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# Physical origin of the anomalous negative W 4*f* surface core-level shifts in the initial oxidation of submonolayer Ba on a W(110) surface

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The electronic changes of a polarized Ba/W(110) surface during the incipient oxidation have been investigated by synchrotron-radiation photoemission spectroscopy. The slight $O_2$ adsorptions ($\leqslant 0.15$ L) induce both interfacial W 4*f* (Ba-coordinated W) and Ba 4*d* core levels to shift concurrently toward smaller binding energies, and the intensity of Ba 5*d* states increases sharply. We have proposed a model in terms of the 5*d* hybridization effect to explain the physical origin of the oxygen-induced anomalous negative chemical shifts of W and Ba core levels and to correlate chemical shifts to local changes of surface chemical reactivity.

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## I. INTRODUCTION

Chemical modification of alkali and alkali-earth metals covered transition metal surfaces by coadsorbed oxygen has been found interesting because this frequently results in strong alteration of both chemical states and electronic structures of interfaces.[1–9] For instance, adsorption of oxygen leads to an anomalous negative chemical shift of alkali core levels, a drastic work function (WF) reduction, and the promoting effect of alkali metals in catalysis. In particular, the unusual negative chemical shift of Ba core levels in BaO overlayer[5] is largely discussed in terms of strong covalent bonding between the O 2*p* states and Ba 5*d* bands, due to the partial occupancy of the empty Ba 5*d* orbitals upon oxidation.[10,11] The increased density of 5*d* states implies that the core hole is more efficiently screened, this would reduce the effective potential and hence the core-level binding energies (BEs).[10–13] In fact, the screening capability of the core-ionized system is closely related to the charge distribution near the core-excited atom and the surface chemical activity;[14,15] thus, this information is also of significance for the catalytic surface oxidation by 5*d* metals.

In recent decades, a full-potential-linearized augmented-plane-wave (FLAPW) calculation for the electronic structure of a $c(2\times2)$ BaO overlayer on W(001) has shown that the chemical bonding of this surface is very complex and involves significant interactions between both the adsorbated Ba and oxygen atoms and the W substrate. In particular, the 5*d*-like surface states of the W substrate is found to play a crucial role in the overlayer-substrate interaction; i.e., a covalent bonding is formed between the W 5*d*-like surface states and both Ba 5*d* and O 2*p* states.[9] Moreover, we have demonstrated experimentally that a strong covalent Ba-W bonding indeed occurs through Ba(5*d*)-W(5*d*) hybridization in the polarized metallic Ba adlayer on W(110), which results in negative shifts of both Ba and W core levels via a greater extra-atomic screening of 5*d* electrons.[16] Also, a chemical study of BaO/W surface reported that a complicated bonding of this cathode surface is described as strongly ionic bonds between Ba and the O/W substrate, whereas O binds covalently to W; and the presence of O enhances the transfer of charge from Ba into the W substrate, lowering the WF.[8]

In order to investigate the complicated oxygen-induced electronic changes of submonolayer Ba/W(110), we present a high-resolution surface core-level shift (SCLS) study to investigate the electronic interaction between a polarized Ba overlayer on W(110) surface and the adsorbing oxygen. As SCLS is directly related to the redistribution of charge in the outer electron orbitals due to the modification of the structural environment at the surface, the shape of the core levels and their energy positions are thus sensitive to the local chemical reactivity and electronic change at the interface and can provide direct insight into the nature of the interface bond.[17–20] In the present work, surface sensitive W 4*f* photoemission with synchrotron radiation can give rise to the sufficiently narrow spectral features, this makes it possible to observe the very small chemical shifts in W 4*f* core levels of the topmost-layer W atoms induced by the adsorbate-substrate interaction during various $O_2$ dosages. Upon slight exposure to $O_2$, both Ba-induced W 4*f* and Ba 4*d* core levels move simultaneously towards lower BEs, and the emission of Ba 5*d* states near Fermi level ($\boldsymbol{E}_{\mathbf{F}}$) increases sharply. The concurrent negative shifts of both W 4*f* and Ba 4*d* peaks have not been reported in previous studies of oxidized alkali-metal adlayers on metallic surfaces. Especially, the anomalous negative shift of the interfacial W 4*f* core level has been obtained in this study for the first time. As photoemission measurements of metal oxides typically show core level BEs that are higher than those of the elemental metal, this positive shift is fundamental to oxidation reactions. Thus, our study for the oxygen-induced electronic changes of submonolayer Ba/W(110) is of significant scientific interest to surface chemical reactivity in the incipient stage of the catalytic oxidation of 5*d* metals covered transition metal surfaces.

## II. EXPERIMENT

Photoemission experiments were performed at the National Synchrotron Radiation Research Center in Hsinchu, Taiwan. The details can be found elsewhere.[16,21] In short, photoelectrons were collected via a hemispherical analyzer in an UHV chamber with a base pressure of $3\times10^{-11}$ Torr.

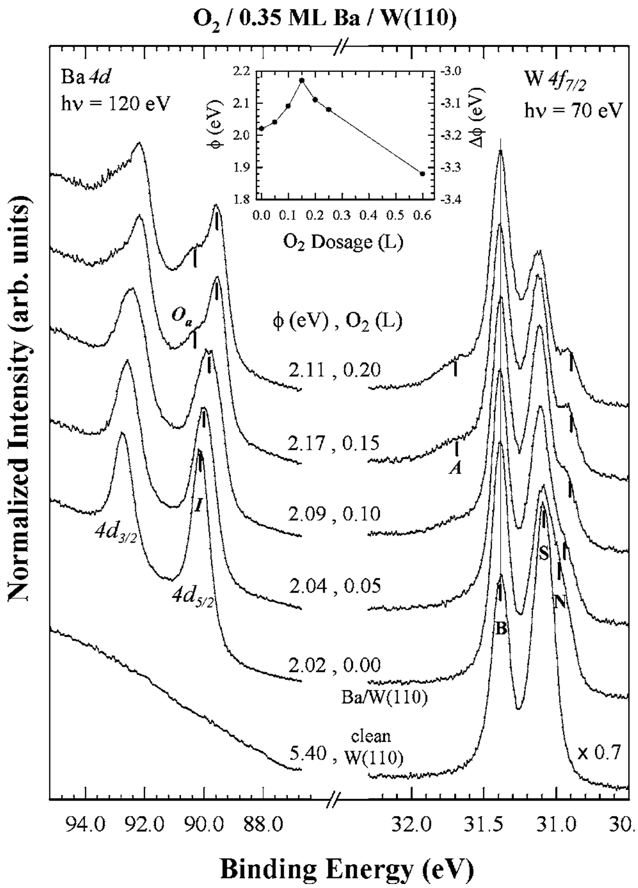

FIG. 1. W $4f_{7/2}$ and Ba $4d$ core level spectra from various $O_2$ dosages on 0.35 ML Ba-covered W(110) surface at room temperature. Symbols **B**, **S**, and **N** denote emission from bulk, surface and Ba-coordinated W atoms, respectively. Component ***I*** is from the Ba adatoms; ***A*** and ***$O_a$*** are oxygen-induced features. Also shown in the inset is the work function versus oxygen dosages.

All photoemission spectra were normalized to the photon flux, which was monitored by a gold mesh in front of the sample. The surface sensitivity was optimized by selecting 70 eV photon energy for W $4f$ spectrum in order to minimize the escape depth of photoelectrons. The total instrumental energy resolution was better than 72 meV. Ba was evaporated from a thoroughly outgassed SEAS getter source. The Ba thickness was chosen to be 0.35 ML, where the WF is the lowest and a transition from polarization to depolarization occurs.[16] This oxygen-free surface is hereafter denoted as Ba/W. The oxidation of the Ba/W surface at RT was conducted on backfilling the chamber with $O_2$ (purity 99.999%). The oxygen dose is given in Langmuir units ($1\ \text{L}=1.0\times10^{-6}$ Torr s).

## III. RESULTS AND DISCUSSIONS

Figure 1 shows the evolution of a set of W $4f_{7/2}$ and Ba $4d$ core-level spectra with progressive exposures of the Ba/W surface to $O_2$. In Fig. 1, the clean W $4f_{7/2}$ spectrum clearly exhibits two well distinct peaks, i.e., bulk (**B**) and surface (**S**) components. The strong surface emission **S** is similar to the results reported by Riffe *et al.*[22] Upon Ba adsorption, clean surface emission **S** reduces strongly in intensity, while in the meantime, a Ba-induced component **N** starts to develop as a shoulder structure on the lower-BE side of the surface peak **S**.[16] The **N** component originates from the Ba-coordinated W atoms. While for Ba $4d$ core-level spectra recorded at 120 eV photon energy, only one interfacial component (***I***) appears at BE of 90.12 eV in the unexposed Ba/W interface. The negative SCLSs of both **N** and ***I*** components result from the increased W($5d$)-Ba($5d$) hybridization.[16] Upon further exposure, both **N** and ***I*** components shift concurrently toward smaller BEs and stop at 0.15 L. Moreover, the oxygen adsorption reduces the intensities of both **N** and ***I*** components considerably. With $O_2$ exposure at 0.10 L, an oxidized W $4f$ component (***A***) occurs as a broad shoulder at BE of ~0.3 eV higher than peak **B**, and a new Ba $4d$ component (***$O_a$***) appears on the higher BE side of the ***I*** peak at 90.32 eV. The WF (inserted in Fig. 1) increases from 2.02 to 2.17 eV for 0.0–0.15 L, but decreases with further exposure. This observation is unlike the typical behavior of the WF change with initial oxidation on low-coverage alkali-metal overlayers.[1–4]

TABLE I. Summary of the Gaussian width $\Gamma_G$ (meV) determined from the least-squares fits in Fig. 2.

| | 0.0 L | 0.05 L | 0.10 L | 0.15 L | 0.20 L |
|---|---|---|---|---|---|
| **B** | 78.66 | 78.66 | 78.66 | 78.66 | 88.76 |
| **S** | 118.55 | 116.38 | 117.82 | 114.75 | 121.18 |
| **N** | 140.58 | 136.90 | 127.72 | 119.19 | 115.88 |
| ***A*** | | | 137.91 | 143.87 | 141.91 |
| **O1a** | | | | 229.59 | 277.56 |

In order to obtain more precise qualitative as well as quantitative information available from W $4f$ core-level data during the early oxidation regime, it is necessary to correctly decompose the lineshape of the spectra into different components representative of surface, bulk and interface reaction products. A nonlinear least-squares curve fitting routine was then used to determine the peak composition of the spectra. The fitting function was a Doniach-Šunjić lineshape convoluted with a Gaussian instrumental function. To fit a spectrum with a given oxygen coverage, we implanted a few constraints stated as follows: for the bulk and surface components, the lifetime widths (Lorentzian width) $\Gamma_L$ and the asymmetric index $\alpha$ were fixed at the values of those in the clean W(110) surface;[16,22] as for the **N** component, $\Gamma_L$ and $\alpha$ were fixed at the values of 53 meV and 0.050, respectively, ascertained from the Ba/W interface.[16] The values obtained for these parameters remained constant regardless of $O_2$ coverage. The Gaussian width $\Gamma_G$ was allowed to vary in the fits, and best-fit values for $\Gamma_G$ are given in Table I.

The fitted results of four W $4f_{7/2}$ core level spectra (from unexposed Ba/W, 0.05 L, 0.15 L, and 0.20 L $O_2$-covered surfaces) are displayed respectively in Fig. 2. Both the binding energies and the intensities of different W $4f_{7/2}$ components shown in Fig. 2 versus $O_2$ dosage are plotted in Fig. 3. In Fig. 2, the W $4f_{7/2}$ spectrum of the Ba/W interface actu-

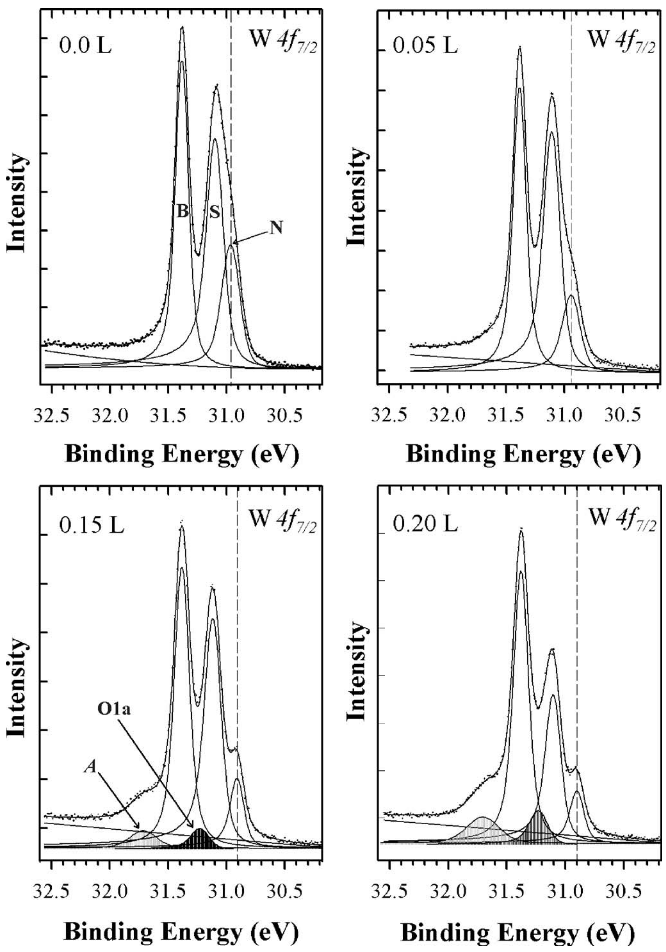

FIG. 2. Decomposition of the W $4f_{7/2}$ spectra of clean Ba/W(110) interface and its evolution as a function of oxygen coverage. The dots represent the experimental data, while the line in between is the result of the fit.

ally consists of three peaks at 31.39, 31.00, and 30.98 eV, respectively. These peaks are assigned to the bulk (**B**), surface (**S**) and Ba-coordinated (**N**) tungsten atoms, respectively. Upon $O_2$ exposures from 0.05 L to 0.15 L, the **N** component moves toward lower BE, and its intensity reduces faster than that of both **B** and **S** components. The negative shift of **N** stops at 0.15 L. Within the accuracy of the peak-fitting analysis, the SCLS of **N** is −84 meV. The physical origin of this oxygen-induced anomalous negative SCLS of **N** will be discussed later. As shown in Table I, the $\Gamma_G$ of **N** decreases gradually with increasing dosing, indicating that the adsorption sites of the Ba atoms on W(110) surface become more ordered induced by the increased $O_2$ doses.

However, the BEs of both **S** and **B** remain unshifted. The intensities of both **S** and **B** decrease slowly from 0.00–0.15 L, then after 0.15 L **S** reduces considerably, while **B** still remains strong. These results of W 4*f* core level spectra clearly show that a more localized interaction has formed between the Ba-coordinated W atoms and oxygen when $O_2$ exposure below 0.15 L, i.e., oxygen initially prefers to adsorb on top of the polarized Ba adatoms, resulting in depolarization of the surface and an increase in the WF.[23]

Upon adsorption of 0.10 L, a small oxidized component (***A***) emerges at 31.71 eV and grows monotonically with increased dosing. At 0.15 L, a second oxidized component (**O1a**) appears at 31.24 eV, but increases very slowly after 0.2 L. The ***A*** oxidized component originates from the surface W atom bound to two oxygen atoms, while **O1a** is attributed to the singly-coordinated W atom. The atomic origins of ***A*** and **O1a** components are the same as the assignments of **O2** and **O1a** peaks reported by Riffe *et al.*[24] The evolutions of both ***A*** and **O1a** oxidized components as function of oxygen dosing have been discussed in detail in a previous paper.[21]

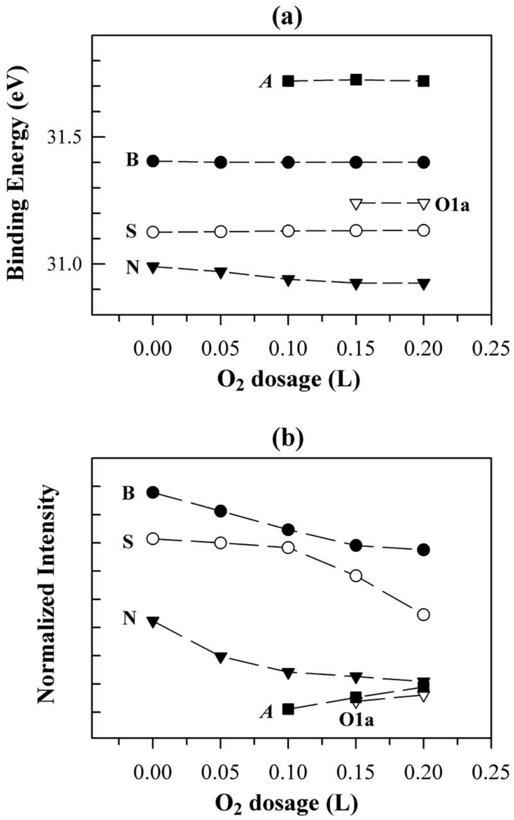

FIG. 3. (a) Binding energies and (b) intensities of the various components of W $4f_{7/2}$ core levels in Fig. 2 versus $O_2$ exposure.

Figure 4 displays the corresponding valence band (VB) spectra of the Ba/W interface exposed to the same dosages as in Fig. 1, which were recorded at a photon energy of 55 eV. The binding energies and the intensities of different surface states versus $O_2$ exposure are displayed in Fig. 5. Figure 4 shows at the bottom the clean W(110) spectrum, in which three surface states are clearly visible at 0.40 (***S***1), 0.95 (***S***2) and 1.41(***S***3) eV, and two bulk states at 2.10 (***B***1) and 3.23(***B***2) eV.[16] Upon Ba adsorption, the $E_F$ remains strong, and all the surface states attenuate in intensity. Moreover, ***S***1 and ***S***2 shift away from $E_F$, and their downward shifts are about 60 and 50 meV, respectively. However, ***S***3 splits into two states, i.e., one (***S***3) still remains at 1.41 eV, the other (***S***3′) moves to 1.62 eV, which are similar to the results of Gd/W(110).[25] These shifts of surface states result from W(5*d*)-Ba(5*d*) hybridization.[16] The emission near the $E_F$ originates primarily from the Ba 5*d* state.[16,26] As seen in Fig. 5, exposure of the Ba/W to 0.05 L substantially increases the intensity of Ba 5*d* state and three hybridized states, ***S***1, ***S***3 and ***S***3′, without affecting their energy posi-

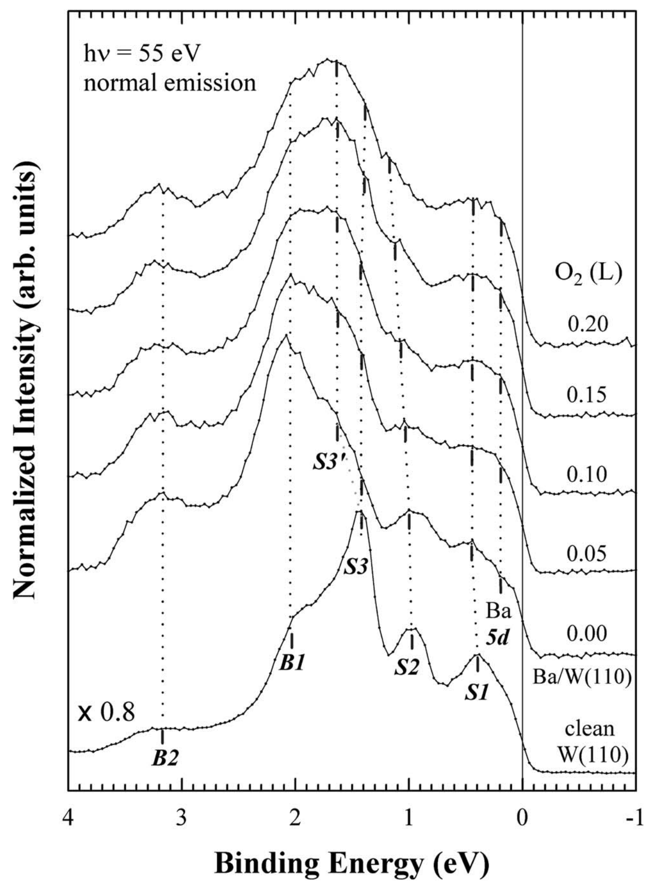

FIG. 4. Normal-emission valence band photoemission spectra corresponding to the same O$_2$ dosages as in Fig. 1. Prefix symbols **S** and **B** represent surface and bulk states, respectively.

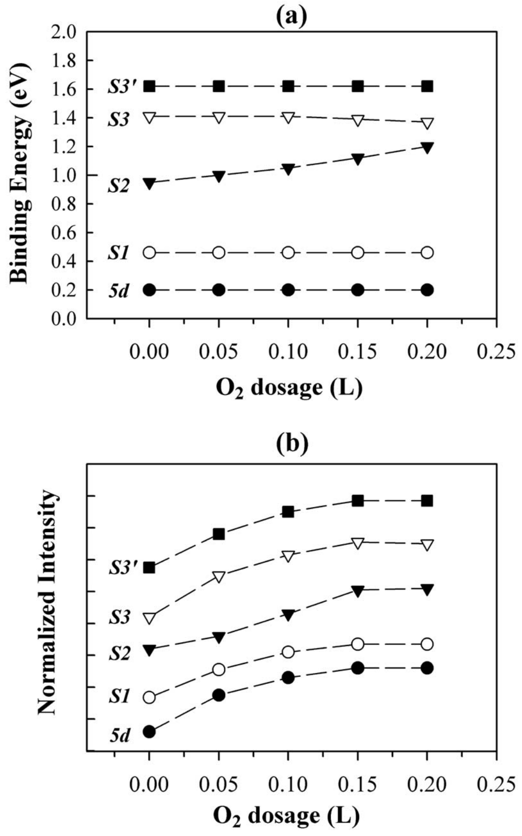

FIG. 5. (a) Binding energies and (b) intensities of different surface states in Fig. 4 versus O$_2$ exposure.

tions. In contrast, the developing ***S***2 state moves toward higher BE. On further exposure to 0.15 L, the growth of Ba 5*d* state and four hybridized states stops. It should be noted that the growth of Ba 5*d* state and four hybridized states is accompanied by the further negative shifts of both **N** and ***I*** components.

The enhanced emission in the vicinity of $\boldsymbol{E}_{\mathbf{F}}$ upon oxidation provides a direct evidence of the increased density of Ba 5*d* state. The increased occupancy of Ba 5*d* orbital enhances the final-state screening efficiency of the Ba 4*d* cores and causes the 5*d* orbital to participate in covalent bond with oxygen.[10,11] This explains the further negative shift of the Ba 4*d* cores upon oxidization. Also, the sharp $\boldsymbol{E}_{\mathbf{F}}$ excludes the concern of the referencing problem in the normal oxide film, and indicates that the Ba adatoms adjacent to oxygen are in a metallic medium. The persistence of this metallicity should result from Ba(5*d*)-O(2*p*) hybridization,[27] which leads to the increased density of Ba 5*d* state. This hybridization buffers the local charge redistribution so as to achieve charge neutrality at the Ba atoms, thereby resulting in a covalent bonding between Ba and O.

The most striking result of the present system is the further negative shift of the **N** component of the W 4*f* peak induced by chemisorbed oxygen. In our previous study of Ba adsorption on W(110),[16] the increased W(5*d*)-Ba(5*d*) hybridization would result in a negative shift of the interfacial component **N**. Therefore, we speculate that for O$_2$ adsorption below 0.15 L the populous Ba 5*d* states due to Ba(5*d*)-O(2*p*) hybridization would supply the extra screening charges with 5*d* character at the Ba-coordinated W atoms through the strong W(5*d*)-Ba(5*d*) hybridization, thereby giving rise to the better-screened component **N** in Fig. 2. Thus, this anomalous negative shift happens with certainty that there is an enhanced emission of W(5*d*)-Ba(5*d*) hybridized states. As revealed in Figs. 2 and 4, the further negative shift of **N** is indeed accompanied by the growth of four hybridized states. This explanation is also supported by the two observations that upon exposure above 0.15 L (1) the variations of the intensities of four hybridized states as well as Ba 5*d* emission are nearly zero (see Fig. 5) and (2) the negative shifts of both **N** and ***I*** peaks stop at 0.15 L. These observations can be understood by the fact that the filling of Ba 5*d* state is completed at 0.15 L so that there is no extra 5*d* electron contribution in final-state screening of both **N** and ***I*** peaks.[12] So, the increased 5*d*-hybridization contribution to the oxygen-induced further negative shift of the interfacial W 4*f* peak (**N**) is evidenced.

In addition, in our oxidized system the change of WF appears to be directly correlated to the oxygen-induced SCLS of both **N** and ***I*** peaks. Below 0.15 L, the negative shifts of both **N** and ***I*** peaks are attributed to the increased 5*d* screening, resulting from Ba(5*d*)-O(2*p*) hybridization. This covalent hybridization introduces an additional barrier for the adsorbing oxygen, which reduces the promotional efficiency of the Ba adatoms. Consequently, the incorporation of oxygen below the Ba overlayer becomes impossible. Therefore, oxygen favors atop the Ba atom and lead to depolarization of the Ba adlayer and an increased WF. Above 0.15 L, the filling of Ba 5*d* state is completed, and this causes no extra 5*d*-screening contribution to the shifts of both **N** and ***I*** peaks, and no additional Ba 5*d* orbital is in covalent bond with oxygen.[10] Thus, the activation barrier for oxygen dissociation is reduced; that is, oxygen atoms can penetrate underneath the Ba adatoms, consequently leading to an undepolarization[28] of the Ba adlayer and a decreased WF.

## IV. SUMMARY

In summary, upon the adsorption of oxygen ($\leqslant$0.15 L) on the polarized 0.35 ML Ba-covered W(110) surface, the high-resolution photoemission study shows that both the Ba-induced W 4*f* (**N**) and the Ba 4*d* (***I***) components simultaneously exhibit negative SCLSs, and the emission of Ba 5*d* state increases sharply. These effects are attributed to the strongly polarized covalent Ba-W interactions that still dominate in early oxidation; i.e., the Ba(5*d*)-W(5*d*) hybridization continues to play a key role during slight oxidation, and promotes the hybridization of empty Ba 5*d* states and O 2*p* orbitals. The Ba(5*d*)-O(2*p*) hybridization increases the population of Ba 5*d* state, leading to a negative shift of the ***I*** peak through 5*d* screening. The occupancy of the Ba(5*d*)-W(5*d*) hybridized state is in turn enhanced, thereby supplying the extra screening charges with *d* character at the Ba-reacted W atoms. This effect results in a further negative shift of the **N** peak. The interpretation for the negative SCLSs of both **N** and ***I*** components is evidenced by the growths of Ba 5*d* state and four hybridized states. These results clearly demonstrate that charge rearrangement is the dominant effect in the surface chemical reactivity of our slightly oxidized surface.

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[1] R. A. d. Paola, F. M. Hoffmann, D. Heskett, and E. W. Plummer, J. Chem. Phys. **87**, 1361 (1987).

[2] F. Xu and A. Bonanno, Phys. Rev. B **50**, 11283 (1994).

[3] Q. B. Lu, R. Souda, D. J. O'Conner, and B. V. King, Phys. Rev. Lett. **77**, 3236 (1996).

[4] L. Surnev, G. Rangelov and M. Kiskinova, Surf. Sci. **179**, 283 (1987).

[5] K. Jacobi, C. Astaldi, B. Frick, and P. Geng, Phys. Rev. B **36**, 3079 (1987).

[6] A. Lamouri, W. Muller, and I. L. Krainsky, Phys. Rev. B **50**, 4764 (1994).

[7] L. A. Hemstreet and S. R. Chubb, Phys. Rev. B **47**, 10748 (1993).

[8] W. Müller, J. Vac. Sci. Technol. A **6**, 1072 (1988).

[9] L. A. Hemstreet, S. R. Chubb, and W. E. Pickett, Phys. Rev. B **40**, 3592 (1989).

[10] G. K. Wertheim, J. Electron Spectrosc. Relat. Phenom. **34**, 309 (1984).

[11] P. S. Bagus, G. Pacchioni, C. Sousa, and F. Parmigiani, Chem. Phys. Lett. **196**, 641 (1992).

[12] 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).

[13] M. Aldén, H. L. Skriver, and B. Johansson, Phys. Rev. Lett. **71**, 2449 (1993).

[14] M.-L. Shek, J. Hrbek, T. K. Sham and G.-Q. Xu, Phys. Rev. B **41**, 3447 (1990).

[15] J. E. Ortega and F. J. Himpsel, D. Li and P. A. Dowben, Solid State Commun. **91**, 807 (1994).

[16] T.-W. Pi, I.-H. Hong, and C.-P. Cheng, Phys. Rev. B **58**, 4149 (1998); Surf. Rev. Lett. **4**, 1197 (1997).

[17] D. M. Riffe, G. K. Wertheim, and P. H. Citrin, Phys. Rev. Lett. **64**, 571 (1990).

[18] J. N. Andersen, M. Qvarford, R. Nyholm, J. F. van. Acker, and E. Lundgren, Phys. Rev. Lett. **68**, 94 (1992).

[19] K. Andersson, A. Nikitin, L. G. Pettersson, A. Nilsson, and H. Ogasawara, Phys. Rev. Lett. **93**, 196101 (2004).

[20] A. Baraldi, S. Lizzit, G. Comelli, M. Kiskinova, R. Rosei, K. Honkala, and J. K. Norskov, Phys. Rev. Lett. **93**, 046101 (2004).

[21] I.-H. Hong, C.-P. Cheng, and T.-W. Pi, Surf. Sci. **601**, 1726 (2007).

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

[23] T. C. Leung, C. L. Kao, W. S. Su, Y. J. Feng and C. T. Chan, Phys. Rev. B **68**, 195408 (2003).

[24] D. M. Riffe and G. K. Wertheim, Surf. Sci. **399**, 248 (1998).

[25] O. Rader and A. M. Shikin, Phys. Rev. Lett. **93**, 256802 (2004).

[26] K. A. Kress and G. J. Lapeyre, Phys. Rev. Lett. **28**, 1639 (1972).

[27] W. E. Pickett, Phys. Rev. Lett. **73**, 1664 (1994).

[28] D. Heskett, D. Tang, X. Shi, and K.-D. Tsuei, Chem. Phys. Lett. **199**, 138 (1992); J. Phys.: Condens. Matter **5**, 4601 (1993).