

Anomalous Decrease of the Work Function of a Carbide-modified W(110) Surface Induced by Hydrogen Chemisorption

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Electronic property of hydrogen adatoms on a carbide-modified W(110) surface, W(110)(15 × 3)R14°-C, was investigated by means of angle-resolved photoelectron spectroscopy. The work function of the surface decreases anomalously with hydrogen exposure. The hydrogen adatom polarizes positively due to bond formation with surface carbon atoms, resulting in the work-function decrease by as large as 1.0 ± 0.1 eV at saturation.

Electronic interaction between hydrogen and a metal surface has been of considerable interest because of its importance in the field of fuel cell technology, heterogeneous catalysis, and hydrogen storage. Surface scientists have investigated hydrogen-induced changes in the electronic properties of the metal surfaces.¹ The work function is one of the most important parameters that characterize the electronic property of the metal surface. The hydrogen chemisorption usually induces an increase in the work function of the metal surfaces.¹ Among numerous experimental data on the hydrogen-induced change in work function, there are only a few exceptional cases; the hydrogen chemisorption induces a decrease in work function of, e.g., Pt(111), Fe(110), and W(110) surfaces.²⁻⁵ However, the absolute values of the work-function change, $|\Delta\Phi|$, are small in these exceptional cases ($|\Delta\Phi| = 230, 95, \text{ and } 450 \text{ meV}$ for Pt(111), Fe(110), and W(110) surfaces, respectively).^{2,3,5} In this paper, we report that hydrogen induces a decrease in the work function of a carbide-modified W(110) surface, W(110)(15 × 3)R14°-C, with anomalously large $|\Delta\Phi|$, which was revealed by means of angle-resolved photoelectron spectroscopy (ARPES). The electronic state of hydrogen adatoms on the W(110)(15 × 3)R14°-C surface is discussed.

The details of the experimental apparatus have been described in our previous report.⁶ A W(110) single crystal was cleaned by heating to ca. 1500 K in 1×10^{-6} Pa of oxygen and subsequent flashing to ca. 2300 K in an ultra high vacuum (a base pressure of 2×10^{-8} Pa). The W(110) surface was exposed to 10 L (Langmuir, 1 L = 1.33×10^{-4} Pa·s) of ethylene at 300 K. After evacuation of ethylene, the sample was heated to ca. 1500 K. From the sample thus prepared, we observed a clear (15 × 3)R14° low-energy electron diffraction (LEED) pattern. An Auger electron spectroscopy study has reported that a carbon coverage of the (15 × 3)R14°-C surface is ca. 0.64 monolayer.⁷ The surface with hydrogen adsorbates was prepared by exposing the sample to H₂ gas at a temperature (T) of 120 ± 20 K. Gas exposures were estimated by an uncorrected ion gauge, which was placed 20 cm away from the sample.

ARPES measurements were performed at a vacuum ultraviolet beamline (BL-7B) of the Photon Factory, High Energy Accelerator Research Organization (KEK-PF), Japan.⁸ The spectra were measured at photon energies, $h\nu$, of 22 and 25 eV, and $T = 120 \pm 20$ K. Light-incident and electron-emission

angles were set at 45 and 0° (normal emission), respectively, from the surface normal. Electron binding energies are referred to the Fermi level, E_F . The energy and angle resolutions were estimated to be 0.15 eV and 2°, respectively, in the present experimental condition. We obtained the work function, Φ , of the sample by measuring the cutoff energy, E_{cutoff} , on the high-binding-energy side in the photoelectron spectrum, as follows; $\Phi = h\nu - E_{\text{cutoff}}$. The absolute work function has an uncertainty of ±0.2 eV mainly due to an uncertainty in the absolute photon energy. On the other hand, the work function obtained has a statistical error of ±2% or less, which was evaluated by repeating the measurements. In the present experimental setup, the work function of the clean W(110) surface was obtained to be 5.3 ± 0.2 eV. This value agrees well with that in a previous report.⁵

We determined the work function of the W(110)(15 × 3)R14°-C surface to be 5.2 ± 0.2 eV, which is almost the same as that of the clean W(110) surface. It decreases monotonically down to 4.2 ± 0.2 eV with the hydrogen exposure. Figure 1 shows the work-function change, $\Delta\Phi$, from that of the bare (15 × 3)R14°-C surface as a function of the hydrogen exposure along with the cutoff region of the photoelectron spectra at different hydrogen exposures. The saturation exposure at $T = 120 \pm 20$ K is found to be approximately 2500 L. In the simplest model, the work-function change is ascribed to an electronic polarization of the hydrogen adatoms. The work-function decrease implies that the hydrogen adatoms are polarized positively, so that a potential barrier for electron emission is lowered. Note that the $|\Delta\Phi|$ value at saturation is very large (1.0 ± 0.1 eV), compared with the Pt(111), Fe(110), and W(110) surfaces. Therefore, the polarization of the adatom at the (15 × 3)R14°-C surface is much larger than those at the pure metal surfaces. The ability of the (15 × 3)R14°-C surface to produce the hydrogen

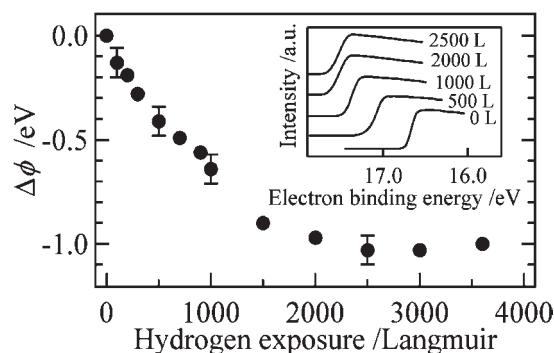


Figure 1. Work-function change from the W(110)(15 × 3)R14°-C surface as a function of hydrogen exposure. The data were taken at $T = 120$ K. Error bars indicate statistical errors. Inset: Cutoff region of the photoelectron spectra of the surface at different hydrogen exposures measured at the photon energy of 22 eV.

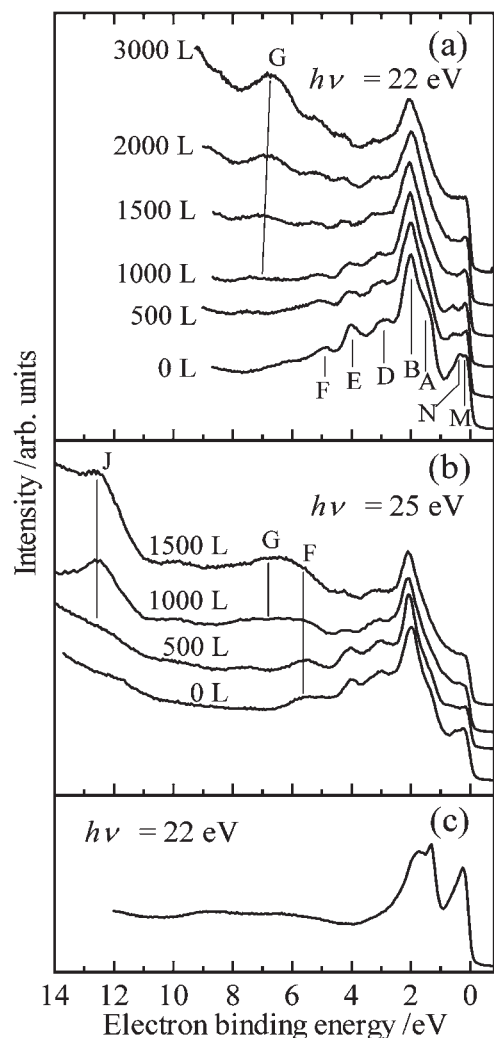


Figure 2. Panels (a) and (b): Angle-resolved photoelectron spectra of the W(110)(15 × 3)R14°-C surface measured at different hydrogen exposures. Panel (c): Angle-resolved photoelectron spectrum of the W(110) surface. The hydrogen exposures and the photon energies ($h\nu$) are given.

adatoms with large positive polarization will be useful in the field of fuel cell technology and heterogeneous catalysis.

Figure 2a shows the normal-emission photoelectron spectra of the W(110)(15 × 3)R14°-C surface at different hydrogen exposures ranging from 0 to 3000 L. In the spectrum at 0 L, seven spectral features are discernible at about 0.2, 0.4, 1.5, 2.0, 3.0, 4.0, and 5.0 eV (labeled as M, N, A, B, D, E, and F, respectively). Features M, A, and B are ascribed to electronic states of the W(110) substrate because they are also observed for the clean W(110) surface as shown in Figure 2c.⁹ Although features N, D, and F were not observed for the clean surface, they are ascribed to bulk bands of the W(110) substrate. Detailed study on the electronic structure of the (15 × 3)R14°-C surface indicates that these bulk bands appear in the spectrum of (15 × 3)R14°-C surface via the Umklapp process according to the carbon-induced (15 × 3)R14° periodicity of the surface lattice.¹⁰ On the other hand, feature E originates from an electronic state of the (15 × 3)R14°-C surface.¹⁰ The hydrogen chemisorption changes the spectral profile near E_F and derives a broad spectral feature in

the vicinity of 7.0 eV (labeled as G). These changes are generally observed for the hydrogen chemisorption on transition metals based on the electronic interaction between the H 1s orbital and metal d bands.¹ Feature G is ascribed to a so-called split-off state from the d bands.¹ The emergence of this split-off state indicates formation of W–H bonds at the carbide-modified surface. Figure 2b shows the photoelectron spectra measured at $h\nu = 25$ eV. The hydrogen-induced feature, G, is also discernible above 1000 L. Because of overlapping with bulk-band feature F, the peak position of feature G at 1500 L seemingly changes from ca. 7.0 eV at $h\nu = 22$ eV to ca. 6.5 eV at $h\nu = 25$ eV. In addition to feature G, the hydrogen chemisorption derives a broad feature in the vicinity of 12.5 eV (labeled as J). A photoelectron-spectroscopy study for ethylene adsorption on the W(110) surface shows that a C–H bond state is observed as a spectral feature at a binding energy of 11.2 eV.¹¹ Because this binding energy is close to that of feature J, we tentatively assigned feature J to an electronic state formed through interaction between the H 1s orbital and sp bands of surface carbon atoms. The present ARPES results indicate that the hydrogen adatoms make bonds with both the tungsten and carbon atoms on the surface. Because the electronegativity of carbon is relatively large (2.5), the bond formation with the carbon atoms is likely to induce the positive polarization of the hydrogen adatoms, resulting in the work-function decrease of the surface.¹²

Finally, we mention a structural change of the W(110)(15 × 3)R14°-C surface induced by the hydrogen chemisorption. It can contribute to the work-function change. The exposure of the surface to hydrogen did not change significantly the (15 × 3)R14° LEED pattern. Although the significant changes in the photoelectron spectrum are induced by the exposure, they are attributed to the electronic interaction between the hydrogen adatom and the surface atoms as described above. These results indicate that the hydrogen chemisorption does not change the geometric structure. Therefore, the work-function change is solely ascribed to the electronic interaction.

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