Second-layer surface core-level shift on Rh(111)

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By synchrotron radiation high-resolution core-level photoemission we have found that the $3d_{5/2}$ core-level spectrum of Rh(111) presents, in addition to a well resolved component shifted by -460 meV with respect to the bulk peak, also another component, opposit in sign, shifted by $+71$ meV. Photoelectron diffraction has allowed to attribute the two components to surface and sub-surface Rh atoms, respectively. Our findings are in very good agreement with recent *ab initio* density functional theory calculations and show that on Rh(111) initial state effects dominate over the screening contribution.

I. INTRODUCTION

The importance of the role of subsurface species in catalysis is nowadays well established.[1–6] The penetration of atomic species such as hydrogen, carbon, nitrogen, and oxygen into the deeper layers of a metal is an important step, not yet well characterized, for a wide set of phenomena, such as the formation of intermediate species during chemical reactions and surface oxidation. However, most of the surface science experimental techniques are not distinctly sensitive to the first, second, and deeper layers of a solid. Moreover, a few techniques, such as low-energy ion scattering, which can probe the surface composition layer by layer, are usually partially destructive, i.e., they induce irreversible modifications of the surface composition and geometry. Finally the scattering techniques sensitive to subsurface layers yield information about the surface geometry but not on the electronic structure of subsurface atoms.

In this context, the advent of high-energy resolution synchrotron based beamlines allows to apply the x-ray photoelectron spectroscopy (XPS) technique to distinguish, taking advantage of the chemical shift, the atoms sitting at the surface from those present in deeper layers. The physical quantity named Surface Core-Level Shift (SCLS) is the difference between the core-level electron binding energy of the surface and the bulk atoms,[7] and reflects their differences in the local density of states. SCLS provides valuable information about the electronic structure of clean semiconductor and metal surfaces and of atomic and/or molecular interaction with solid surfaces.[8–11] By comparison with theoretical calculations, it allows also to quantify the electronic screening of the core hole created in the photoemission process.

Apart from berillyum surfaces, where surface atoms in the first, second, third, and fourth layer generate clearly distinguishable surface core-level components,[12–17] there are several other metal surfaces where subsurface core-level-shifted components have been revealed. The most important example is the (110) surface of Ta (Ref. 18), where, despite the close-packed geometry, Riffe and Wertheim have found a second-layer component at $+65$ meV with respect to the bulk peak, with the same sign of the first-layer component at $+360$ meV. Other surfaces where second-layer core-level peaks _ have been revealed are W(110),[19] W(111),[20] Ru(10$\bar{1}$0),[21] Ru(0001),[22] Rh(100),[23] and Rh(110).[23]

For Rh(111) the $3d_{5/2}$ core-level spectrum showed only one surface-shifted component, at about -500 meV with respect to the bulk peak.[24–26] This experimental finding, is however, in contrast with very recent *ab initio* density functional theory (DFT) calculations (including final state effects), which, besides a surface component at -459 meV, predict the presence of a second-layer peak at $+69$ meV.[26] This theoretical prediction is at variance with what usually measured, i.e., a second-layer SCLS with the same sign of that of the first-layer one.

In order to further investigate this intriguing problem, we have measured the Rh(111) $3d_{5/2}$ core level at high-energy resolution and low temperature ($T=20$ K). A very careful analysis of the experimental results has indeed evidenced the presence of a second-layer core-level-shifted component at $+71$ meV, i.e., opposite in sign with respect to the first-layer component, in excellent agreement with the theoretical predictions.

Our results demonstrate that particular attention has to be paid in analyzing core-level spectra because of the presence of subsurface core-level components, as reported by Riffe and Wertheim.[18,19] These findings prove that synchrotron ra-

diation high-energy resolution XPS measurements, in conjunction with multidimensional least-square data analysis, can be successfully used to probe the electronic structure of subsurface layers of $4d$ transition metals, even in the case of small surface core-level shifts.

II. EXPERIMENTAL

The measurements have been performed at the SuperESCA beamline of Elettra.[27] Photon energies $h\nu$ ranging between 350 and 450 eV with a resolving power of the order of 10 000 have been used for the Rh $3d_{5/2}$ core-level measurement. The spectra have been collected by means of a double pass hemispherical electron energy analyzer with mean radius of 150 mm,[28] equipped with a 96-channel detector.[29] At the photoelectron kinetic energies used in our experiment (40–140 eV) the analyzer acceptance angle is $\pm1.5°$.

In order to minimize the effect of phonon broadening, the sample was mounted on a liquid helium cryostat, which permits to cool the sample down to 20 K.The overall energy resolution under these experimental conditions is about 50 meV, as determined by measuring the width of the Fermi level of a Ag polycrystal. The binding energy scale has been calibrated with respect to the Fermi level measured under the same experimental conditions. The background pressure in the experimental chamber was 6×10^{-11} mbar. Nevertheless, in order to keep the surface contamination at a very low level (below 0.005 ML), the sample was annealed to 570 K at intervals of 10 min. This results in desorption of the main contaminants, such as hydrogen, carbon monoxide, and water. It is, in fact, well known that even very small amounts of adsorbed impurities can modify the shape of the core-level spectra, as they generate new surface core level-shifted components at different binding energies with respect to the clean surface case.

The Rh(111) sample, a 8-mm diameter disc oriented along the (111) direction within 0.1°, was cleaned using the standard procedures for Rh surfaces,[30,31] consisting in cycles of Ar ion sputtering ($T=300$ K, $E=3$ keV), oxygen treatments ($T=700–1100$ K, $p=1\times10^{-7}$ mbar) and a final hydrogen treatment in order to remove residual oxygen ($T=300–600$ K, $p=5\times10^{-8}$ mbar). These procedures generate a well ordered and clean surface, as characterized by sharp and low background low-energy electron diffraction (LEED) spots, and flat XPS C1s and O1s regions.

The spectra were fitted by using a sum of Doniach-Sunjic[32] (DS) functions, which combine a Lorentzian width Γ with the Anderson singularity index α, convoluted with a Gaussian function that describes the phonon bradening, the instrumental resolution, and any inhomogeneous broadening. A linear background was included in the fitting procedure.

III. RESULTS AND ANALYSIS

The high-resolution Rh $3d_{5/2}$ core-level spectrum measured at 20 K, at a photon energy of 407 eV and at normal emission, is shown in Fig. 1(a). At first sight, it appears to be
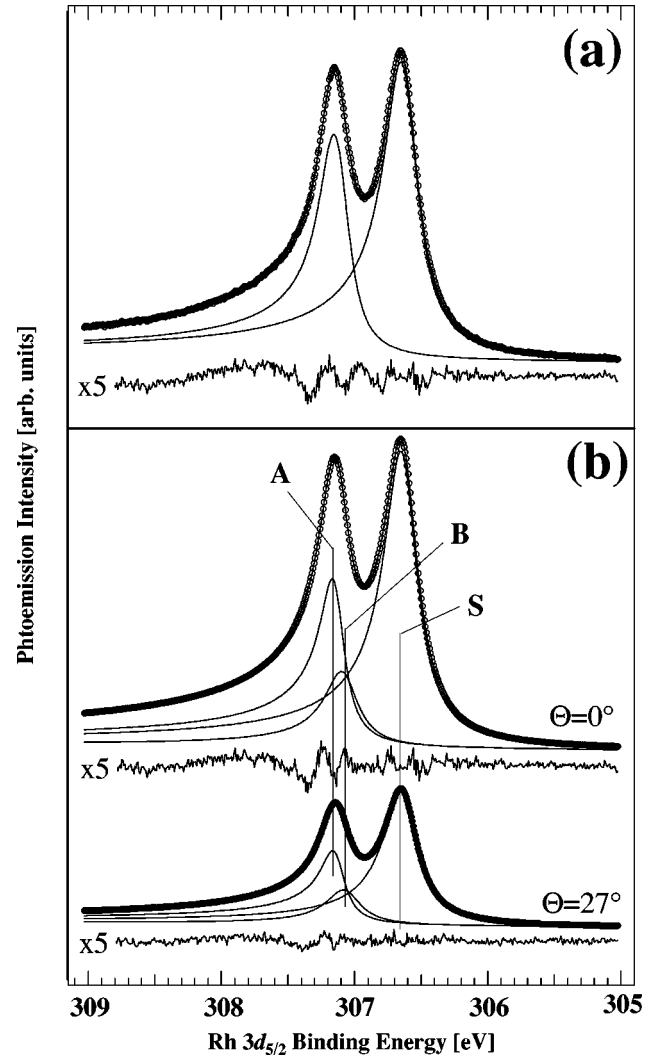

FIG. 1. (a)Rh $3d_{5/2}$ core-level spectrum acquired at normal emission and at $T=20$ K. Photon energy is h$\nu=407$ eV. Shown as solid lines are two DS line shape convoluted with gaussians and the residual of the fit multiplied by 5. (b) Rh $3d_{5/2}$ core-level spectra acquired at the same photon energy and sample temperature. Emission angles are 0° and 27° from the sample normal. These curves have been fitted by using three DS convoluted with gaussians. A (subsurface) and S (surface) components have same line shape parameters.

composed of only two peaks. As previously reported, the higher binding energy component at 307.15 eV binding energy is assigned to bulk atoms, while the lower binding energy peak is originated by surface atoms.

A closer inspection, though, reveals that even the best fit reported in the figure, obtained with two DS functions with different $\Gamma(\Gamma_{surface}=267$ meV, $\Gamma_{bulk}=183$ meV) and $\alpha(\alpha_{surface}=0.167, \alpha_{bulk}=0.232)$ and convoluted with gaussians of different widths, is not satisfactory, as indicated by the strong modulation present in the residual. Deconvolution with just two components, shifted by 497 meV, is therefore not sufficient to describe the lineshape of the Rh(111) $3d_{5/2}$ core-level spectrum. It is important to note that the energy spectrum range where the residual modulates is be-

tween 306.8 and 307.6 eV, just in correspondence of the higher binding energy component. This strongly supports the idea that the second-layer component is hidden underneath the "bulk" peak. This is not surprising since the second layer atoms in the Rh(111) surface have 12 nearest neighbors, same as the bulk atoms and therefore should display a similar SCLS.

The first attempt to improve the quality of the fit has been done by using three peaks: one for the surface layer (S), one for the second layer, and the last for the rest of the bulk atoms (A and B peaks). As in the two-peaks case, Γ and α parameters have been let free in the fitting procedure, but kept same for the A and S peaks. The gaussian width has been found to be always very similar to the experimental resolution and therefore has been fixed at 50 meV. This is a sign that at 20 K the energy resolution largely dominates over the phonon contribution to the gaussian broadening. In order to make a more precise determination of the fitting parameters, we have analyzed in parallel two spectra acquired at 372 eV photon energy with different surface sensitivity (normal emission and $\Theta = 27°$). In Fig. 1(b) we report the best fit obtained by using two surface components (S and A peaks) with the same line shape and a bulk component (B) with different line shape. Lorentzian and asymmetry parameters for the A and S components are 0.270 eV and 0.125, while for the B peak they are 0.170 eV and 0.290. Also in this case the fit is unsatisfactory. The same happens if we force the peaks A and B to have the same line shape, attributing to both a bulklike atomic behavior, and allow a different line shape for the lower binding energy peak. These preliminary results strongly indicate that the spectrum has to be fitted with three components, each one with different line shape values.

The problem in analyzing the Rh$3d_{5/2}$ core-level spectra with three independent components is the large number of free parameters, which has to be included in the fit: even though we keep the gaussians width fixed at 50 meV, there are two line shape values, the intensity and the position for each peak, which, together with the linear background, result in a total number of 14 parameters. Moreover, since the higher binding energy peaks are close to each other, we expect the line shape parameters of these components to be highly correlated when performing the fit. The Rh case is particularly complicated if compared, for example, to Ru surfaces. The reason is that the asimmetry parameter α is for both bulk and surface Rh atoms, always much larger (between 0.17 and 0.25) than for Ru(10$\bar{1}$0) (Ref. 21) ($\alpha = 0.08$) and Ru(0001) (Ref. 22) ($\alpha = 0.085$), where a subsurface layer component was revealed. This can be due to the different density of states at the Fermi level for these two metals, as shown in Refs. 23,27. The larger is the α parameter, the larger is the broadening effect on the core-level peaks, which at the end renders even more complicated the data analysis.

In order to rationalize the data analysis procedure, we have mapped the evolution of the χ^2 as a function of each of the two parameters, following the procedure *proposed* by Riffe and Wertheim[18] to identify the subsurface core-level-shifted component on Ta(110). In parallel, the evolution of a third free parameter is controlled. This procedure allows us
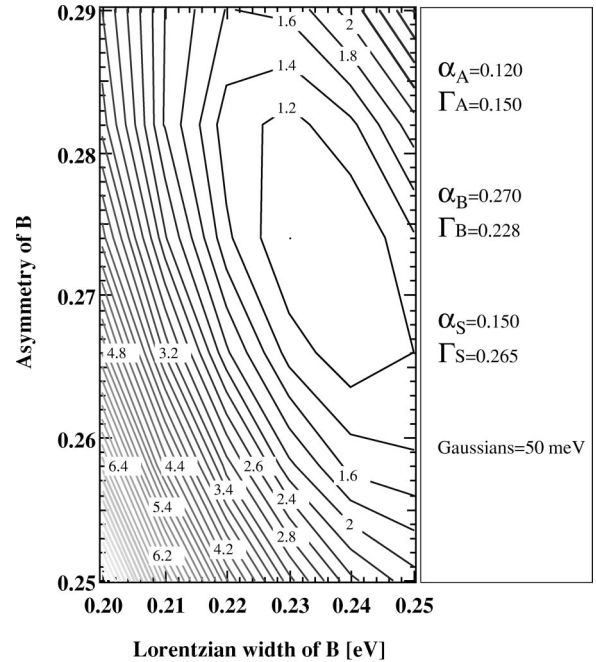

FIG. 2. Contour plot of χ^2/χ_{min} for α_B vs Γ_B. In the right panel are summarized the best values of the line shape parameters obtained for A, B, and S components.

to determine the aforementioned correlation between parameters. For example, as shown in Fig. 2, for the spectrum measured at normal emission and $h\nu = 407$ eV, the asymmetry and the Lorentzian of the B peak are strongly correlated: with increasing α, Γ diminuishes.

We have generated and analyzed nearly 40 χ^2 contour plots with Γ, α and binding energy position of the three peaks as variables. This procedure allowed an accurate determination of the fitting parameters. There are, in fact cases in which the contour plots present a deep minimum, which therefore forces the parameters to precise values. The results for the best line shape parameters are summarized in the right panel of Fig. 2.

In order to evaluate more accurately the binding energy position of the surface core-level-shifted components, the quantity which we want to extract from the data, we have made a further step by measuring the core-level spectra at different polar emission angles. In this way we expect that, because of photoelectron diffraction and different photoelectron escape depth conditions, the ratio of the intensities of the A and B components modulate to a certain degree. Several spectra have been measured at different emission angles from the sample normal, at a photon energy of 407 eV. The spectra, measured between 305.3 and 307.2 eV electron binding energy, have been fitted by using the same line shape parameters reported in the panel of Fig. 2, allowing only the binding energy positions as free parameters.

A selection of the spectra acquired for different polar emission angles are reported in Fig. 3. The results of the fits and the residuals are a futher proof of the goodness of the line shape parameters obtained with the multidimensional least-square data analysis. We found that the core-level shifts of peaks S and A with respect to the B component are equal
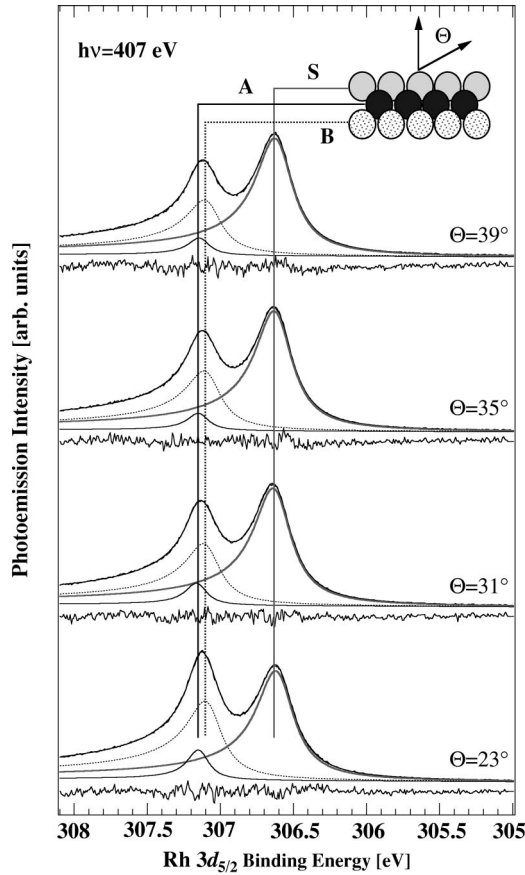
FIG. 3. (a)Rh $3d_{5/2}$ core-level spectra acquired at $T=20$ K and $h\nu=407$ eV. Emission angles Θ range from 23° to 39°.

FIG. 4. Measured (filled markers) and calculated (open markers) modulation function $[I(\theta)\text{-}I_0]/I_0$ of A (upper panel), S (middle panel), and B (lower panel) core-level components for a polar scan. $h\nu=372$ eV.

to $+71\pm8$ meV and -460 ± 10 meV, respectively. These results, if compared with first principles theoretical findings,[26] which predict a shift of -459 meV and $+71$ meV for the surface and subsurface peaks, respectively, strongly support the idea that the B component is originated by the bulk atoms, while the higher binding energy component A is due to the second-layer atoms. We would like to point out how state-of-the-art first principles calculations on SCLS and high-resolution core-level photoemission experiments with synchrotron radiation now normally agree within a few tenth of meV.

It is important to note that, even if our results are in very good agreement with the theoretical prediction, our experimental SCLS determination is not yet a clear-cut answer to the problem of peak assignment. In order to univocally determine, within a fully experimental approach, the origin of the A and B components, we have therefore performed a Photoelectron Diffraction (PED) experiment. In principle one would simply expect that going to higher photon energies, because of the larger inelastic mean-free path, it would be possible to suppress, together with the surface peak, also the second-layer component. However, as we have previously demonstrated on Ru(0001),[22] the main origin of strong modulation in the peak intensities of first- and second-layer Ru atoms is not inelastic damping, but photoelectron interference. It is not therefore possible to disentangle the two components by considering only the inelastic scattering con-
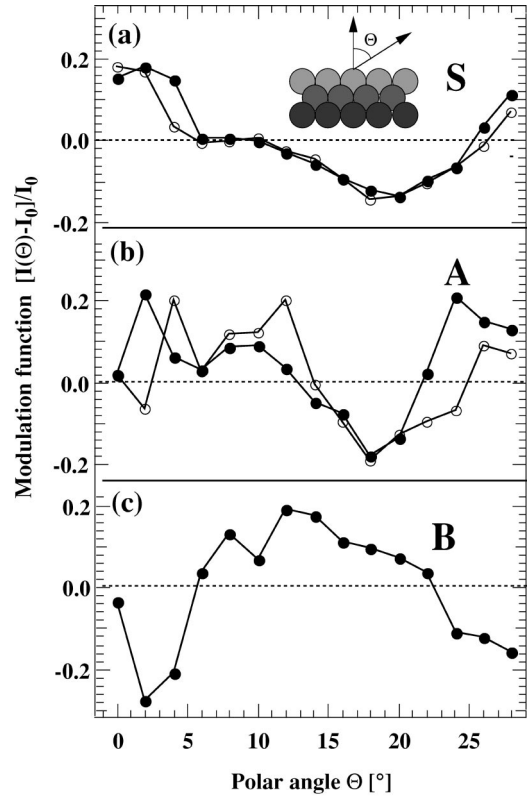
tribution. For this reason, we have measured about 20 high-resolution $3d_{5/2}$ spectra at emission angles ranging from normal emission to 28°.

In Fig. 4 the results of such a scan recorded at 372 eV photon energy are shown as filled markers. We plot the modulation function for the S, A, and B components. This quantity is defined as $[I(\theta)\text{-}I_0]/I_0$, where $I(\theta)$ is the peak intensity as a function of the polar emission angle and I_0 is the average peak intensity over the polar scan both for the S and B components, reported in Figs. 4(a) and 4(b), respectively. The modulation function presents a minimum at approximately 18°, while the bulk intensity behaves very differently [Fig. 4(c)]. To identify the components, we have simulated the modulation functions for first- and second-layer atoms, using the MSCD package program,[33] which calculates on the basis of multiple scattering theory the elemental and state-specific core-level photoelectron diffraction pattern. The Rh(111) structural parameters used in the simulation have been taken from a previous LEED IV work.[34] The simulated modulation function for the surface atoms, reported in Fig. 4(a) as open markers, very well agree with the experimental data, while the curve for the subsurface atoms closely resembles the modulation function of the A component [Fig. 4(b)]. Therefore, we can confirm that the higher binding energy component stems from the second-layer atoms, as predicted by theory.[26]

Our results clearly indicate that, due to photoelectron diffraction effects, care has to be taken in assigning the origin

of core level peaks on the basis of their intensities. Indeed, in our case, considering only inelastic damping, one would have expected for 39° emission angle a second-layer component about four times lower than the surface component. This is not the case, as photoelectron diffraction reduces the intensit ratio between second and first layer (I_A/I_S) by another factor of ≈ 2.

IV. DISCUSSION

The most interesting finding of our experimental results, which still remains unexplained, is the evidence of a second-layer SCLS at higher binding energy with respect to the bulk peak, while the first-layer component stays on the other energy side. This is different to what has been observed for example on Ta(110), where second-layer atoms originate a surface core level shift with the same sign of that produced by first-layer atoms.[18]

In a simple initial state picture the surface core-level shift for a transition metal surface such as Rh can be explained as due to the d-band narrowing at the surface because of the reduced atomic coordination with respect to the bulk. In this approximation the second-layer atoms on Rh should behave like the bulk atoms and, should not originate a distinguishable SCLS. However, we can propose two different reasons. First of all the first-to-second layer distance of a metal surface often differs from the interlayer bulk distance, because of the broken translational simmetry at the surface. A reduced first-to-second layer distance mimics an increased coordination and should enhance the band narrowing effect. The second hypothesis is that, even in an unrelaxed configuration, the electronic charge distribution at the surface is rearranged and this obviously influences the d-band width of the second layer.

The first hypothesis is questioned by the LEED experimental results,[34] which evidenced a practically unexpanded first-to-second-layer distance, as usual for close-packed metal surfaces, compared to the more open surfaces that normally exhibit a substantial top-layer spacing contraction. The second hypothesis is therefore more reliable and can be understood in terms of redistribution of valence electrons at the surface, as for the case of electron density Friedel oscillations at the surface: this could originate an oscillatory damping of the SCLS when going from outer to inner surface layers. This interpretation is supported by the results of the *ab initio* calculations.[26] The initial state contribution to the second-layer SCLS is almost +100 meV, just in the opposite direction to the initial state contribution to the first-layer SCLS, which is −385 meV. Moreover, also on Rh(100) we have recently found a second-layer surface core-level shifted component at a binding energy of +82 meV with respect to

the bulk peak, thus following the same trend than on Rh(111),[35] in agreement again with theoretical calculations.[36] Our experimental results and interpretations for the subsurface CLS therefore indicate that the initial state effect dominates over the screening contribution in the interpretation of the SCLS of Rh surfaces, as stated by Citrin and Wertheim.[37,38]

Another point that has to be taken into account to describe the first and second-layer SCLS behavior is the final state contribution. The α parameter found in the data analysis indicates that the screening is larger for the first-layer ($\alpha_S = 0.15$) than for the second layer atoms ($\alpha_A = 0.12$). This behavior is not new and has been already observed for alkali[39,40] as well for transition[23,41−43] metal surfaces. This means in our case that the density of polarizable states at the Fermi level, which is responsible for the screening, is larger for the first-layer atoms than for subsurface atoms. These considerations, although qualitative, well agree with the results of the DFT calculations: the final state contribution in the second layer, −29 meV, is much smaller than the contribution evaluated for the first layer, which results to be −74 meV.

V. SUMMARY

We have measured the $3d_{5/2}$ core-level spectrum of Rh(111) with high-energy resolution and at low temperature. Our results evidence the presence of an apparently anomalous second-layer component at +71 meV with respect to the bulk peak, in very good agreement with theoretical predictions. Possible explanations of the different sign in SCLS for first- and second-layer atoms have been proposed. In particular initial state effects seem to be dominating in the total surface core-level shift on Rh(111). This study represents the first step of a general project that aims to study the electronic structure modifications induced by atomic penetration into subsurface layers. Subsurface species can significantly modify the electronic structure of both, second- and first-layer atoms, and this results in modified surface core-level spectra. Therefore, the SCLS approach seems to be a quite encouraging technique because of its intrinsic selectivity to different surface layers.

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[1] G. Eilmsteiner, W. Walkner, and A. Winkler, Surf. Sci. **352**, 263 (1993).

[2] Z.B. Guvenc, X.W. Sha, and B. Jackson, J. Chem. Phys. **115**, 9018 (2001).

[3] T. Kammler, S. Wehner, and J. Kuppers, Surf. Sci. **339**, 125 (1995).

[4] H. Okuyama, W. Siga, N. Takagi, M. Nishijima, and T. Aruga, Surf. Sci. **401**, 344 (1998).

[5] C. Daitzchmann, C. Aharoni, and M. Ungarish, Surf. Sci. **244**, 362 (1991).

[6] I.J. Malik and J. Hrbek, J. Phys. Chem. **95**, 10188 (1991).

[7] N. Mårtensson and A. Nilsson, in *Application of Synchrotron Radiation*, edited by. W. Eberhrdt, Springer Series in Surface Sciences Vol. 35 (Springer, Berlin, 1994).

[8] O. Björneholm, A. Nilsson, H. Tillborg, P. Bennich, A. Sandell, B. Hernnäs, C. Puglia, and N. Mårtensson, Surf. Sci. **315**, L983 (1994).

[9] J.N. Andersen, M. Qvarford, R. Nyholm, S.L. Sorensen, and C. Wigren, Phys. Rev. Lett. **67**, 2822 (1991).

[10] A. Baraldi, S. Lizzit, and G. Paolucci, Surf. Sci. **457**, L354 (2000).

[11] A. Baraldi, S. Lizzit, G. Comelli, and G. Paolucci, Phys. Rev. B **63**, 115410 (2001).

[12] L.I. Johansson, P.A. Glans, and T. Balasubramanian, Phys. Rev. B **58**, 3621 (1998).

[13] J.N. Andersen, T. Balasubramanian, C.O. Almbladh, L.I. Johansson, and R. Nyholm, Phys. Rev. Lett. **86**, 4398 (2001).

[14] A. Baraldi, S. Lizzit, K. Pohl, P. Hofmann, and S. de Gironcoli (unpublished).

[15] H.I.P. Johansson, L.I. Johansson, E. Lundgren, J.N. Andersen, and R. Nyholm, Phys. Rev. B **49**, 17 460 (1994).

[16] S. Lizzit, K. Pohl, A. Baraldi, G. Comelli, V. Fritzsche, E.W. Plummer, R. Stumpf, and P. Hofmann, Phys. Rev. Lett. **81**, 3271 (1998).

[17] L.I. Johansson, H.I.P. Johansson, E. Lundgren, J.N. Andersen, and R. Nyholm, Surf. Sci. **321**, 17460 (1994).

[18] D.M. Riffe and G.K. Wertheim, Phys. Rev. B **47**, 6672 (1993).

[19] D.M. Riffe, G.K. Wertheim, P.H. Citrin, and D.N.E. Buchanan, Phys. Scr. **41**, 1009 (1990).

[20] G.K. Wertheim and P.H. Citrin, Phys. Rev. B **38**, 7820 (1988).

[21] A. Baraldi, S. Lizzit, G. Comelli, A. Goldoni, P. Hofmann, and G. Paolucci, Phys. Rev. B **61**, 4534 (2000).

[22] S. Lizzit, A. Baraldi, A. Groso, K. Reuter, M.V. Ganduglia-Pirovano, C. Stampfl, M. Scheffler, M. Stichler, C. Keller, W. Wurth, and D. Menzel, Phys. Rev. B **63**, 205419 (2001).

[23] M. Zacchigna, C. Astaldi, K.C. Prince, M. Sastry, C. Comicioli, M. Evans, and R. Rosei, Phys. Rev. B **54**, 7713 (1996).

[24] J.N. Andersen, D. Hennig, E. Lundgren, M. Methfessel, R. Nyholm, and M. Scheffler, Phys. Rev. B **50**, 17 525 (1994).

[25] A. Beutler, E. Lundgren, R. Nyholm, J.N. Andersen, B. Setlik, and D. Heskett, Surf. Sci. **371**, 381 (1997).

[26] M.V. Ganduglia-Pirovano, M. Scheffler, A. Baraldi, S. Lizzit, G. Comelli, G. Paolucci, and R. Rosei, Phys. Rev. B **63**, 205415 (2001).

[27] A. Baraldi, M. Barnaba, B. Brena, D. Cocco, G. Comelli, S. Lizzit, G. Paolucci, and R. Rosei, J. Electron Spectrosc. Relat. Phenom. **76**, 145 (1995).

[28] A. Baraldi and V.R. Dhanak, J. Electron Spectrosc. Relat. Phenom. **67**, 211 (1994).

[29] L. Gori, R. Tommasini, G. Cautero, D. Giuressi, M. Barnaba, A. Accardo, S. Carrato, and G. Paolucci, Nucl. Instrum. Methods Phys. Res. A **431**, 338 (1999).

[30] A. Baraldi, J. Cerda, J.A. Martin-Gago, G. Comelli, S. Lizzit, G. Paolucci, and R. Rosei, Phys. Rev. Lett. **82**, 4874 (1999).

[31] A. Baraldi, S. Lizzit, D. Cocco, and G. Paolucci, Phys. Rev. B **57**, 3811 (1998).

[32] S. Doniach and M. Sunjic, J. Phys. C **3**, 185 (1970).

[33] Yufeng Chen and Michel A. Van Hove, http://electron.lbl.gov/mscdpack/

[34] C.-M. Chan, P.A. Thiel, J.T. Yates, Jr., and W.H. Weinberg, Surf. Sci. **76**, 296 (1978).

[35] A. Baraldi, S. Lizzit, A. Novello, G. Comelli, and R. Rosei (unpublished).

[36] S. de Gironcoli (private communication).

[37] P.H. Citrin, G.K. Wertheim, and Y. Baer, Phys. Rev. Lett. **41**, 1425 (1978).

[38] P.H. Citrin and G.K. Wertheim, Phys. Rev. B **27**, 3176 (1983).

[39] G.K. Wertheim, D.M. Riffe, and P.H. Citrin, Phys. Rev. B **49**, 2277 (1994).

[40] G.K. Wertheim, D.M. Riffe, and P.H. Citrin, Phys. Rev. B **45**, 8703 (1992).

[41] D.M. Riffe, G.K. Wertheim, and P.H. Citrin, Phys. Rev. Lett. **63**, 1976 (1989).

[42] D.M. Riffe, W. Hale, B. Kim, and J.L. Erskine, Phys. Rev. B **51**, 11 012 (1995).

[43] A. Baraldi, G. Comelli, S. Lizzit, R. Rosei, and G. Paolucci, Phys. Rev. B **61**, 4534 (2000).