by adsorption or alloying. The perturbations affecting core electrons have always been considered a local phenomenon due to the spatial localization of the orbitals. In the past 10 years, the substantial improvement of high-energy resolution core level photoelectron spectroscopy, along with the parallel development of density functional theory, has allowed for an increasingly accurate determination of the SCLSs. Nowadays, a direct comparison between experimental and theoretical data is possible, and an excellent agreement-typically within few tens of meV-has been attained for many systems.

More specifically, core level photoelectron spectroscopy has been employed to investigate a number of clean and oxygencovered transition metal (TM) surfaces. The interaction of oxygen with 4d and 5d metals has traditionally attracted a great deal of interest due to several reasons. Firstly, it has long provided a general model to study the mechanisms involved in simple adsorbate-substrate interactions; secondly, it represents the first step in the oxidation process and hence plays a key role in a number of industrially relevant catalytic reactions. Significant efforts have therefore been devoted to the spectroscopic characterization of bulk and surface late TM oxides 5^{-8} as well as of the chemisorption states formed upon oxygen exposure of various TM surfaces,⁴ in particular W,⁹ Ru,¹⁰⁻¹² Rh,^{13,14} Pt,¹⁵ and Ta.^{16,17}

As pointed out in previous works,^{9,10,13} oxygen adsorption induces the appearance of distinct SCL components in the 3d or 4f core level spectra of the metal substrate due to nonequivalent surface metal atoms characterized by a different coordination to the adsorbates. The changes occurring in the local oxygen adsorption configurations during exposure are

Received: May 18, 2012 Revised: October 17, 2012 Published: October 17, 2012 directly reflected in the evolution of the photoemission intensities of the different SCL components of the substrate.

Early photoemission studies on various TMs already showed evidence of a link between the oxygen coverage and the BE of the SCL components originating from surface metal atoms bonded to a different number of adsorbates.^{10,13} A trend in this sense emerged from the analysis of the Ru $3d_{S/2}$ core level spectra acquired in correspondence of the different stoichiometric structures formed upon oxygen adsorption on Ru(0001).¹⁰

A relevant issue, which has not yet been addressed in detail, concerns the effects induced by oxygen adsorption on the SCLSs not only of the first nearest neighbor (NN) substrate atoms but also of the surrounding atoms further away. This is precisely the focus of the present work. In order to thoroughly investigate this issue, we applied a combined experimental and computational approach to the analysis of oxygen adsorption on Re(0001).

In the first part of our study, we acquired a set of high energy resolution Re $4f_{7/2}$ core level spectra of the clean surface, where two spectral contributions, separated by 95 ± 10 meV, were resolved and attributed to bulk and surface Re atoms. The effects of oxygen adsorption on the substrate core levels were subsequently addressed by carrying out an uptake experiment in which the time evolution of the core level spectra of both the substrate and the adsorbate atoms was monitored during oxygen exposure of the Re surface at 300 K. In parallel, we performed a series of DFT simulations to determine the adsorption configuration and to calculate the SCLSs of the spectral components originating from non-equivalent Re atoms at different oxygen coverages.

The structure of this paper is as follows. The experimental section provides technical information on the sample preparation procedure and on the experimental setup. This part is followed by a description of the DFT computational procedures used to calculate the structure and the SCLSs of clean and oxygen-covered Re(0001). The experimental and theoretical results for the Re $4f_{7/2}$ core levels of the clean and oxygen-covered surface are then reported in two separate sections, followed by the final discussion, in which a thorough comparison between experiments and theory is presented.

TECHNIQUES

Experimental Section. The measurements were performed at the SuperESCA beamline¹⁸ of the Elettra synchrotron radiation facility in Trieste, Italy. The photoemission spectra were collected by means of a Phoibos 150 mm mean radius hemispherical electron energy analyzer from SPECS, equipped with an in-house developed delay line detector.

The experimental setup combines high-energy resolution with fast data acquisition rates, thus making it possible to perform fast XPS experiments in which the core level evolution can be monitored *in situ* under adsorption conditions. The spectra presented in this work were acquired at a rate of 7 s per spectrum. The overall energy resolution (taking into account both the electron energy analyzer and the photon beam) was within 50 meV in all measurements.

The Re(0001) single crystal was mounted on a cryostat manipulator with four degrees of freedom. In the lowtemperature measurements, the sample was cooled by liquid nitrogen and heated by electron bombardment from hot tungsten filaments mounted behind it. The temperature of the sample was monitored by means of a C type thermocouple directly spot-welded on one side of the specimen. The sample was cleaned by repeated annealing cycles up to 1250 K in an oxygen background ($p(O_2) = 5 \times 10^{-7}$ mbar), followed by flash annealing to 2000 K. At the end of the treatment a very sharp (1 × 1) LEED pattern with low background intensity was obtained, and the XPS spectrum did not show any residual traces of carbon, oxygen, or other contaminants. During the measurements the base pressure was always kept below 2 × 10^{-10} mbar.

The spectra shown in this paper were all fitted to Doniach– Šunjič (DS) functions¹⁹ convoluted with a Gaussian distribution. The DS profile comprises a Lorentzian width Γ , which accounts for the finite core hole lifetime, and a singularity index α , related to the asymmetric shape of the spectra, which arises from core hole screening effects. The vibrational fine structure, along with any instrumental or inhomogeneous broadening, contributes to the Gaussian width *G*. The background was assumed to be linear. The BEs of the core level components are all referred to the Fermi level, measured under the same experimental conditions.

Theoretical Section. Calculations were performed using density functional theory^{20,21} with exchange-correlation effects included at the level of the PBE-GGA²² functional. We used the Projector Augmented Wave²³ method as implemented in VASP^{24,25} to account for the core electrons of both Re and O atoms, with the 6s and 5d electrons of Re and the 2s and 2p electrons of O explicitly included in the valence. We used a plane-wave kinetic energy cutoff of 400 eV.

The (0001) surface of Re was modeled using a slab with a thickness of 8 layers, with the atoms of the bottom cell (2 layers) kept fixed at their bulk positions, while all the other atoms were allowed to relax. A vacuum interspace of at least 13 Å was used to minimize the interaction between periodic images of the slab along the direction perpendicular to the surface, resulting in a supercell of 30 Å along the *z*-axis. On the surface plane, in order to consider a range of oxygen coverages, we employed a (6 × 2) supercell for the majority of the calculations.

Calculations were carried out both for the clean surface and for the following oxygen coverages: 1/6, 1/4, 1/3, 5/12, 1/2, 2/3, 3/4, 11/12, and 1 ML (where 1 ML = 1.52×10^{15} atoms/ cm²). Preliminary calculations to determine the most stable oxygen configuration on the (0001) surface were performed on a smaller (2 × 2) supercell. For these calculations we used a Monkhorst–Pack k-point sampling of $9 \times 9 \times 1$ k-points, while for the larger supercells this was reduced to $3 \times 9 \times 1$. In all the calculations the energy was minimized until the forces acting on the atoms were smaller than 0.03 eV/Å.

Surface core-level shifts have been calculated for the clean as well as for the various oxygen-covered surfaces that we have considered above. Core-level bindings for both bulk and surface atoms have been estimated in the so-called final-state approximation, as follows: first a standard calculation is performed on the fully relaxed system (bulk or slab). Then, in a subsequent calculation, an electron from the chosen core level of a particular atom is excited to the lowest conduction band, and the valence electronic structure is relaxed at fixed atomic configuration. The energy difference between these two calculations provides an estimate of the core level binding energy. This estimate does not include the effect of coreelectron screening, as the other core electrons remain fixed at the electronic configuration with which the PAW potential was

The Journal of Physical Chemistry C

generated; the valence-electron structure is however relaxed, and thus screening from valence electrons is included. Although this procedure is not capable of providing an accurate estimate of the core level binding energy, due to the neglect of core electron relaxation effects, the error incurred can be expected to be relatively insensitive to the chemical environment.²⁶ The same procedure is then carried out for a bulk atom in a crystal geometry (i.e., a bulk cell without surfaces), thus obtaining the core binding energy for bulk atoms. The SCLS is then given as the difference of core binding energies between the surface and bulk atoms, i.e.

$$SCLS = E_{binding}(surf.) - E_{binding}(bulk)$$
(1)

In our case, core electrons from the 4f shell have been excited to the lowest empty band. According to previous theoretical studies,²⁶ the method used in the present work to calculate the SCLSs yields an accuracy of about 20-50 meV on the results.

In order to assign charges to the individual atoms, we used the method introduced by Bader,²⁷ following, more specifically, the approach implemented by Henkelman and co-workers.²⁸ The method consists of dividing the space into volumes, whose boundaries are determined by a zero charge-flux condition, so that the delimiting surfaces are selected in such a way that the charge density has a minimum along the surface normal. The resulting volumes have an atom at (or close to) their centers. The charge that results from integrating the electron density over a given atom's volume is thus a natural estimate of the electronic charge of that atom.

We also calculated the partial density of states $n_{lm}^i(E)$ of atom *i*, defined as the projection of the density of states onto spherical harmonics Y_{lm}^i centered on the atom:

$$n_{lm}^{i}(E) = \sum_{N} \int_{BZ} d\mathbf{k} \, |\langle Y_{lm}^{i} | \psi_{N\mathbf{k}} \rangle|^{2} \delta(E - E_{N\mathbf{k}})$$
⁽²⁾

with the projection $\langle Y_{lm}^i|\psi_{Nk}\rangle$ calculated by integrating over a sphere of radius $R_i = 1.43$ Å centered on atom *i*. Here ψ_{Nk} is the crystal wave function of band N at wave-vector **k**, and E_{Nk} is the corresponding energy eigenvalue. We define the *p*th moment of the density of states $n_{lm}^i(E)$ as $\mu_p = \int dE \ E^p n_{lm}^i(E)$; μ_0 and μ_1/μ_0 give the total number of states in the band and the band center B_{lm}^i , respectively. In particular, we define the d-band center B_d^i of atom *i* as the ratio μ_1/μ_0 obtained from the partial density of states

$$n_d^i(E) = \sum_{m=-2}^2 n_{2m}^i(E)$$
 (3)

RESULTS

Experimental Results. *Clean Re(0001) Surface.* Before investigating the modifications of the electronic structure induced by oxygen adsorption, in the preliminary part of the work we devoted our attention to the SCLS of clean Re(0001), which, despite the numerous core level photoemission studies on clean and adsorbate-covered 5d transition metals (TM) (see the review by Spanjaard et al.¹), has long been debated in the literature due to its small magnitude.

According to an early measurement,¹ the $4f_{7/2}$ SCLS of Re(0001) is negative (i.e., the surface lies at lower BE than the bulk peak) and amounts to -0.22 eV. In a subsequent work by Ducros et al.,²⁹ the deconvolution of the Re $4f_{5/2}$ spectrum into bulk and surface components led to a smaller estimate, -0.1

eV. One year later, Mårtensson et al. carried out a redetermination of the SCLS of Re(0001) using synchrotron radiation.³⁰ The analysis of the Re $4f_{5/2}$ core level spectrum initially suggested the presence of two components, but the high quality of the fit performed with a single component led the authors to conclude that the actual SCLS of rhenium is $\lesssim 0.1$ eV, thus falling below the experimental resolution attainable at the time. This estimate is consistent with the predictions of a thermodynamic model proposed by Johansson and Mårtensson, in which the SCLS is related to the difference in cohesive energy between the Z and Z + 1 metal.³¹ On the other hand, calculations based on a microscopic model (where the SCLS is considered as the energy shift of the surface d-band center relative to that of the bulk) yielded a value of -0.18 eV.^{1} The most recent high energy resolution XPS study on Re,³² however, reported a positive SCLS of +0.170 eV on a stepped $Re(12\overline{3}1)$ sample. Although this latter value cannot be directly compared to that obtained for Re(0001), it confirms the small magnitude of the SCLS of the Re 4f core levels.

In order to determine the SCLS of clean Re(0001), we acquired a set of high energy resolution Re $4f_{7/2}$ core level spectra of the clean surface. The $4f_{7/2}$ rather than the $4f_{5/2}$ sublevel was selected because the latter is affected by a larger Lorentzian broadening due to Coster-Krönig decay processes inaccessible to the $4f_{7/2}$ levels. A drawback of this choice is the presence of a broad $5p_{3/2}$ component which partially overlaps with the $4f_{7/2}$ level, although with a relatively small overall photoemission intensity. The problem was tackled following the strategy already adopted by Chan et al. in their paper on stepped rhenium.³² More precisely, we collected preliminary spectra at low photon energy ($h\nu = 136$ eV), where the photoioization cross section of the 5p levels is higher, and their spectral deconvolution is therefore easier. We found that the $5p_{3/2}$ component lies at 430 meV lower BE than the Re $4f_{7/2}$ bulk component, with an estimated total full width at halfmaximum (fwhm) of 1 eV, in agreement with the results reported by Chan et al.³² These parameters were pinned down to the values so obtained in all subsequent fits.

A complete set of normal emission high energy resolution Re $4f_{7/2}$ core level spectra was collected using different photon energies, at 80 K, in order to reduce the thermal contribution to the Gaussian broadening of the peaks. Figure 1 shows a selection of spectra recorded at $h\nu = 160$, 180, and 200 eV. Sampling different photon energies in such a small energy range allows to change the relative weight of the two core level components because of photoelectron diffraction effects.

From the analysis of this data set, we identified two spectral contributions, separated by 95 \pm 10 meV and originating from photoemission from bulk and surface Re atoms. In the proceeding, we will use S_b to indicate the bulk peak and S_0 to indicate the SCL component from first layer atoms. The intensity enhancement of the high BE component at photon energies >200 eV suggests the assignment of the latter to bulk photoemission. However, as will be shown below, an unambiguous attribution of the two components was only possible on the basis of (i) DFT calculations and (ii) oxygen uptake experiments, which showed that the peak at lower BE is the most affected by the adsorption. Our findings are in line with the earlier estimate of Ducros et al.,²⁹ who measured a SCLS of -0.1 eV.

In order to derive a reliable estimate of the line shape parameters of the spectra, we applied a best fitting procedure which has already been successfully used in a number of



Figure 1. Selected normal emission Re $4f_{7/2}$ spectra collected at 80 K with three photon energies. The deconvolution into bulk and surface components is shown superimposed; the $5p_{3/2}$ component (indicated only by a dashed line) has also been included in the fit. The residual spectra, magnified by a factor 6, are shown above the corresponding spectra.

studies,^{33–35} where the χ^2 is contoured as a function of two independent parameters at a time, until a global minimum in the phase space is located. The results obtained in the present case are summarized in Table 1. The reliability of our fits is proved by the almost structureless residual, as can be seen in Figure 1.

Table 1. Line Shape Parameters and BE Positions of Re $4f_{7/2}$ Bulk, Surface and Second Layer Core Level Components, Both for the Clean Surface and for the Oxygen Saturated Sample at T = 300 K

Re 4f _{7/2} CLS component	Γ (meV)	α	G (meV)	SCLS (meV)
S _b (bulk)	65 ± 5	0.050 ± 0.010	90 ± 5	
S ₀ (clean)	100 ± 5	0.105 ± 0.015	30 ± 5	-95 ± 10
S ₁ (oxygen saturation)	100 ± 10	0.090 ± 0.010	180 ± 10	$+345 \pm 25$
S ₂ (oxygen saturation)	100 ± 10	0.090 ± 0.010	180 ± 10	+690 ± 25
S ₃ (oxygen saturation)	100 ± 10	0.090 ± 0.010	180 ± 10	+980 ± 25
2nd layer (oxygen saturation)	65 ± 5	0.050 ± 0.010	90 ± 5	+90 ± 20

Oxygen-Covered Re(0001) Surface. In the second part of our work, we studied the effects of oxygen adsorption on the core levels of the substrate. To this purpose, we carried out an uptake experiment at 300 K, by monitoring the evolution of the Re $4f_{7/2}$ and the O 1s core levels while exposing the sample to an increasing oxygen pressure (from 1×10^{-9} to 1×10^{-7} mbar), until saturation was reached. The oxygen coverage was calibrated from the oxygen uptake curve, as obtained from the

photoemission intensity of the corresponding O 1s core level spectra.

Similar oxygen chemisorption experiments have already been carried out in the past on various TM surfaces, including Ru(0001),¹⁰ $Ru(10\overline{10})$,¹¹ Rh(111),¹³ Rh(100),³⁶ W(110),⁹ Ir(111),³⁴ Pt(111),¹⁵ Pd(111),³⁷ Pd(110),³⁸ Ta(111),¹⁷ and Ta(110).¹⁶ This kind of measurements is an important source of information about the time evolution of the adsorbed surface phases and on the instantaneous configurations of the non-equivalent populations of first-layer atoms coordinated to a different number of adsorbates.

Oxygen on Re(0001) is known to adsorb dissociatively at room temperature, leading to the formation of an overlayer with (2×2) periodicity. In an early investigation, this pattern was attributed to a (2×1) structure with three domains rotated by 120° from each other.³⁹

Figure 2 shows a selection of O 1s spectra acquired during the uptake at increasing exposure values. The sequence of



Figure 2. A selection of O 1s spectra acquired during the uptake experiment at 300 K. The O 1s photoemission intensity (which is proportional to the oxygen coverage), normalized to its saturation value $(I/I_{\rm SAT})$, is indicated besides each spectrum. The oxygen uptake curve (reported in the inset) shows that saturation is reached at about 10 langmuirs.

spectra can be fitted to a single peak up to the saturation coverage. In order to prevent fitting artifacts—mainly arising from the low intensity of the spectrum at the beginning of the uptake—both the Lorentzian and the Gaussian fwhm, as well as the asymmetry parameter, were held fixed to the values found for the high-energy resolution O 1s core level spectrum recorded at the end of the uptake. The monotonic increase of the photoemission intensity of the O 1s signal during the uptake is accompanied by the parallel shift of the peak to lower BEs.

Following the results of earlier DFT calculations,⁴⁰ and in analogy to what is observed on the majority of close-packed transition metal surfaces, we assumed that oxygen adsorbs preferentially in 3-fold hollow sites also on Re(0001). This hypothesis was later born out by our DFT simulations, which proved that the site yielding the highest adsorption energy is the hcp hollow site.

In order to determine the changes taking place in the local configurations of surface Re atoms during exposure, we measured the Re $4f_{7/2}$ SCLSs induced by oxygen adsorption. The evolution of the substrate core levels during oxygen exposure shows similar trends to those previously reported for oxygen adsorption on other 4d and 5d TM surfaces.^{9,10,13}

As already illustrated in the previous section, the spectrum of the clean surface exhibits two components (S_b and S_0). As the oxygen coverage increases, the intensity of S_0 progressively drops to zero (Figure 3). This is a clear experimental evidence that the component at lowest BE originates from surface atoms.



Figure 3. Selection of high energy resolution Re $4f_{7/2}$ spectra collected during the oxygen uptake experiment at 300 K. The deconvolution into bulk and surface components is shown superimposed. The clean surface component is indicated by S_0 , while the components labeled as S_1 , S_2 , and S_3 are due to first-layer substrate atoms coordinated to 1, 2, and 3 oxygen atoms, respectively. The oxygen coverage is reported on the right. In the top panel a high energy resolution Re $4f_{7/2}$ core level spectrum ($h\nu = 160 \text{ eV}$) at saturation coverage is presented, together with the deconvolution into bulk, first-layer, and second-layer components.

At the same time, we observe the sequential appearance of three new oxygen-induced core level components on the high BE side of the bulk, labeled as S_1 (yellow curve), S_2 (orange), and S_3 (red) in Figure 3. Following the trends observed for the oxygen-induced SCLSs on other substrates,^{4,10,13,34} we assign these components to surface Re atoms bonded to one (S_1), two (S_2), and three (S_3) oxygen atoms, respectively.

The fitting parameters of the three components, reported in Table 1, were obtained as follows.

We first constrained the line shape parameters and BEs of S_b and S_0 to the values obtained from the Re $4f_{7/2}$ spectrum of the clean surface. In principle, an oxygen-induced BE shift of the uncoordinated surface component (S_0) is to be expected upon adsorption, but the large number of fitting parameters and the reduced BE separation between S_b and S_0 would make the estimate unreliable. We thus fixed S_0 at its zero-coverage BE and pinned the line shape parameters of both S_b and S_0 down to their clean surface values. In order to estimate the line shape parameters and BEs of the three oxygen-induced SCL components (S_1 , S_2 , and S_3), we assumed, as a first-order approximation, an equal asymmetry, Lorentzian, and Gaussian fwhm for all the peaks.

We initially fixed the Γ and α parameters of the three components to the same values found for S_0 , but keeping a different Gaussian width, to take into account a possible larger inhomogeneous broadening of the oxygen-induced components. The so-obtained set of parameters was then refined by releasing the constraint on the asymmetry of S_1 , S_2 , and S_3 in order to detect possible differences in the electron—hole pair excitation probability between uncoordinated and oxygen-coordinated Re atoms (owing to substrate—adsorbate charge transfer mechanisms). The same was done for the Lorentzian width. However, no further improvement was observed after these runs. We hence decided to describe the three O-induced components with a common set of parameters.

Besides the analogy with previous cases reported in the literature, the following observation supports our assignment of the oxygen-induced SCL components. If we term $\Delta E_{i,0}$ the BE separation between S_i and S_0 (where the index *i* indicates the number of O-Re bonds and runs from 1 to 3), we observe that: $\Delta E_{1,0} = 440$ meV, $\Delta E_{2,0} = 785$ meV, and $\Delta E_{3,0} = 1075$ meV. This means that the values $\Delta E_{i,0}$ are roughly proportional to the oxygen coordination of the corresponding species of surface Re atoms. A similar, more clear-cut trend in this sense has been detected in the past for a number of adsorbate (and coadsorbate)/substrate systems,^{10,13,34,41} which were found to obey the additivity rule for adsorbate-induced SCLSs: $\Delta E_{i,0}$ = $i\Delta E_{1,0}$ ¹⁴ This equation indicates that the BE shifts of the SCL components originating from non-equivalent substrate atoms scale linearly with the number of O-Re bonds, provided that the contribution of final state effects is not too large.

Another effect accompanying oxygen adsorption is the appearance of a new core level component at about 90 meV higher BE than the bulk. This peak is rather broad, with an estimated Gaussian fwhm of 175 ± 10 meV. Since there is no evident mathematical relation between its CLS and that of the four SCL components previously described, we tentatively attributed this feature to second-layer Re atoms. This interpretation is firstly supported by qualitative considerations. In the absence of adsorbates, since the bulk and second layer atoms have the same coordination, their core level states are expected to be energetically very close, so that they cannot be experimentally resolved. Oxygen adsorption, on the other hand, modifies the local electronic structure, inducing a measurable energy splitting between the bulk and the second-layer component. This point will be addressed in further detail in the discussion.

In order to limit the number of degrees of freedom in the fit, preventing nonphysical effects due to the reduced separation between bulk and second-layer component, the CLS of the latter was constrained to a constant value during the uptake.

The second-layer component was fitted using the same parameters of S_b on the basis of two considerations: (i) bulk and second-layer atoms have the same coordination number $C_N = 12$; therefore, they experience a similar local environment; (ii) the BE shift between the two peaks is too small to determine two separate sets of parameters. To remove possible correlation effects among the fitting coefficients (and thus improve the quality of our fits), also in this case we made a series of contour plots to map the evolution of the χ^2 as a function of the selected parameters.

Oxygen adsorption leads to two primary effects: (i) a change in the relative weights of the SCL components at increasing coverage (clearly visible in Figure 4a), which reflects the evolution of the populations of differently coordinated Re atoms; (ii) a shift to higher BEs of all the oxygen-induced Re $4f_{7/2}$ SCL components during the exposure (see Figure 4b).

In our fits, the BE of S_0 was constrained to the clean surface value during the whole uptake. Although, in fact, a coverage-dependent BE shift of S_0 is to be expected, as for the other



Figure 4. (a) Integrated intensity of the clean and oxygen-induced first-layer components of the Re $4f_{7/2}$ spectra shown in Figure 2 as a function of the oxygen coverage. (b) CLS evolution of the different first-layer components at increasing oxygen coverage.

components¹⁰ (as indicated by the DFT simulations), such a restriction was required to avoid overfitting. This constraint, however, does not significantly affect the SCLSs of S_1 , S_2 , and S_3 , which are well separated from S_0 .

The analysis of the intensity curves of the Re $4f_{7/2}$ SCL components, reported in Figure 4a, yields insight into the surface arrangement of oxygen atoms at different coverages.

At the beginning of the uptake, all surface Re atoms contribute to the intensity of S_0 because there are no oxygen adatoms available to form bonds.

Since in the present case the saturation coverage was initially unknown, we started from the assumption of adsorption at 3fold sites to estimate the saturation value of the oxygen coverage.

The first stage of the uptake is characterized by a linear decrease of the photoemission intensity of S_0 (accompanied by the proportional increase of S_1). This behavior is explained by considering that, for each oxygen atom which adsorbs in a 3fold site, the intensity contribution of three Re atoms moves from S_0 to S_1 . Following this reasoning, the intersection between the linear fit to S_0 and the coverage axis must occur at 1/3 ML.14 On this basis, we calibrated the whole oxygen coverage scale up to its saturation coverage, which turns out to be 0.70 \pm 0.12 ML. The error bar associated with the oxygen coverage was estimated by performing a number of linear fits of S_0 considering every time a different fitting range—within the linear region of the curve. The most intriguing results of the present work actually came from the analysis of the coveragedependent evolution of the adsorbed oxygen phases on Re(0001) and of the corresponding local configurations of the substrate atoms. Again, oxygen on $Ru(0001)^{10}$ and on $Ru(10\overline{1}0)^{11}$ were taken as reference models. In the case of Ru(0001), a LEED analysis allowed to detect the formation of three ordered adlayers as the oxygen coverage increases from 0 to 0.75 ML: namely, a $p(2 \times 2)$, a $p(2 \times 1)$, and a $p(2 \times 2)$ -30 structure.⁴²⁻⁴⁴ Although a detailed characterization of the

adlayers formed during oxygen exposure was not carried out for Re(0001), it is known from previous studies that oxygen forms an overlayer with a (2×2) periodicity,³⁹ so that a basic scheme of the adsorption geometries at different coverages can be proposed, at least on the local scale.

The intensity of the S_1 component, for instance, increases almost linearly up to ~0.25 ML, where it reaches a maximum and subsequently starts decreasing (Figure 4a). The parallel appearance of S_2 marks the onset of a new local configuration, in which a fraction of first-layer Re atoms are coordinated with two oxygen atoms. The crossover between the two curves (S_1 and S_2) occurs at about 0.50 ML coverage. Finally, the rise of the S_3 signal, which becomes detectable already above ~0.3 ML, reflects the increasing number of first-layer Re atoms which are coordinated with three oxygen atoms.

The presence of different components at the same coverage and their relative intensity evolution does not reflect the trends expected if only stoichiometric surface structures (like the $p(2 \times 2)$ at 0.25 ML and the $p(2 \times 1)$ at 0.5 ML) were formed. This observation suggests that, at the temperature and O₂ pressures considered, oxygen exposure results in an overlayer lacking long-range order, in which the presence of the stoichiometric structures is limited to the local scale. Under these conditions, oxygen adsorption would therefore proceed through the simultaneous formation of short-range ordered patches of distinct surface phases. An analogous behavior had indeed been observed by Ynzunza et al.⁹ for oxygen adsorption on W(110), where LEED measurements performed during the uptake confirmed the absence of long-range ordered structures on the surface.

It is interesting to observe that, even at saturation, a coverage of 1 ML cannot be reached. An analogous limitation has been reported in the past also for Ru(0001) and has been related to the dissociation process involved in oxygen adsorption on close packed TM surfaces.¹⁰ In fact, each oxygen molecule requires two adjacent 3-fold sites to break the O=O bond and accommodate two oxygen atoms, so that, as the oxygen coverage increases, the number of available 3-fold sites—in particular, of 3-fold sites at adjacent positions—progressively decreases, thus hampering the process of oxygen adsorption at high coverage.

Concerning the oxygen-induced surface components (S_1 , S_2 and S_3), a monotonic shift to higher BEs is observed for all the peaks. The three curves in Figure 4b show a smooth behavior over the entire coverage range. More precisely, the measured overall BE shifts of the three components (namely, the difference between the initial and final values of the BE of each component) are ~110 meV for S_1 , ~100 meV for S_2 , and ~70 meV for S_3 .

Theoretical Results. *Clean Surface.* On the relaxed clean surface all Re atoms are fixed on the same plane, but the interlayer distances are allowed to vary with respect to the corresponding bulk value. We obtain a minimum energy for a first interlayer spacing of 2.10 Å, to be compared with the bulk interlayer spacing of 2.23 Å. An oscillatory behavior of the interplanar distances around the bulk value is then found as we move toward deeper crystal layers (2.32 Å between the second and the third layer, 2.17 Å between the third and the fourth, etc.). This behavior is consistent with a general trend observed in a number of structural investigations on TM single crystals.^{45,46}

In order to make a comparison with the experiments, the core level BEs for both bulk and surface atoms were calculated

in the so-called final-state approximation. We obtain for S_0 a value of -130 meV, which is in fair agreement with the experimentally determined value of -95 meV. Possible reasons for the difference will be discussed more extensively in the final section of the paper.

Oxygen Adsorption: Surface Core Level Shifts. In the calculations, we considered three possible oxygen adsorption sites, namely the *on-top* site, directly above a surface atom, and two hollow sites, the hcp and the fcc site.

In agreement with previous calculations,⁴⁰ and in line with what has been found on the (0001) surface of other hcp TMs such as Ru,⁴⁷ we find that oxygen is most strongly adsorbed in the hcp site and least strongly in the on-top configuration. More specifically, for the $p(2 \times 2)$ structure at 0.25 ML, we obtained a binding energy of 3.69 eV for oxygen in the hcp site, 3.12 eV for the fcc site, and 2.62 eV for the on-top configuration. In the most stable configuration at 0.25 ML, the oxygen atom is found 1.22 Å above the surface plane, at a distance of 2.05 Å from the three nearest surface Re atoms. At 1 ML oxygen coverage the distance between the oxygen atoms and the surface plane increases slightly, reaching 1.25 Å. Interestingly, on the fully oxygen-covered surface the distance between substrate planes close to the surface nearly recovers the bulk value.

From our calculations at intermediate oxygen concentrations, we can determine the oxygen atomic binding energy as a function of the coverage, according to the formula

$$E_{\rm b} = \frac{1}{n_{\rm O}} \left(E_{\rm Re} + \frac{n_{\rm O}}{2} E_{\rm O_2} - E_{\rm ReO} \right) \tag{4}$$

where E_{ReO} is the energy of the Re slab with n_{O} adsorbed oxygen atoms per supercell, E_{O_2} is the energy of the oxygen molecule, and E_{Re} that of the clean Re slab. As can be seen in Figure 5, the calculated BE has a low-coverage value close to 3.7



Figure 5. Calculated oxygen adsorption energies on Re(0001) as a function of the coverage. For the 0.25 ML oxygen coverage, two non-equivalent adsorption configurations have been simulated.

eV, which decreases steadily with increasing coverage, reaching 3.35 eV at 1 ML coverage. The dependence on coverage is fairly linear, with some deviation at intermediate coverages. Our results generally agree with those recently published by Kaghazchi and Jacob.⁴⁰

We then performed calculations to determine the SCLSs of the oxygen-covered surface for the different coverages considered in this study. In order to understand the evolution of the CLS of S_1 , S_2 , and S_3 originating from non-equivalent local configurations, we could not restrict ourselves to the simulation of stoichiometric structures (such as the $p(2 \times 2)$, the $p(2 \times 1)$, or the $p(2 \times 2)$ -3O). Instead, for each selected oxygen coverage a set of non-equivalent atomic configurations was considered, and to this purpose, larger simulation cells were used (see Figure 6). This method allowed us to quantitatively estimate the effect on the CLSs ensuing not only from directly bonded oxygen atoms but also from the presence of adatoms located at further than NN positions. The numerical values of the SCLS are shown superimposed to the corresponding experimental results in Figure 7. As a general observation, we notice a good consistency with the experimental data, since both the magnitude of the SCLSs and their upward trends at increasing oxygen coverage are well reproduced. More specifically, our calculations indicate that the SCLS of a given Re atom is sensitive not only to the number of O atoms it is directly bonded to, but it also depends on the atoms adsorbed at second and third NN sites. The number of these atoms is small at low coverage but gets larger as the oxygen concentration grows. The parallel increase in the BE of surface Re atoms with increasing coverage (which leads to the upward trend visible in Figure 7) indicates a correlation between the SCLSs of the adsorbate-induced surface components and the number of O-Re bonds, which is however affected by the interactions with second and third NN oxygen adatoms.

DISCUSSION

For the clean Re(0001) surface, a fair agreement is found between experimental data and DFT simulations. As already mentioned, theoretical calculations predict a SCLS of -130 meV, to be compared with the experimentally determined value of -95 meV. In addition, they indicate the presence of a second and third layer component at higher (+1 meV) and lower (-30 meV)meV) BE with respect to the bulk peak, respectively. However, the magnitude of these CLSs is so small that the corresponding components cannot be experimentally isolated in the Re 4f_{7/2} spectrum. The presence of unresolved features at a BE close to that of the bulk can be held accountable for two main effects: (i) the observed difference between the DFT-predicted and the experimentally measured SCLS of clean Re(0001) (in this case, in fact, the experimentally determined BE of the bulk component is actually an average over the spectral distribution of many components); (ii) the Gaussian broadening of the bulk peak, which cannot be interpreted as a pure phonon effect, but should be rather ascribed to the additional presence of second and deeper layer components. The larger Gaussian fwhm of the bulk with respect to the surface component is in fact at odds with the behavior expected from the enhanced thermal lattice vibrations of first layer atoms.

On the other hand, a second layer component becomes experimentally observable during oxygen exposure, although only above 0.5 ML coverage. DFT calculations indeed proved that the spectral distribution of second layer Re atoms evolves at increasing oxygen coverage (Figure 8), and that its center of mass shifts to higher BEs during the exposure. More precisely, the average second layer CLS amounts to +38 meV at 1/4 ML, +61 meV at 1/2 ML, and +61 meV at 3/4 ML, which compare fairly well with our experimental estimate of 90 meV (for coverages higher than 0.5 ML). The average theoretical CLSs have also been reported as blue bars in Figure 8 for each oxygen coverage. Since oxygen occupies the 3-fold hcp sites of Re(0001), adsorption leads to the appearance of two nonequivalent populations of subsurface atoms, with and without an oxygen atom above. A closer inspection of the DFT data shows that the second-layer atoms without an oxygen adsorbate above experience a smaller CLS (to lower BE), while the



Figure 6. DFT-simulated structural models for oxygen adsorption. A set of non-equivalent cells with distinct local geometries was modeled in such a way to span the coverage range between 0 and 1 ML. The stoichiometric structures are indicated in bold.



Figure 7. Coverage-dependent evolution of the SCLSs of the Re $4f_{7/2}$ components due to non-equivalent populations of surface atoms. The DFT-calculated results have been plotted as colored marks; the corresponding experimental trends are shown superimposed for comparison as gray hollow circles. Multiple DFT values at the same coverage correspond to distinct local atomic configurations, with the same coordination but non-equivalent simulation cells (see e.g. Figure 6 for 1/4, S/12, and 1/2 ML).



Figure 8. Comparison between the experimentally measured CLSs of second-layer Re atoms and the DFT-calculated BE distribution of the Re $4f_{7/2}$ subsurface components, at different oxygen coverages. The average theoretical CLS of second-layer Re atoms (blue bars) is also reported for each coverage. For fitting purposes, the BE of the second-layer component was held fixed to a constant value at all coverages.

subsurface Re atoms with an O atom above experience a significant shift to higher BE, by more than 100 meV.

These considerations once more support the relevance of non-local effects on the CLSs of the substrate, since even second-layer atoms, which are not involved in bond formation with the adsorbates, sense the presence (and distribution) of oxygen atoms on the top layer.

Good agreement is also found between calculated and experimental values in the case of the core level analysis of the Re substrate during oxygen adsorption. With reference to Figure 7, where the SCLSs of the different oxygen-induced SCL components are plotted as a function of the oxygen coverage, we notice, in particular, that an excellent correspondence is found for the S_1 and S_2 components in the whole coverage range, while, in the case of S_3 , the average calculated CLS at saturation coverage (~1065 meV) is somewhat larger than the experimentally estimated value of 980 meV.

The effect of indirect metal-oxygen interactions on the SCLSs of the oxygen induced Re $4f_{7/2}$ components is well illustrated in Table 2, where the SCLSs of some selected first layer Re atoms-found in distinctive configurations-are reported for different oxygen coverages. More specifically, we chose surface metal atoms characterized by an equal number of first and second NN oxygen atoms, but a distinct number of third NN. From the table, it is evident how even a change in the number of third NN adatoms, which is considered a long-range effect, leads to significant differences in the SCLSs of otherwise equivalent Re atoms. As a general trend, we observe that a higher number of third NN adatoms (which basically means a higher effective coordination of the metal atom considered) is associated with a larger SCLS of the corresponding Re $4f_{7/2}$ component. In quantitative terms, if we consider the SCLSs of the singly bonded Re atoms (top section of Table 2), we notice that they increase by \sim 20 meV for each additional O adsorbate at third NN position.

A reason for the differences in the SCLSs is to be looked for in the charge transfer effects from Re to a more electronegative species like oxygen.

In order to further explore this issue, we calculated some relevant physical quantities related exclusively to the initial neutral state, and we investigated their link to the DFT-

Table 2. SCLSs of Singly and Multiply Coordinated Surface Re Atoms with an Equal Number of First and Second NN O, but Distinct Numbers of Third NN^a

O coverage (ML)	no. of 1st NN O bonds (no. of 1st NN O atoms)	no. of 2nd NN O atoms	no. of 3rd NN O atoms	SCLS (meV)
1/4	1	0	0	+215
1/4	1	0	2	+213
1/4	1	0	2	+239
1/4	1	0	3	+2/9
1/3	1	0	3	+262
1/3	1	0	4	+288
5/12	1	0	3	+263
5/12	1	0	4	+290
5/12	1	0	2	+241
5/12	1	0	3	+257
5/12	1	0	4	+299
1/2	2	2	2	+617
1/2	2	2	5	+786
2/3	2	3	3	+667
2/3	2	3	4	+743
2/3	2	3	3	+665
2/3	2	3	4	+742
11/12	2	3	5	+761
11/12	2	3	6	+797
2/3	3	0	4	+1004
2/3	3	0	6	+1130
2/3	3	0	4	+1003
2/3	3	0	6	+1129
11/12	3	3	4	+1033
11/12	3	3	5	+1095

"Note: in those cases in which non-equivalent Re atoms were found to have the same number of first, second, and third NN oxygen atoms, we averaged the SCLSs of the non-equivalent configurations.

calculated SCLSs of the oxygen-induced Re $4f_{7/2}$ core level components. More precisely, we computed the effective charge of surface Re atoms and the surface-projected d-band center and studied their link to the SCLSs.

It is here important to recall that SCLSs include the contribution of both initial and final state effects, mainly ensuing from core—hole screening by valence electrons following the photoemission event. As explained in detail in the Theoretical Section, the SCLSs were therefore calculated in the so-called final-state approximation, thus taking into account both initial and final state effects.

The calculations for the atomic charge were carried out on the cell reported at the bottom center of Figure 6, which corresponds to 1/2 ML coverage, since this structural model is representative of a range of distinct local adsorption configurations. An isolated surface Re atom has a nominal charge of 7, which means it has 7 electrons available to form bonds with other atoms. Oxygen adsorption induces a partial charge withdrawal from the surface metal atoms, thus reducing their effective charge. The data reported in Figure 9 for the effective charge per atom were calculated taking into account also the indirect (second and third order) oxygen-metal interactions. The linear relationship between the SCLSs and the effective atomic charge confirms the importance of non-local effects in determining the electronic structure of first layer metal atoms.

The other relevant initial-state parameter we calculated is the surface-projected d-band center; more specifically, we focused on its relationship with the DFT-computed SCLSs of the



Figure 9. DFT-calculated SCLSs as a function of the effective charge per surface Re atom. The calculations were performed for the structural model displayed in the bottom center of Figure 6, corresponding to an oxygen coverage of 1/2 ML.

oxygen-induced Re $4f_{7/2}$ components. Figure 10 displays the SCLSs of the surface Re atoms calculated for the simulation



Figure 10. Evolution of the DFT-calculated SCLSs of non-equivalent surface Re atoms as a function of the surface-projected d-band center, at different oxygen coverages. The calculations were performed on the structural models presented in Figure 6.

cells of Figure 6, as a function of the surface-projected d-band center. It is acknowledged that the surface d-band center of a metal is a key parameter in determining the chemical reactivity of transition metal surfaces. This link was first investigated by Hammer and Nørskov,^{48,49} who observed how the position of the d-band center of a metal affects the ability of surface d-electrons to form bonds with the adsorbates.

Within an initial state picture, the SCLS of the clean substrate is due to the narrowing of the surface d-band caused by the lower coordination of surface atoms with respect to bulk atoms. In order to preserve neutrality, the surface d-band center shifts downward or upward, depending on whether the band is less or more than half-filled. Conversely, the adsorption of a strongly electronegative species-like oxygen-leads to a broadening of the surface d-band, which in turn induces a shift of the d-band center to higher BEs. Accordingly, a higher number of adsorbate-metal bonds results in a larger surface dband broadening, and thus in an increased downward shift of the surface d-band center. Previous studies on different adsorption systems $^{10,41,50-52}$ have pointed out a linear correlation between the initial state contribution to the adsorbate-induced SCLSs and the surface-projected d-band center. Both these quantities, in fact, are related to the change in the Kohn and Sham surface potential upon chemisorption, although they are measured in the core and valence band, respectively. As for O and N adsorption on Rh surfaces, 36,51 also in the case of O adsorption on Re the CLs toward higher BEs is linked to the charge transfer from the surface to the O

The Journal of Physical Chemistry C

atoms, thus leading to a more attractive potential. Actually, also other effects besides charge transfer should be taken into account, namely environmental and configurational effects. For example, the oxygen-induced charge depletion of the surface dband weakens the bonds between first- and second-layer Re atoms, resulting in an increased first interlayer spacing, which would in turn lead to a surface d-band narrowing. More specifically, at zero coverage the calculated distance between first and second layer is 2.098 Å; at intermediate coverages, the first layer is slightly corrugated, with an average interlayer spacing of 2.11 Å at 0.25 ML, 2.11 Å at 0.5 ML, and 2.16 Å at 0.75. Finally, at 1 ML coverage the two layers are uniformly separated by 2.19 Å, a value close to the bulk interlayer distance (2.23 Å). This phenomenon counteracts the broadening effect of oxygen adsorption on the surface d-band. For this reason, the oxygen-induced first interlayer relaxation cannot be held accountable for the observed trends in the SCLSs and does not override the overall linear relationship between SCLSs and surface atomic charge.

As can be seen in Figure 10, a qualitatively linear behavior is found also for the total oxygen-induced SCLSs vs surfaceprojected d-band center. This proves that the dominant contribution to the SCLSs comes from initial-state effects.

CONCLUSIONS

By using high energy resolution core level photoemission spectroscopy and DFT calculations, we investigated the morphology and the electronic structure of clean and oxygen-covered Re(0001).

The data analysis of the clean surface pointed out the presence of two components in the Re $4f_{7/2}$ core level spectrum, which we assigned to photoemission from bulk and surface Re atoms. The experimentally estimated SCLS (-95 meV) turns out to be in fair agreement with theoretical predictions (-130 meV).

The effects of oxygen adsorption on Re(0001) were investigated by monitoring the evolution of the Re $4f_{7/2}$ core levels during oxygen exposure at 300 K. Similarly to what observed in other adsorbate/TM systems, oxygen chemisorption on Re(0001) leads to a suppression of the photoemission signal from the clean surface, along with the appearance of new oxygen-induced SCL components, due to non-equivalent populations of surface Re atoms with a distinct number of O–Re bonds. As a general trend, the SCLSs of differently coordinated Re atoms are observed to shift toward higher BEs as the oxygen coverage increases.

The evolution of the O-induced SCLSs as a function of the oxygen coverage was further addresses by DFT, by performing calculations on a set of simulation cells (characterized by distinct local configurations) corresponding to different oxygen coverages. The theoretically calculated values, which reproduce fairly well the experimentally observed trends, indicate a substantial contribution of the non-local O–Re interactions to the SCLSs. Not only, in fact, are the CL states of Re(0001) affected by the formation of direct bonds with oxygen atoms, but they are also sensitive to the interactions with second and third NN adatoms.

A linear relationship is indeed found between the theoretical Re $4f_{7/2}$ SCLSs and the DFT-calculated effective charge per Re atom, which receives a contribution also from non-local interactions.

We also addressed the link between the oxygen-induced SCLSs and the surface-projected d-band center, which plays a

key role in determining the initial state configuration. In an initial state picture, SCLSs are related to a modification of the Re valence 5d bandwidth, due either to the reduced coordination of the atoms in the first layer or to the interaction with the O 2p levels, which results in the formation of bonding and antibonding states, thus broadening the band. Our results actually show a fairly linear dependence of the total SCLSs on the surface-projected d-band center, thus indicating that initial state effects are largely predominant on possible core hole screening mechanisms occurring in the final state.

AUTHOR INFORMATION

Corresponding Author

*E-mail: alessandro.baraldi@elettra.trieste.it.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The work of E.R.H. was funded by the Spanish Ministry of Science and Innovation through project FIS2009-12721-C04-03 and by the Leverhulme Trust through a Visiting Professorship to UCL. Calculations were performed on the HECTOR national service (UK) and at the Legion UCL Research Computing Facility. D.A. and A.B. acknowledge the Royal Society for support. A.B. acknowledges the Universita' degli Studi di Trieste for the Finanziamento per Ricercatori di Ateneo.

REFERENCES

(1) Spanjaard, D.; Guillot, C.; Desjonqueres, M.; Treglia, G.; Lecante, J. Surf. Sci. Rep. 1985, 5, 1.

(2) Egelhoff, W. J. Surf. Sci. Rep. 1987, 6, 253-415.

(3) Andersen, J. N.; Hennig, D.; Lundgren, E.; Methfessel, M.; Nyholm, R.; Scheffler, M. *Phys. Rev. B* **1994**, *50*, 17525–17533.

(4) Baraldi, A. J. Phys.: Condens. Matter 2008, 20, 093001.

(5) Lundgren, E.; Mikkelsen, A.; Andersen, J.; Kresse, G.; Schmid, M.; Varga, P. J. Phys.: Condens. Matter 2006, 18, R481-R499.

(6) Gustafson, J.; Mikkelsen, A.; Borg, M.; Lundgren, E.; Köhler, L.; Kresse, G.; Schmid, M.; Varga, P.; Yuhara, J.; Torrelles, X.; Quirós, C.; Andersen, J. N. *Phys. Rev. Lett.* **2004**, *92*, 126102.

(7) Lundgren, E.; Kresse, G.; Klein, C.; Borg, M.; Andersen, J.; Santis, M. D.; Gauthier, Y.; Konvicka, C.; Schmid, M.; Varga, P. *Phys. Rev. Lett.* **2002**, *88*, 2461031.

(8) Todorova, M.; Lundgren, E.; Blum, V.; Mikkelsen, A.; Gray, S.; Gustafson, J.; Borg, M.; Rogal, J.; Reuter, K.; Andersen, J.; Scheffler, M. Surf. Sci. 2003, 541, 101–112.

(9) Ynzunza, R.; Denecke, R.; Palomares, F.; Morais, J.; Tober, E.; Wang, Z.; de Abajo, F.; Liesegang, J.; Hussain, Z.; Hove, M. V.; Fadley, C. Surf. Sci. **2000**, 459, 69–92.

(10) Lizzit, S.; Baraldi, A.; Reuter, K.; Ganduglia-Pirovano, M.; Stampfl, C.; Scheffler, M.; Stichler, M.; Keller, C.; Wurth, V.; Menzel, D. *Phys. Rev. B* **2001**, *63*, 205419.

(11) Baraldi, A.; Lizzit, S.; Paolucci, G. Surf. Sci. 2000, 457, L354.

(12) Reuter, K.; Scheffler, M. Surf. Sci. 2001, 490, 20-28.

(13) Ganduglia-Pirovano, M.; Scheffler, M.; Baraldi, A.; Lizzit, S.; Comelli, G.; Paolucci, G.; Rosei, R. *Phys. Rev. B* **2001**, *63*, 205415.

(14) Baraldi, A.; Lizzit, S.; Comelli, G.; Kiskinova, M.; Rosei, R.; Honkala, K.; Nørskov, J. *Phys. Rev. Lett.* **2004**, *93*, 046101.

(15) Puglia, C.; Nilsson, A.; Hernnäs, B.; Karis, O.; Bennich, P.; Mårtensson, N. Surf. Sci. **1995**, 342, 119–133.

(16) Treglia, G.; Desjonqueres, M. C.; Spanjaard, D.; Lassailly, Y.; Guillot, C.; Jugnet, Y.; Duc, T. M.; Lecante, J. J. Phys. C: Solid State Phys. **1981**, *14*, 3463–3473.

(17) van der Veen, J. F.; Himpsel, F. J.; Eastman, D. E. *Phys. Rev. B* **1982**, *25*, 7388–7397.

The Journal of Physical Chemistry C

(18) Baraldi, A.; Comelli, G.; Lizzit, S.; Kiskinova, M.; Paolucci, G. *Surf. Sci. Rep.* **2003**, *49*, 169–224.

- (19) Doniach, S.; Sunjic, M. J. Phys. C: Solid State Phys. 1970, 3, 285–291.
- (20) Hohenberg, P.; Kohn, W. Phys. Rev. 1964, 136, B864-B871.
- (21) Kohn, W.; Sham, L. J. Phys. Rev. 1965, 140, A1133-A1138.

(22) Perdew, J. P.; Burke, K.; Ernzerhof, M. Phys. Rev. Lett. 1996, 77, 3865–3868.

- (23) Blöchl, P. E. Phys. Rev. B 1994, 50, 17953-17979.
- (24) Kresse, G.; Furthmüller, J. Phys. Rev. B 1996, 54, 11169-11186.
- (25) Kresse, G.; Joubert, D. Phys. Rev. B 1999, 59, 1758-1775.
- (26) Köhler, L.; Kresse, G. Phys. Rev. B 2004, 70, 165405.
- (27) Bader, R. F. W. Atoms in Molecules A Quantum Theory; Oxford University Press: New York, 1990.
- (28) Tang, W.; Sanville, E.; Henkelman, G. J. Phys.: Condens. Matter 2009, 21, 084204.
- (29) Ducros, R.; Fusy, J. J. Electron Spectrosc. Relat. Phenom. 1987, 42, 305.
- (30) Mårtensson, N.; Saalfeld, H.; Kuhlenbeck, H.; Neumann, M. Phys. Rev. B 1989, 39, 8181.
- (31) Johansson, B.; Mårtensson, N. Phys. Rev. B 1980, 21, 4427-4457.
- (32) Chan, A.; Wertheim, G.; Wang, H.; Ulrich, M.; Rowe, J.; Madey, T. *Phys. Rev. B* **2005**, *72*, 035442.
- (33) Riffe, D.; Wertheim, G. Phys. Rev. B 1993, 47, 6672-6679.
- (34) Bianchi, M.; Cassese, D.; Cavallin, A.; Comin, R.; Orlando, F.; Postregna, L.; Golfetto, E.; Lizzit, S.; Baraldi, A. *New J. Phys.* **2009**, *11*, 063002.
- (35) Ferrari, E.; Galli, L.; Miniussi, E.; Morri, M.; Panighel, M.; Ricci, M.; Lacovig, P.; Lizzit, S.; Baraldi, A. *Phys. Rev. B* **2010**, *82*, 195420.
- (36) Bianchettin, L.; Baraldi, A.; de Gironcoli, S.; Vesselli, E.; Lizzit, S.; Comelli, G.; Rosei, R. J. Phys. Chem. C 2009, 113, 13192.
- (37) Klötzer, B.; Hayek, K.; Konvicka, C.; Lundgren, E.; Varga, P. Surf. Sci. 2001, 482-485, 237.

(38) Westerström, R.; Weststrate, C.; Resta, A.; Mikkelsen, A.; Schnadt, J.; Andersen, J.; Lundgren, E.; Schmid, M.; Seriani, N.; Harl, J.; Mittendorfer, F.; Kresse, G. *Surf. Sci.* **2008**, *602*, 2440–2447.

(39) Ducros, R.; Housley, M.; Piquard, G. Phys. Status Solidi A 1979, 56, 187.

- (40) Kaghazchi, P.; Jacob, T. Phys. Rev. B 2011, 83, 035417.
- (41) Lizzit, S.; Zhang, Y.; Kostov, K. L.; Petaccia, L.; Baraldi, A.; Menzel, D.; Reuter, K. J. Phys.: Condens. Matter 2009, 21, 134009.
- (42) Lindroos, M.; Pfnür, H.; Held, G.; Menzel, D. Surf. Sci. 1989, 222, 451–463.

(43) Pfnür, H.; Held, G.; Lindroos, M.; Menzel, D. Surf. Sci. 1989, 220, 43-58.

(44) Stampfl, C.; Schwegmann, S.; Over, H.; Scheffler, M.; Ertl, G. *Phys. Rev. Lett.* **1996**, *77*, 3371–3374.

(45) Hove, M. V.; Weinberg, W.; Chan, C. Low Energy Electron Diffraction, 3rd ed.; Springer: Berlin, 1986.

- (46) Davis, H.; Noonan, J. Surf. Sci. 1983, 126, 245-252.
- (47) Stampfl, C.; Scheffler, M. Phys. Rev. B 1996, 54, 2868-2872.
- (48) Hammer, B.; Nørskov, J. K. Nature 1995, 376, 238-240.
- (49) Hammer, B.; Morikawa, Y.; Nørskov, J. K. *Phys. Rev. Lett.* **1996**, 76, 2141–2144.
- (50) Ganduglia-Pirovano, M. V.; Scheffler, M. Phys. Rev. B 1999, 59, 15533-15543.
- (51) Bianchettin, L.; Baraldi, A.; de Gironcoli, S.; Lizzit, S.; Petaccia, L.; Vesselli, E.; Comelli, G.; Rosei, R. *Phys. Rev. B* **2006**, *74*, 045430.
- (52) Pehlke, E.; Scheffler, M. Phys. Rev. Lett. 1993, 71, 2338–2341.