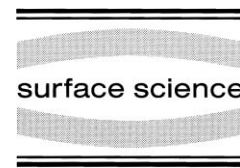




ELSEVIER

Surface Science 430 (1999) L515–L520



www.elsevier.nl/locate/susc

Surface Science Letters

## Alkali metal (Li, K) induced reconstructions of the W(001) surface

H.W. Kim <sup>a</sup>, J.R. Ahn <sup>a</sup>, J.W. Chung <sup>a,\*</sup>, B.D. Yu <sup>b</sup>, M. Scheffler <sup>b</sup>

<sup>a</sup> Department of Physics, and Basic Science Research Institute, Pohang University of Science and Technology, 790-784 Pohang, South Korea

<sup>b</sup> Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin-Dahlem, Germany

Received 14 October 1998; accepted for publication 11 January 1999

### Abstract

The adsorption of Li and K atoms on the (001) surface of tungsten is found to exhibit remarkable differences in the surface core-level shifts (SCLS) of the W 4f level and in adsorbate-induced changes of the transition temperature of the substrate surface reconstruction. Density-functional theory calculations suggest that these results reflect mainly the different bonding geometry of the adatoms, and, for example, the adsorption of potassium is largely affected by an adsorbate-induced reconstruction of the substrate (dimerization of W atoms). © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Density functional calculations.; Photoelectron spectroscopy; Reconstruction

It is widely accepted and understood that metal atoms adsorbed on a metal substrate assume a high-coordination site. However, recent studies showed that this needs not always be the case: For example, for the adsorption of K on Al(111) it was found that the adatom site switches from a hollow site (the highest-coordination site) to an on-top site (the lowest-coordination site) as the coverage is increased [1]. This phenomenon was explained in terms of the strongly repulsive adsorbate–adsorbate interaction of the partially ionized alkali-metal (AM) adatoms. The present paper deals with a substrate from the middle of the

transition metal series. Here the stronger covalent nature of bonding, provided by the half-filled d shell, may affect the simple ‘rule of a preference of high-coordination sites’ for AM adatoms, and/or the strong electron-lattice coupling, for example, due to a Kohn anomaly, may affect the simple picture. Indeed, we will present the first experimental and theoretical evidence of a breakdown of the ‘rule of a preference of high-coordination sites’. The work employs measurements of surface core-level shifts (SCLS) and density-functional theory (DFT) total-energy calculations, and reports results for two AM adatoms, namely Li and K, adsorbed on a (001) surface of tungsten. This substrate was chosen since the clean W(001) surface exhibits a well known reconstruction,

\* Corresponding author. Fax: +82-562-279-3099.

E-mail address: jwc@postech.ac.kr (J.W. Chung)

driven by a Kohn anomaly [2,3], in which the surface atoms are shifted parallel to the surface assuming a zig-zag arrangement [4,5].

SCLS were measured for both, the adsorbate and the substrate atoms, and it was monitored how the transition temperature ( $T_c$ ) of the phase transition of the clean W(001) surface [ $c(2 \times 2) \rightarrow 1 \times 1$ ] [6,7] is affected by the adsorption. Our study reveals that Li and K behave very differently, and we argue that the local AM-substrate geometry, and the accompanied nature of the chemical bond, actuate the observed effects. This conclusion is substantiated by DFT results for adsorption energies, geometries and SCLS, which show that Li adatoms occupy hollow sites and K adatoms prefer the bridge geometry. Also the assumed substrate geometries are importantly different for the two adatoms.

Photoemission measurements for W  $4f_{7/2}$ , K  $3p$ , and Li  $1s$  were performed at the synchrotron beam line 2B1, the Pohang light source using unpolarized photons of energy 78 eV. The optimum energy resolution of the analyzer was 140 meV. To determine the change in the transition temperature, ( $\Delta T_c$ ), of the substrate surface reconstruction and its dependence on adsorbate coverage, we measured the intensity of a half-order low-energy electron diffraction (LEED) spot of the clean  $c(2 \times 2)$  reconstructed surface as a function of temperature for various AM coverages. The background pressure of the ultra-high vacuum chamber was maintained below  $6 \times 10^{-11}$  Torr during the entire course of the experiment. Contamination of the surface was minimized by thoroughly outgassing the AM getter source keeping the pressure below  $5 \times 10^{-10}$  Torr during AM evaporation. The sample was cooled below 52 K using a cold finger maintained at 20 K and heated using electron beam bombardment up to 2500 K. The SCLS spectra were analyzed by a well-known routine [8,9]. The background was subtracted before fitting the spectra with several peaks of the Doniach–Sunjic type lineshape convoluted with a Gaussian instrumental function.

Below  $T_c = 200$  K the clean W(001) surface exhibits a  $c(2 \times 2)$  reconstruction see Fig. 3a [6,7]. Upon adsorption of Li or K on the reconstructed surface and for coverages below 0.5 monolayers

(1 ML =  $1.0 \times 10^{15}$  atoms  $\text{cm}^{-2}$ ), we do not observe a change of the surface periodicity. But for higher coverage (up to 1 ML) and Li adsorption the half-order LEED spots disappear and the LEED pattern becomes indicative of a  $(1 \times 1)$  substrate periodicity. In difference, for K adsorption the surface transforms into an intermediate geometry at coverage  $\theta = 0.5$  ML, which becomes again  $c(2 \times 2)$  when the coverage increase further.

Fig. 1 shows the progressive changes in SCLS of the W  $4f_{7/2}$  level induced by Li (1a) and K adsorption (1b). The spectrum at the bottom from the clean ( $\theta = 0$ ) surface was analyzed with three peaks,  $S_B$ ,  $S_U$  and  $S_S$  due to photoemission from bulk, second-layer and surface W atoms as in previous work [8,10–12].

For the AM covered surface, another peak  $S_{Li}$  ( $S_K$ ) for the contribution from the W surface atoms directly bonded to Li (K) atoms has been added in the fits Fig. 2a. The resulting fit curves are shown as solid curves in Fig. 1.

The results of the fits are summarized in Fig. 2b for the variation of  $S_S$  ( $\circ$ ,  $\bullet$ ) and  $S_U$  ( $\triangle$ ,  $\blacktriangle$ ) components with increasing  $\theta$ . It is clearly seen that Li induces maximum shifts of  $199 \pm 11$  meV (for the  $S_S$  peak) and  $87 \pm 3$  meV (for the  $S_U$ ) with respect to the corresponding energies of the zig-zag reconstructed clean W(001) surface. The values for the K adsorbate are significantly smaller:  $52 \pm 17$  meV for the  $S_S$  peak and  $36 \pm 8$  meV for the  $S_U$  peak. Indeed, shifts as large as those observed here for Li have never been reported previously for AM adsorbed on metal surfaces. We also note that the relatively small shifts ( $\leq 28$  meV) observed for Na, K and Cs adsorbates on the close-packed (110) tungsten surface were interpreted to signify a metallic picture for the AM–substrate interaction [10,11]. This interpretation, however, is not consistent with our observation of the much greater shifts induced by Li, which we take as yet another sign that the experimental identification of the nature of the AM–substrate bond is not without problems [13].

In order to understand the above described experimental results we performed electronic-structure, total-energy and SCLS calculations for the Li and K adsorption on the W(001) using DFT. We employed the local-density approximation for

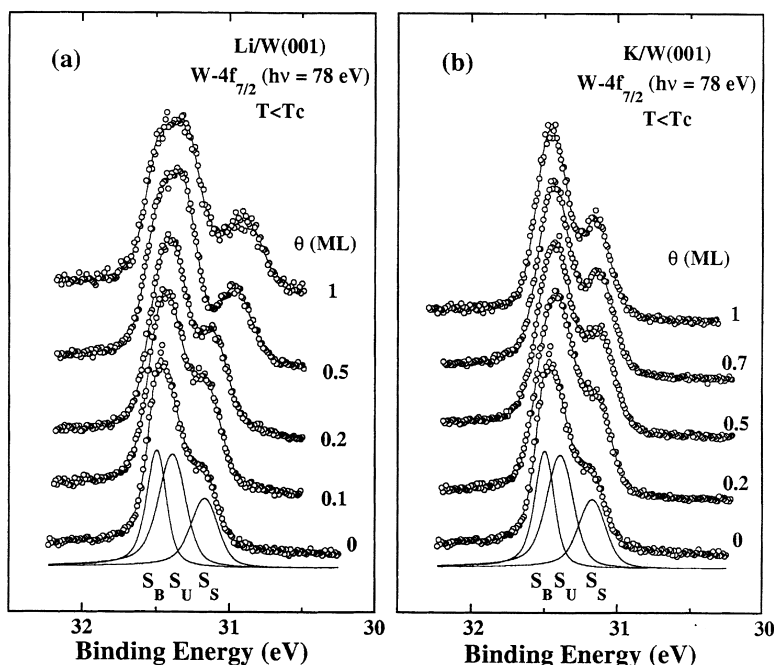


Fig. 1. Evolution of  $W 4f_{7/2}$  peak with increasing AM coverage  $\theta$ ; (a) Li and (b) K. The bottom spectrum from the clean surface consists of three peaks (see text for details).

the exchange-correlation functional [14,15] and used norm-conserving, fully separable pseudo-potentials [16,17]. The basis set consists of plane waves up to a kinetic energy of 30 Ry. The calculated lattice constant for the tungsten crystal is  $a_0 = 3.15 \text{ \AA}$ , and the bulk modulus is  $B_0 = 3.24 \text{ Mbar}$ , which agree well with the measured values,  $a_0^{\text{exp}}$ ,  $b_0^{\text{exp}}$ , as with other calculations [18].

The surface was simulated by a repeated slab, consisting of five W layers with AM adatoms on both sides of the slab. We used our theoretical lattice constant for the W slab, a  $c(2 \times 2)$  surface periodicity, and the  $\mathbf{k}$ -space integration was replaced by a summation over a uniform mesh of 36  $\mathbf{k}$ -points in the surface Brillouin zone (SBZ) of the  $c(2 \times 2)$  cell (displaced from  $\bar{\Gamma}$ ). All geometries were optimized by allowing adatoms and top-layer substrate atoms to relax up to the points where the forces were smaller than  $0.05 \text{ eV \AA}^{-1}$ ; atoms in deeper layers were kept at bulk positions. We also performed test calculations using a more extensive set of parameters, as for example, a slab

of seven W layers, a 35-Ry cutoff energy, and 16  $\mathbf{k}$ -points in the SBZ. From these studies we conclude that the numerical accuracy of our total-energy is better than 0.03 eV.

Table 1 summarizes the calculated results for the total energies at the fourfold hollow, the twofold bridge and the on-top site on the W(001) surface. When the adsorption calculations are performed without allowing the substrate to reconstruct we find that the fourfold hollow site, that is, the highest coordination for the adsorbate, has the lowest total energy for both AMs, Li and K, which conforms with the expected behavior for metal adatoms on metal surfaces. However, when the substrate surface is allowed to reconstruct, K favors the twofold bridge site over the fourfold hollow site, while Li stays on the fourfold hollow site (compare Table 1). This finding is consistent with the above described experimental observations.

The results listed in Table 1 show that the substrate reconstruction mainly affects the adsorption energies at the bridge site. Fig. 3c represents

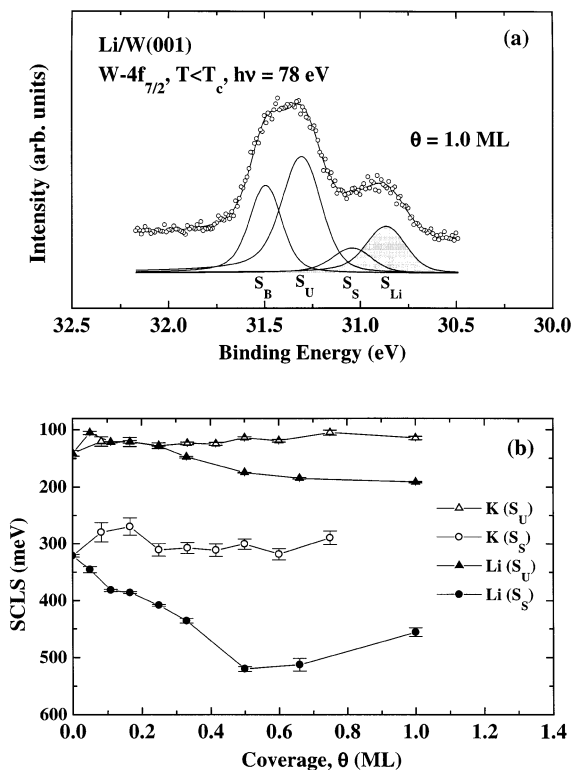


Fig. 2. (a) A representative fit of the W 4f<sub>7/2</sub> peak at  $\theta = 1.0$  ML showing the four peaks; (b) changes of SCLS with  $\theta$  for  $S_S$  (○, ●) and  $S_U$  (△, ▲) peaks induced by Li- (solid) and K- (empty) adsorption.

the fully relaxed atomic geometry at the bridge site. In contrast to the zigzag arrangement of tungsten atoms of the clean  $c(2 \times 2)$  W(001) surface [4,5], Fig. 3c displays the formation of tung-

Table 1

Calculated results of total energy difference  $\Delta E_{tot}$  for Li and K at different adsorption sites. The calculations were performed for both the unreconstructed and reconstructed structures of the AM adsorbed surface using the  $c(2 \times 2)$  cell. The corresponding energy for the fourfold hollow site is used as a reference

Site	$\Delta E_{tot}^{unr}$		$\Delta E_{tot}^r$	
	Li	K	Li	K
Hollow	0	0	0	0
Bridge	0.53	0.16	0.24	-0.16
On-top	0.86	0.27	0.87	0.27

sten dimers. The dimer distances are 2.69 Å for the Li adsorbate and 2.63 Å for the K adsorbate. These distances are slightly shorter than the theoretical atomic distance of 2.73 Å in bulk tungsten. The lower total energy for K at the bridge site is a consequence of two competing contributions, namely, the energy gain due to the dimerization (or reconstruction) of the surface tungsten atoms,  $E_r$ , and the bond energy cost,  $E_b$ , which accounts for the difference between the fourfold hollow and the twofold bridge site of the unreconstructed surface.

Our total energy calculations (see Table 1) show that the substrate dimerization energies for both Li and K are quite similar,  $E_r = 0.29$  and 0.32 eV, respectively <sup>1</sup>. But the loss in bond energy,  $E_b$ , is very different:  $\sim 0.58$  eV for Li and  $\sim 0.18$  eV for K <sup>2</sup>. This significant difference in adsorbate–substrate bonding energies between Li and K reflects the size effect of AM atoms. As a consequence,  $E_r \geq E_b$  for the K adsorption, which explains why K assumes the bridge site. We note in passing that a noticeable difference in adsorbate–substrate bonding energies between Li and K is also found when on-top and bridge adsorption are compared:  $\sim 0.33$  eV (Li) and  $\sim 0.11$  eV (K).

The above results referred to a  $c(2 \times 2)$  surface cell. Interestingly, for lower adsorbate coverage and a  $p(2 \times 2)$  K-adsorbate structure the adsorption energy for the bridge site and a dimer-reconstructed substrate is 0.38 eV lower than that for the hollow site adsorption (unreconstructed substrate surface). Thus, while the repulsive adsorbate–adsorbate interaction is clearly present (it is smaller for the deeper-into-surface adsorbed Li), it does not represent the (only) driving force for the unusual adsorption of K at a low coordination site. As discussed below, the reconstruction represents a key factor, and this is largely due to an electronic (density of states, DOS) effect.

The theoretically identified adsorption sites of Li and K on the  $c(2 \times 2)$  structure of the W(001) surface are supported by our measurements of

<sup>1</sup>  $E_r$  is the total energy difference between the reconstructed and unreconstructed structures of the AM adsorbed surface.

<sup>2</sup> We calculate  $E_b$  ( $\sim 2\epsilon_b$ ) using the energy cost in breaking a single AM–W bond  $\epsilon_b = 0.29$  and 0.09 eV for Li and K, respectively, estimated at the on-top site where reconstruction is not allowed. The accuracy of our analysis is less than 0.05 eV.

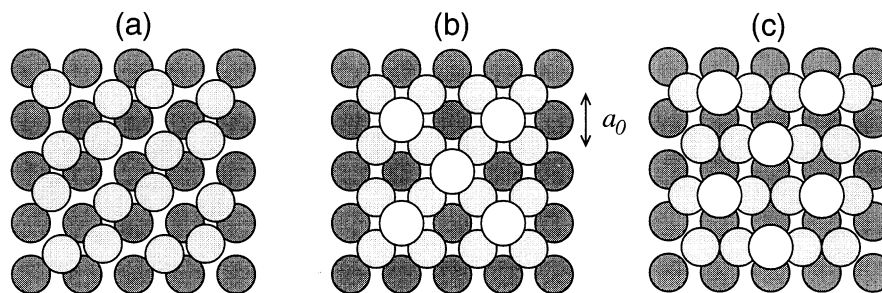


Fig. 3. Top view of: (a) the zigzag reconstructed clean W(001) and the AM/W(001) surface with adatoms (○); at (b) the fourfold hollow sites, (c) the twofold bridge sites. The gray scale of the atoms reflects their heights.

how  $\Delta T_c$  of the clean substrate reconstruction changes upon AM adsorption. Fig. 4 presents the results of our  $\Delta T_c$  measurements where (again) a remarkable difference between Li and K is evident. While adsorption of K increases  $T_c$  by as much as ca 60 K near 0.2 ML, adsorption of Li has nearly no effect. Roelofs et al. observed that the adsorption of oxygen decreases  $T_c$  while that of hydrogen increases it [19]. They argued that the two different atoms may affect  $T_c$  in the opposite way simply by occupying different sites, the hollow site and the bridge site for O and H, respectively. With the same argument the adsorption of K adatoms at the bridge site and Li adatoms at the hollow site explains the behavior of  $\Delta T_c(\theta)$  in Fig. 4.

We also performed DFT calculations for SCLS for the W 4f level, using the final-state theory of Pehlke and Scheffler [20]. The obtained SCLS

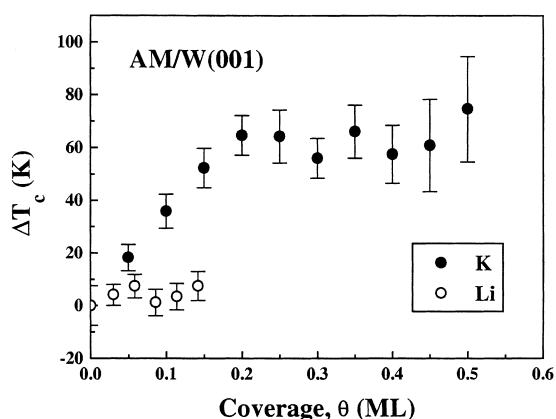


Fig. 4. The effects on  $T_c$  of the clean W(001) reconstruction by AM adsorption. Note the remarkable difference in  $\Delta T_c$  induced by Li and K.

from the surface W atoms was 228 meV for the Li adsorption at the hollow site, while it was only 29 meV for the K adsorption at the bridge site. These numbers agree well with our experimental results. The calculations also show that these shifts are much more sensitive to the reconstruction of surface W atoms than to the adsorbate–substrate interaction. Indeed the obtained SCLS for the K adsorption at the hollow site changed to 187 meV, thus, much more than that at the bridge site.

In Fig. 5, we present the typical behavior of the calculated projected DOS of the surface W atoms for the unreconstructed (Fig. 5a) and the recon-

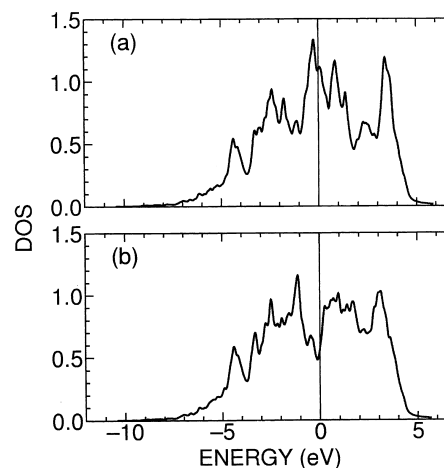


Fig. 5. Surface-W-atom projected DOS (states/eV-atom) for the (a) unreconstructed and (b) reconstructed K-covered W(001) surfaces. The K adatom adsorbs at the twofold bridge site. The corresponding DOS plots for Li at the bridge site also show similar features. The energy zero is set to be at the Fermi energy  $E_F$ . The muffin-tin radius of 2.25 bohr for W atoms is used in calculating the site-projected DOS.

structed (Fig. 5b)  $c(2 \times 2)$  structures of the AM (Li, K)-covered W(001) surface with the adatoms adsorbed at the bridge site. The most striking feature is a large DOS at  $E_F$  as found similarly for the unreconstructed clean W(001) surface [21]. This peak disappears as the surface reconstructs. Since the energy (at least the contribution from the electron kinetic energy) is lowered by eliminating the large DOS at  $E_F$ , the AM-induced dimer reconstruction at the bridge site may be driven primarily by the desire to lower the DOS at the Fermi level, similar to a Jahn–Teller-like or Kohn–anomaly-like instability and the general rule that poly-atomic systems tend to attain a geometry of high electronic hardness. This mechanism is also behind the fact that metals in the middle of the periodic table assume the bcc structure in difference to their neighbors which crystallize with fcc or hcp symmetry. In summary, significant differences between Li and K are observed both in the SCLS of the W  $4f_{7/2}$  peak and in changes of  $\Delta T_c$  of the clean  $c(2 \times 2)$  surface reconstruction. Our DFT calculations reveal that these differences arise essentially by the competition between the energies associated with the local AM–W bonding and the AM-induced surface reconstruction.

### Acknowledgements

The authors (Kim, Ahn, Chung) acknowledge the partial supports from BSRI 97-2440, the

Seo-Am Fund and KOSEF through the ASSRC at Yonsei University.

### References

- [1] J. Neugebauer, M. Scheffler, Phys. Rev. Lett. 71 (1993) 577.
- [2] R. Tosatti, in: E. Bertel, M. Donath (Eds.), Electronic Surface and Interface States on Metallic Systems, World Scientific, 1995, pp. 67–89, and references therein.
- [3] K.S. Shin et al., Surf. Sci. 385 (1997) L978.
- [4] M.K. Debe, D.A. King, Phys. Rev. Lett. 39 (1977) 708.
- [5] M.K. Debe, D.A. King, Surf. Sci. 81 (1979) 193.
- [6] T.E. Felter et al., Phys. Rev. Lett. 38 (1977) 1138.
- [7] I.K. Robinson et al., Phys. Rev. Lett. 62 (1989) 1294.
- [8] J.F. van der Veen et al., Phys. Rev. B 25 (1982) 7388.
- [9] J.J. Joyce et al., J. Electron Spectrosc. Relat. Phenom. 49 (1991) 31.
- [10] D.M. Riffe et al., Phys. Rev. Lett. 64 (1990) 571.
- [11] D.M. Riffe et al., Phys. Rev. B 49 (1994) 4834.
- [12] P. Soukiassian et al., Phys. Rev. B 31 (1985) 1341.
- [13] C. Stampfl, M. Scheffler, Surf. Rev. Lett. 2 (1995) 317.
- [14] D.M. Ceperley, B.J. Alder, Phys. Rev. Lett. 45 (1980) 566.
- [15] J.P. Perdew, A. Zunger, Phys. Rev. B 23 (1984) 5048.
- [16] X. Gonze et al., Phys. Rev. B 44 (1991) 8503.
- [17] M. Fuchs et al., Computer Phys. Commun (1999) in preparation.
- [18] A. Khein, Phys. Rev. B 51 (1995) 4105.
- [19] L.D. Roelofs et al., Phys. Rev. B 33 (1986) 6537.
- [20] E. Pehlke, M. Scheffler, Phys. Rev. Lett. 71 (1993) 2338.
- [21] D. Singh, S.-H. Wei, H. Krakauer, Phys. Rev. Lett. 57 (1986) 3292.