Atomic Scale Purification of Re Surface Kink States with and without Oxygen Chemisorption

Yanguang Nie,‡ Jisheng Pan,‡ Weitao Zheng,§ Ji Zhou,‖ and Chang Q. Sun*,†,§,‖

‡School of Electrical and Electronic Engineering, Nanyang Technological University, Singapore 639798
†Institute of Materials Research and Engineering, A*STAR, Singapore 117602
§School of Materials Science, Jilin University, Changchun 130012, China
‖State Key Lab of New Ceramics and Fine Processing, Department of Material Science & Engineering, Tsinghua University, Beijing 100084, China
*Institute of Quantum Engineering and Micro-nano Energy, Key Laboratory of Low-Dimensional Materials and Application Technologies, Xiangtan University, Changsha 411105, China

ABSTRACT: Understanding the energetic behavior of bonds and electrons localized in the surface of skin depth or within the atomic-scaled zones surrounding under- and heterocoordinated atoms such as vacancy defects and adsorbate impurities has long been pursued by the community since the invention of scanning tunneling microscopy/spectroscopy. Such atomic scale, zone selective information is particularly important for one to control the process such as catalytic reaction, corrosion protection, growth nucleation, and quantum friction. Here we demonstrate that a simple technique of the photoelectron residual spectroscopy (PRS) can readily reveal such information from the Re(0001) and the Re(1231) surfaces with and without oxygen chemisorption, for instance. Under the guidelines of the BOLS incorporated tight-binding theory, we have decomposed the photoelectron spectra with derivatives of the Re 4f5/2 binding energy of 40.015 ± 0.004 eV for an isolated Re atom and its bulk shift of 2.629 eV and the effective coordination number for each spectral component. A subtraction of the reference spectrum collected at the normal (0°) emission angle from the one collected at a larger emission angle (75°) from the same surface has led to the skin-depth residual energy states in the bottom edge of the Re 4f band, indicating clearly the undercoordination-induced quantum entrapment as the PRS filters out the bulk and background information. Applying the same PRS process to the Re(1231) surface before and after being chemisorbed with oxygen has enabled the purification of the oxygen chemisorption states with even lower binding energy due to the stronger O–Re bonds formation at the surface.

1. INTRODUCTION

The energetic behavior of bonds and electrons associated with surface kinks or stripes has attracted tremendous interest because of their impact on the catalytic dynamics, crystal growth, corrosion protection, quantum friction, wetting, welding, and melting due to the under-coordinated atomic environment compared with the smooth surface. For example, the rough Re(1121) and Re(1130) surfaces have shown reactivity of three orders higher in magnitude for the ammonia synthesis than that of the smooth Re(0001) surface.1,2 The activation energy of N2 dissociation magnitude for the ammonia synthesis than that of the smooth surface. For example, the rough Re(1121) and Re(1130) surfaces have shown reactivity of three orders higher in magnitude for the ammonia synthesis than that of the smooth Re(0001) surface.1,2 The activation energy of N2 dissociation because of the anisotropy of surface free energy.

The smooth Re(0001) and the rough Re(1231)surfaces with and without oxygen chemisorption have been studied using high-resolution X-ray photoelectron spectroscopy (XPS).2,3–11 The surface core level shift (SCLS) has been well-resolved1,10,12–15 with unfortunately debatable assignments of the number, the order, and the direction of the shift of the components, as well as the reference point from which the components shift. Some groups13,15 reported that the 4f5/2 level shifts negatively by an amount of 0.10 to 0.22 eV from the Re bulk value, as the reference, to the upper energy (smaller absolute value in magnitude). Some others13,14 suggested a 0.125 eV positive SCLS (or go deeper in energy) for the same Re(0001) surface from the same bulk reference. The latter was attributed to the “initial—final states” effect,13 indicating that the SCLS is related to the difference in cohesive energies between the Z and Z+1 metal, where Z is the atomic number of the particular element concerned in the periodic...
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2. PRINCIPLES

2.1. BOLS-TB Theory. According to the band theory, as an intrinsic constant and the reference from which the $v$th level shifts, the specific $v$th energy level of an isolated atom, $E_v(0)$, is determined by the integral of the intra-atomic potential, $V_{\text{atom}}(r)$, and the specific wave function of an atom at the specific $i$th atomic site, $|\psi_i\rangle$. Upon the involvement of the bulk crystal potential $V_{\text{cry}}(r)$, the binding energy will shift from the origin $E_v(0)$ to the $E_v(12)$ by an amount of $E_v(12) - E_v(0)$ that is proportional to the cohesive energy per bond at equilibrium

$$E_v(12) - E_v(0) = <\psi_i | V_{\text{cry}}(r) | \psi_i > + \sum_{j=1}^{j=z} <\psi_i | V_{\text{cry}}(r) | \psi_j > = \alpha \left( 1 + \frac{e^\beta}{\alpha} \right) \approx \alpha \quad (1)$$

The coordination number $z = 0$ and $12$ represents for an atom in isolated state and in the bulk. The sum is over all $z$ neighbors of the specific $i$th atom. The term $e^\beta/\alpha \ll 1$ because $<\psi_i | V_{\text{cry}}(r) | \psi_j > = \delta_{ij}$ with $\delta_{ij}$ being the Kronic function (if $i = j$, $\delta_{ij} = 1$, otherwise, $\delta_{ij} = 0$). Any process of bond energy modification provides perturbation to the crystal potential and hence generates a new component in the specific $v$th band, which can be resolved using the XPS or synchrotron spectroscopy, as illustrated in Figure 1a.

According to the bond-order-length-strength (BOLS) correlation mechanism, the shorter and stronger bonds between undercoordinated atoms cause local densification and quantum entrapment of energy and charge at sites surrounding undercoordinated atoms. This entrapment provides perturbation $\Delta H$ to the local Hamiltonian and hence a positive CLS due to the undercoordination. Incorporating the BOLS into the tight-binding (TB) approximation, we have

$$V_{\text{cry}}(\Delta H) = V_{\text{cry}}(r)[1 + \Delta H]$$

$$\Delta E_v(\Delta H) = [E_v(12) - E_v(0)] \times [1 + \Delta H]$$

where

$$1 + \Delta H = E_z / E_0 = \left\{ \begin{array}{ll} C_z^{-m} & \text{(bond contraction)} \\ t & \text{(bond nature alteration)} \\ p & \text{(polarization screening)} \end{array} \right\}$$

$$= d_z/d_0 = 2/[1 + \exp[(12 - z)/(8z)]] \quad (2)$$

The bond nature indicator $m = 1$ for metals has been optimized. The possible origins for the Hamiltonian perturbation include the following:

(i) Undercoordination induced bond contraction and the associated bond energy gain.

(ii) Chemical reaction induced bond nature alteration.

Figure 1. Schematic illustrations of (a) the undercoordination-induced positive core level shift of various components from that of an isolated atom $E_v(0)$, which satisfies the constraint: $\Delta E_v(z_i) / \Delta E_v(12) = C_z^{i-1}$ with $C_z$ being the bond contraction coefficient. $A$, $P$, and $S$ represents the components arising from the surface kink atoms, polarization, and surface sublayers. The $E_v(0)$ and $\Delta E_v(12)$ are intrinsic constants disregarding the crystal orientation or the surface chemical treatment. (b) Atomic configurations of the clean Re(0001) and (1231) surface. The right panel in (b) shows the atomic kink edge of the (1231) with high fraction of undercoordinated atoms.

Table. A giant 0.17 eV positive SCLS for the Re(1231) surface has been concluded by Chan et al. through changing the incident photon energy and altering the emission angles in measurements. An XPS or a synchrotron spectroscopy collects more information from the surface at larger emission angles or with lower incident beam energies. Although the physics and chemistry of the undercoordinated Re surface and kink atoms have been extensively investigated, understanding the behavior of electrons and bonds localized in the surface of skin-depth has been far from clear. Therefore, a method purifying the spectral information confined within the outermost one or two atomic layers is highly desired.

However, gaining bond and electronic information from the surface-covering sheet of skin depth is beyond the scope of the scanning tunneling microscopy/spectroscopy (STM/S) because STM/S collects information only from the open side of the surface about electrons with energies near the Fermi level. Comparatively, the XPS collects statistic and volumetric information about the binding energies of electrons in the valence band and below from the mixture of surface, subsurface, and bulk up to nanometers in depth. The challenge is how to attack the challenge faced by the STM/S and the XPS to gain atomic scale, zone selective, localized, and quantitative information of the bonding and electronic dynamics. The objective of this communication is to show that a proper process of data collection and processing has enabled us to solve this problem.
(iii) Charge polarization induced crystal potential screening and splitting.

The physical indication of eq 2 is that the bond energy gain or crystal potential screening is responsible for the extra components adding to the bulk XPS spectrum. As illustrated in Figure 1a, the amount of the energy shift of each component from the reference point is proportional to the energy of the specific bond at equilibrium. With respect to the bulk shift \( \Delta E_v(z) \), the undercoordination-induced CLS, \( \Delta E_v(z) \), is expressed as \[ \frac{\Delta E_v(z)}{\Delta E_v(12)} = \frac{E_v(z) - E_v(0)}{E_v(12) - E_v(0)} = \frac{C_z}{C_z - 1} > 1 \]

or \[ \Delta E_v(z) = \frac{[E_v(z) - E_v(0)]}{[E_v(12) - E_v(0)]]/C_z \] (3)

According to this relation and the rule of Goldschmidt–Pauling bond contraction,18,19 all of the SCLS should be positive without exception unless polarization becomes dominant. Using this regulation, we have analyzed the XPS data from the (0001), (1010), and (1120) surfaces of Be and Ru,25,26 with derivatives of the effective \( E_v \) values, the lattice strains, the binding energy densities, and the atomic cohesive energies in the outermost three atomic layers. The analysis also derived the specific energy levels of an isolated atom and their bulk shifts of a number of other metals. The layer and orientation resolved \( z \) values of the hcp-structured Be, Ru, and Re should share the same \( z \) values.

2.2. Photoelectron Residual Spectroscopy. One can imagine what will happen in the following processes. Upon executing the proper processes of spectral background correction and spectral area normalization, one can find the difference between two spectra collected from: (i) a surface before and after the surface being chemically or physically conditioned under the same measurement conditions and (ii) the same surface at different emission angles. The residual spectrum keeps only the features due to surface conditioning such as adatoms or different emission angles. The residual spectrum keeps only the features due to surface conditioning such as adatoms or defects formation, adsorption, alloy formation, and so on, in the first case, and the features due to the skin only, in the second, because the XPS collects more bulk information at 0° emission angle than that collected at larger emission angles. Such a process keeps the meaningful information by filtering out the common bulk information and minimizing the influence of the extrinsic factors such as the background uncertainty and the “initial-final states” effect that exist throughout the course of detection.27

2.3. Criteria, Procedures, and Derivatives. Three criteria need to be met in the spectral decomposition and the PRS processing. First, undercoordination induces global positive shift because of the bond energy gain. Second, eq 3 correlates the energy shifts of the spectral components; the number of components in each spectrum may vary slightly depending on the penetration depth of the incident X-ray. Finally, the PRS spectral areas across should conserve.

We first digitized the well-measured spectra and rechecked the background correction using the standard Shirley method. We then conducted the spectral deconvolution for the available Re(0001) and Re(1231) surface collected at 0 and 75° angles with respect to the reported peak values but subject to slightly tuning. The deconvolution based on the criterion of eq 3 derives the energy level of an isolated atoms \( E_0(0) \) and its shift of \( E_0(12) \) as standard for calibration. The \( E_0(0) \) and \( \Delta E_0(12) \) should be intrinsic constants disregarding the experimental or surface conditions. The accuracy of \( E_0(0) \) and \( \Delta E_0(12) \) is subject to volume size of the database. One can ensure the accuracy by collecting and calculating more spectra from different orientations of the same specimen. Using eq 3 as the constraint and the known \( z \) values for Be and Ru surfaces as references,25,26 we can determine the peak energy of each component of the Re surfaces with sufficient accuracy.

In general, the integrated intensity of a spectral peak is weaker for the one collected at larger angles or from the rough surface than that collected at a smaller angle from the smooth surface because of the effect of scattering. The integral intensity of the specific peak is proportional to the total number of electrons emitted from the specimen under the same experimental conditions such as the incident beam energy and temperature. Ideally, the total number of the emitted electrons should be constant. To make all spectra quantitatively comparable, a normalization of all the spectra can minimize the influence of the scattering effect. Having all of the spectra been normalized, we performed the spectral subtraction under the guideline of spectral conservation, which means that the net spectral gain of the resultant PRS is zero. Any improper process of background correction or spectral normalization may lead to the deviation of the PRS from the ideal situation in which the areas above and below the lateral axis are identical. With these criteria, we can get quantitative information from the database that is richer than ever, which should be the purpose of the costive and sophisticated measurements.

3. RESULTS AND DISCUSSION

3.1. Re(0001) and Re(1231) SCLS. Figure 1b illustrates the atomic arrangement of the hcp(0001) and the (1231) surfaces. In contrast to the smooth (0001) surface, the (1231) surface is much rougher with high fraction of undercoordinated kink atoms. It is anticipated that these undercoordinated atoms will generate the entrapped states below the bulk component in the core band. Thanks to the well-measured Re(0001) and (1231) surface, 4f/2 XPS with and without oxygen chemisorption by Mårtensson et al.14 and Chan et al.10 using synchrotron radiation at different emission angles and incident beam energies.

Figure 2 shows the decomposed XPS spectra for the Re(0001) and the (1231) surfaces with the \( z \) values derived from eq 3 as input and the derived information as given in Table 1. The (0001) and the (1231) surfaces are decomposed into three and four components, respectively, which is consistent with those for the hcp-(0001) and (1120) surfaces of Be and Ru.25,26 As the intrinsic quantities, the \( E_0(5/2,0) \) and the \( E_0(5/2,12) \) remain constant disregarding the change in the emission angle or the crystal orientation. From the decomposition, it is noted that the undercoordination-induced CLS is indeed positive and the lowest coordination component shifts most from that of an isolated Re atom. Therefore, choosing the bulk component as the reference point and assigning the shift as negative are improper, which prevents the tabulated information from being extracted.

Including the common B component (\( z = 12 \)), we have a total of 28 possible values of \( E_j(0) \) derived from eq 3

\[ E_j(0) = \frac{C_0E_j(z') - C_zE_j(z)}{C_z - C_0} \]
The z value for each component collectively can improve the accuracy of the effective z value in the differently oriented surface layers. The optimized z value of 2.836 for the outermost (1231) surface layer is lower than the value of 3.506 for the (0001) surface. On the basis of the given criteria, the decomposition of the three spectra has led to the z-dependent binding energy and more information listed in Table 1

\[
E_{4f_{5/2}}(z) = \frac{\langle E_{4f_{5/2}}(0) \rangle \pm \sigma + [E_{4f_{5/2}}(12) - E_{4f_{5/2}}(0)]}{C_z^{-1}} = 40.015 \pm 0.004 + 2.629C_z^{-1}
\]

(4)

### 3.2. PRS-Purified Re (1231) Surface Kink States

Figure 3a shows the PRS of the Re (1231) 4f_{5/2} and 4f_{7/2} bands gained by subtracting the spectrum collected at 0° from the one collected at 75° after background correction and spectral area normalization. The rule of spectral area conservation almost applies to the PRS, indicating that the background correction and spectral area normalization are quantitatively proper. Obvious valleys and peaks appear in the PRS, which can be assigned without any question to the bulk (B) and the undercoordinated kinks with the quantum entrapment (T). Applying eq 4, the T components are dominated by the outermost two atomic layers with the effective z values of 3.6(S_3) and 2.8(S_1), as indicated in Figure 3b. The small feature at the upper edge of the 4f_{7/2} band is contributed from the S_{3} and S_{1} kinks being involved. The PRS could therefore separate the kinks from the mixture of bulk, the skin, and the kink without needing any argument in the B and skin component assignment.

### Table 1. Crystal Orientation and Atomic Layer Resolved Re 4f_{5/2} Shift with Derived Information of the Effective CNs, Local Strain (Cz – 1), Relative Binding Energy Density (Cz^{-1}), and the Relative Atomic Cohesive Energy (z_a/Cz with z_a = z/12) of the Re(0001) and (1231) Surfaces and the z-Dependent CLS

<table>
<thead>
<tr>
<th>i</th>
<th>E_{4f_{5/2}}(z)</th>
<th>z</th>
<th>Cz -1 (%)</th>
<th>Cz^{-1}</th>
<th>z_a/Cz</th>
<th>ref</th>
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<tr>
<td>Re atom</td>
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<tr>
<td>Re(0001)</td>
<td>B</td>
<td>42.645</td>
<td>12</td>
<td>0</td>
<td>1</td>
<td>1</td>
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<tr>
<td>S_{1}</td>
<td>42.794</td>
<td>6.480</td>
<td>-5.319</td>
<td>1.244</td>
<td>0.571</td>
<td>42.67; 13, 42.725^{14}</td>
</tr>
<tr>
<td>S_{2}</td>
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<tr>
<td>S_{3}</td>
<td>43.11</td>
<td>3.506</td>
<td>-15.027</td>
<td>1.918</td>
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</tr>
<tr>
<td>Re(1231)</td>
<td>S_{4}</td>
<td>42.779</td>
<td>6.778</td>
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### Figure 2. Decomposed XPS Re 4f_{5/2} spectra collected from the (a) Re(0001) and the Re(1231) surfaces with (b) 0° (along the surface normal) and (c) 75° emission angles. The constant bulk component locates at 42.645 eV. The intensities of the surface (S_{1} and S_{2}) components increase with the emission angle rendering that of the bulk component.

Giving rise to the mean $\langle E_{\nu}(0) \rangle = \Sigma_{N}E_{\nu}(0)/j$ with the standard deviation of

$\sigma = \left\{ \sum_{28} (E_{\nu}(0) - \langle E_{\nu}(0) \rangle)^2 / (j(j-1)) \right\}^{1/2}$

Increasing the l or the j values can ensure the accuracy of the $E_{\nu}(0)$ (minimize the standard deviation $\sigma$ value). A fine-tuning of
From the spectral bandwidth of the B valley, we can show that the overlap integral $\beta$ is negligible compared with the exchange integral $R$ in the TB approximation of the inner band, as mentioned in eq 1. The width of a core band is $2z\beta$, and the shift of the band from that of an isolated atom is $R + z\beta$. On the basis of the width of the B valley for both the 4f$_{7/2}$ and the 4f$_{5/2}$ bands of $\sim$0.25 eV and the bulk shift of $R + z\beta = 2.629$ eV, we have, $\beta/R \approx 0.1/2.50 = 0.4\%$ only.

3.3. PRS-Purified O−Re(1231) Kink States. Figure 4a,b shows the decomposed 4f$_{7/2}$ band for the Re(1231) surface with and without oxygen chemisorption. Because of the lacking of the oxygen chemisorption spectral data for the 4f$_{5/2}$ band, we turned to analyze the 4f$_{7/2}$ band. A direct decomposition of the spectra for oxygen adsorbed Re(1231) surface using the coordination wise does no longer hold because of the new bond formation between the adsorbate and the metal surface atoms. The O−Re bond formation will increase the crystal potential substantially in the adsorbed region, which will lower the surface states further to deeper energies, as shown in Figure 4b. The O-induced Re 4f$_{7/2}$ positive shift is in line with what is detected.
from oxygen chemisorbed surfaces,28 in which the O 2p states shift positively by $\sim0.5$ eV upon oxide formation. Figure 4c shows the PRS for the Re(1231) surface with and without oxygen adsorption. A valley $B_0$ centered at 40.40 eV is present, being different from the $B$ and the $S_0$ in the referenced PRS of the unadsorbed surface. This difference indicates that the O–Re bond is much stronger and the synchrotron beam with 90 eV collects less information from the bulk and the $S_0$ region. The extra states extending to energy are even lower than the surface states of the clean surface. The PRS has thus enabled us to separate the chemisorbed surface states from the mixture and allowed us to estimate the depth of two atomic layers being involved in the adsorption of oxygen. It has been demonstrated28 that oxygen prefers the central position of a tetrahedron by interacting with two metal atoms through bonding and two through nonbonding lone pairs of electrons.

4. CONCLUSIONS

The XPS spectra for the Re(0001) and Re(1231) surfaces with and without oxygen chemisorption have been analyzed under the guidelines of the BOLS-TB algorithm and the PRS approach. The Re 4f$_{5/2}$ binding energy of 40.015 eV for the isolated Re atom and its bulk shift of 2.629 eV and the layer and Re(1231) surface kink states presenting at the bottom edge of the Re 4f band, which evidence the undercoordination-induced orientation resolved bond relaxation and quantum entrapment of Re atoms and its bulk shift of 2.629 eV and the layer shift positively by 0.5 eV upon oxide formation. Figure 4c shows the PRS for the Re(1231) surface before and after being chemisorbed with oxygen purified the oxygen chemisorption states with even lower binding energy due to the stronger O–Re bonds formed at the surface with two atomic layers being involved. The novel yet simple PRS technique and the associated analytical solution is demonstrated to be more powerful in gaining the local, quantitative information from atomic scaled zone surrounding the under- and the heterocoordinated atomic scaled zone surrounding the under- and the heterocoordinated

AUTHOR INFORMATION

Corresponding Author *E-mail: ecqsun@ntu.edu.sg.

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