

Dynamics of very low energy photoelectrons interacting with image charge of Cs/Cu(111) surface

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We have measured the very low energy photoelectron spectra of Cs-covered Cu(111) surfaces, and determined the mechanism for the appearance of a spike structure due to the interaction of emitted electron with its image charge. At high Cs coverage of 0.10 and 0.14 monolayers (ML), the spike structure appeared at the vacuum level. No such structure was found at low coverage of 0.06 ML. The vacuum level at high coverage lies in the energy gap at the $\bar{\Gamma}$ point in the surface Brillouin zone of the Cu(111) surface, while it lies outside the energy gap at low coverage. These results confirm the validity of our proposed mechanism that the spike structure appears when the vacuum level lies in the energy gap.

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I. INTRODUCTION

Recently we found that a spike structure arising from the energy loss of the photoelectron by interaction with its image charge appears at the vacuum level in very low energy photoelectron spectra.¹⁻³ This spike structure was observed in the Cu(001) and Ag(001) spectra, but not in the Cu(110) and Cu(111) spectra. On the basis of these results we described the dynamics of very low energy photoelectrons near the solid surface as follows. Since the wave vector parallel to the surface k_{\parallel} of the photoelectron excited by a low energy photon is very small, we focus on the electrons at the $\bar{\Gamma}$ point in the surface Brillouin zone. The photoelectron emitted into vacuum can lose energy down to zero kinetic energy (i.e., the energy position of the vacuum level) by interacting with its image charge. The photoelectron can return to the bulk if bulk states (at the $\bar{\Gamma}$ point) are available at the vacuum level. On the other hand, if the vacuum level lies in the energy gap at the $\bar{\Gamma}$ point, the photoelectron that lost energy cannot return to the bulk, and hence the electron population builds up at the vacuum level. Consequently such photoelectrons are collected by the detector and form the spike structure at the vacuum level in the spectra. From the above consideration we proposed a mechanism that the spike structure appears when the vacuum level lies in the energy gap at the $\bar{\Gamma}$ point.

In this paper we demonstrate this mechanism by measuring the photoelectron spectra by varying the energy position of the vacuum level relative to the energy gap. It is widely known that the Cs adsorption on a metal surface leads to a considerable decrease in the work function.⁴⁻⁶ The band structures of the Cu(111) and its Cs-covered surfaces have been well studied theoretically and experimentally.⁶⁻²⁰ For these reasons we have chosen the Cs/Cu(111) surface as a test case. The clean Cu(111) surface has a projected band gap at the $\bar{\Gamma}$ point extending between -0.92 and 4.12 eV relative to the Fermi level (E_F) as shown in Fig. 1.^{7,8} The shaded areas and the dotted line indicate the projected bulk band and a surface state at the $\bar{\Gamma}$ point, respectively. The surface state

lies at ~ 0.4 eV below E_F .⁹ The vacuum level ϕ of the clean Cu(111) surface lies at ~ 4.9 eV,⁹ which is above the upper edge of the band gap. When this surface is covered by Cs, the vacuum level shifts to lower energy with Cs coverage θ [we have defined θ to be 1 monolayer (ML) for a close packed $p(2 \times 2)$ Cs overlayer], reaching ~ 1.5 eV at $\theta=0.5$ ML.⁶ From this coverage dependence of the vacuum level relative to the energy gap, one can expect that the vacuum level of the Cs/Cu(111) surface moves into the energy gap above a certain coverage. Thus if the proposed mechanism is correct, the spike structure should appear in the spectra of the Cs/Cu(111) surface when the vacuum level moves into the energy gap. We have verified this effect in the present experiment.

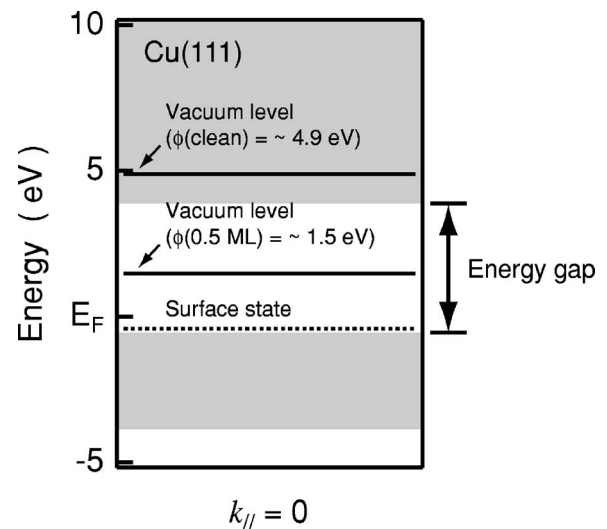


FIG. 1. Projected band structure at the $\bar{\Gamma}$ point of the Cu(111) surface. The shaded areas and the dotted line indicate the projected bulk band and the surface state at the $\bar{\Gamma}$ point, respectively. The vacuum levels ϕ of the clean Cu(111) surface and the 0.5 ML Cs/Cu(111) surface are also shown.

II. EXPERIMENTAL

The sample was set in an ultra-high vacuum chamber with a pressure of $\sim 5 \times 10^{-11}$ mbar. The Cu(111) surface was cleaned by repeated cycles of Ar ion sputtering (600 V, $\sim 1.7 \mu\text{A}$, 1 h) and annealing (690 K, 1 h). The cleanliness and flatness of the surface was confirmed by the sharp spots in the low energy electron diffraction image. The Cs atoms were evaporated onto the Cu(111) surface at room temperature by resistive heating (6.5 A, ~ 2.0 V) of a Cs evaporation source located in front of the surface. The pressure during evaporation was $\sim 7 \times 10^{-11}$ mbar. The Cs coverage θ was obtained by comparing the change of the work function ($\Delta\phi$) measured from the photoelectron spectra with the $\phi(\theta)$ curve reported in the literature.⁶ The typical evaporation rate was 0.01 ML/min.

The experimental configuration of the very low energy photoelectron spectroscopy has been described elsewhere,¹⁻³ and we describe here only the main components. The photon energy of the incident laser beam was tuned by using a picosecond Ti:sapphire laser in combination with second and third harmonic generation crystals. The pulse width and the repetition rate of the laser beam were 2 ps and 82 MHz, respectively. The *p*-polarized laser beam was shined on the sample surface with a spot diameter of $\sim 100 \mu\text{m}$ and with intensity of $\sim 2 \mu\text{W-cw}$ equivalent.

The photoelectrons emitted normal to the sample surface were analyzed by a hemispherical electron energy analyzer. The pass energy and the acceptance angle of the analyzer were set at 0.5 eV and 1° around the surface normal, respectively. To minimize spectral distortion due to stray electric and magnetic fields, and to collect the very low energy photoelectrons effectively, a bias voltage of -7.0 V was applied to the sample with the analyzer entrance hole grounded. We have confirmed that there is no bias voltage dependence of the spectra up to -10 V. Under these experimental arrangements the resolution of the analyzer was 6 meV. The spectral distortion due to the nonlinear (multiphoton) effect²⁰⁻²² and the space charge effect²³ was not observed.

III. RESULTS AND DISCUSSION

Figure 2 shows the very low energy photoelectron spectra of Cs/Cu(111) surfaces at three different Cs coverages. The vertical axis is the photoelectron intensity normalized by the cw-equivalent laser power and the photon energy. The horizontal axis is the final state energy, which is the energy of the photoelectron relative to E_F . The sample temperature was kept at 97 K. The upper and lower cutoff energies coincide with the photon energy and the work function, respectively. The work function is 4.146, 3.702, and 3.368 eV, and the Cs coverage estimated from the work function is respectively 0.06, 0.10, and 0.14 ML. The peaks marked with an arrow correspond to the surface state of the Cu(111) surface,^{6,10,19} and are shifted to the lower energy as the Cs coverage increases. This energy shift is caused by the increase of the occupancy of the surface band as a result of the electrons transferred from Cs atoms.^{10,11} The inset shows the enlarged view of the spectra very close to the vacuum level. At high

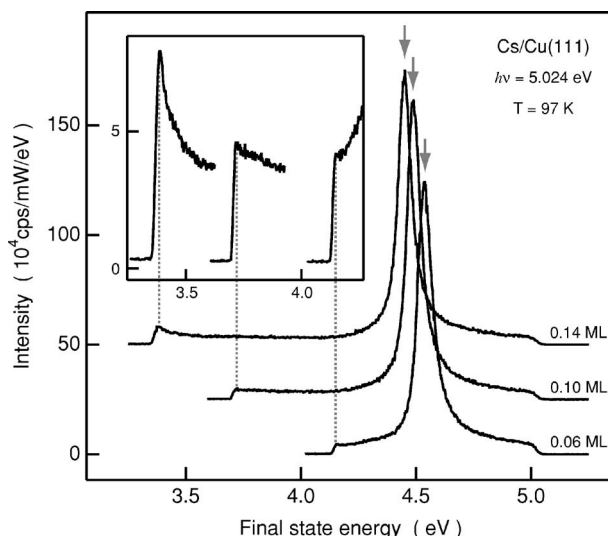


FIG. 2. Very low energy photoelectron spectra of Cs/Cu(111) surfaces taken at the photon energy of 5.024 eV. The peaks marked with arrows correspond to the surface state of the Cu(111) surface. The inset shows the enlarged view of each spectrum around the vacuum level.

coverages of 0.10 and 0.14 ML we see a spike structure at the vacuum level in the spectra, while no such structure exists in the spectrum at low coverage of 0.06 ML.

Now let us examine the relative position between the energy gap and the vacuum level at each coverage. Figure 3 shows the details of the projected band structure at the $\bar{\Gamma}$ point described in Fig. 1 and the location of the vacuum level for each Cs coverage. The vacuum level lies below the upper edge of the band gap at high coverages. On the other hand, it lies above the upper edge of the band gap at low coverage. In other words the vacuum level lies in the energy gap at high coverages, while it lies out of the energy gap at low coverage. For the spike structure to appear, the vacuum level must lie in the energy gap according to our proposed mechanism.

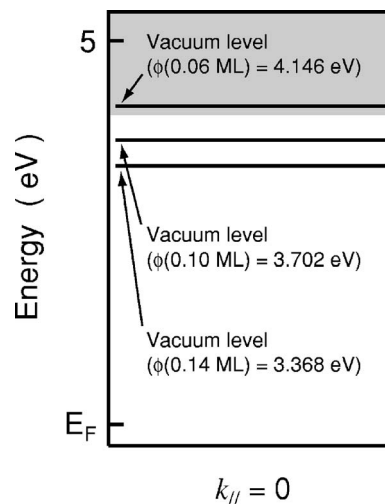


FIG. 3. Projected bulk band at the $\bar{\Gamma}$ point described in Fig. 1 and the location of the vacuum level ϕ for each Cs coverage. Note that the vacuum level at high coverages lies in the energy gap.

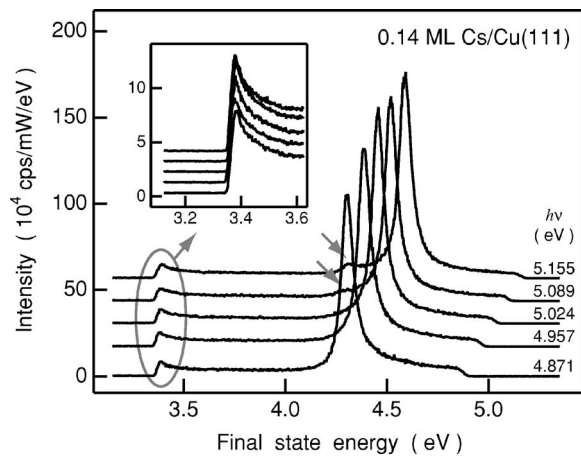


FIG. 4. Photon energy dependence of very low energy photoelectron spectra of 0.14 ML Cs/Cu(111) surfaces. The inset shows the enlarged view of each spectrum around the vacuum level.

Thus the spike structure should appear only in the spectra at high Cs coverages, which we see in the present experimental results.

Next we want to show that the appearance of the spike structure is independent of the incident photon energy. Figure 4 shows the photon energy dependence of the very low energy photoelectron spectra at $\theta=0.14$ ML. The small peaks marked with an arrow originate from bulk band transitions,¹⁰ not from the energy loss of photoelectrons by interaction with the image charge discussed here. As seen in the inset, the appearance of the spike structure does not depend on the photon energy, and neither does the spectral line shape of the spike structure. Although the photon energy dependence of

the spike structure at $\theta=0.10$ ML is not presented here, it is identical to that at $\theta=0.14$ ML. In addition the spike structure is not found in the spectra at $\theta=0.06$ ML taken at various photon energies. Thus we conclude that the spike structure appeared in the spectra because the vacuum level was moved into the energy gap by Cs adsorption. The present results directly demonstrate our proposed mechanism for the appearance of the spike structure.

The spike structure is more pronounced for $\theta=0.14$ ML than for $\theta=0.10$ ML. A possible explanation of this feature is that the photoelectrons are less probable to return into the bulk at $\theta=0.14$ ML, because the vacuum level lies further down in the energy gap at $\theta=0.14$ ML than at $\theta=0.10$ ML. To arrive at a definitive conclusion, measurement of the very low energy photoelectron spectra of Cs/Cu(111) surface with higher Cs coverage is needed in the future.

IV. CONCLUSION

We have performed very low energy photoelectron spectroscopy of the Cs-adsorbed Cu(111) surface. The spike structure arising from the energy loss of photoelectrons by interaction with the image charge was found at the vacuum level in the spectra for $\theta=0.10$ and 0.14 ML, and not for $\theta=0.06$ ML. This coverage dependence confirms our proposed mechanism that the spike structure appears when the vacuum level lies in the energy gap at the $\bar{\Gamma}$ point.

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- ¹R. Arafune, K. Hayashi, S. Ueda, and S. Ushioda, Phys. Rev. Lett. **92**, 247601 (2004).
- ²K. Hayashi, R. Arafune, S. Ueda, and S. Ushioda, Appl. Surf. Sci. **237**, 296 (2004).
- ³R. Arafune, K. Hayashi, S. Ueda, Y. Uehara, and S. Ushioda (unpublished).
- ⁴J. P. Muscat and D. M. Newns, Prog. Surf. Sci. **9**, 1 (1978).
- ⁵N. D. Lang, in *Theory of the Inhomogeneous Electron Gas*, edited by S. Lundqvist and N. H. March (Plenum, New York, 1983).
- ⁶S. Å. Lindgren and L. Walldén, Solid State Commun. **25**, 13 (1978).
- ⁷J. A. Knapp, F. J. Himpsel, A. R. Williams, and D. E. Eastman, Phys. Rev. B **19**, 2844 (1979).
- ⁸E. Knoesel, A. Hotzel, and M. Wolf, J. Electron Spectrosc. Relat. Phenom. **88-91**, 577 (1998).
- ⁹R. Courths and S. Hüfner, Phys. Rep. **112**, 53 (1984), and the references therein.
- ¹⁰S. Å. Lindgren and L. Walldén, Solid State Commun. **28**, 283 (1978).
- ¹¹P. Ahlqvist, Solid State Commun. **31**, 1029 (1979).

- ¹²S. Å. Lindgren and L. Walldén, Phys. Rev. Lett. **43**, 460 (1979).
- ¹³J. P. Muscat and D. M. Newns, Surf. Sci. **84**, 262 (1979).
- ¹⁴R. Dudde and B. Reihl, Surf. Sci. **287-288**, 614 (1993).
- ¹⁵N. Fischer, S. Schuppler, T. Fauster, and W. Steinmann, Surf. Sci. **314**, 89 (1994).
- ¹⁶M. Bauer, S. Pawlik, and M. Aeschlimann, Phys. Rev. B **55**, 10040 (1997).
- ¹⁷D. A. Arena, F. G. Curti, and R. A. Bartynski, Phys. Rev. B **56**, 15404 (1997).
- ¹⁸S. Ogawa, H. Nagano, and H. Petek, Phys. Rev. Lett. **82**, 1931 (1999).
- ¹⁹H. Petek, M. J. Weida, H. Nagano, and S. Ogawa, Surf. Sci. **451**, 22 (2000).
- ²⁰H. Petek, M. J. Weida, H. Nagano, and S. Ogawa, Science **288**, 1402 (2000).
- ²¹U. Höfer, I. L. Shumay, Ch. Reuß, U. Thomann, W. Wallauer, and Th. Fauster, Science **277**, 1480 (1997).
- ²²M. Aeschlimann, C. A. Schmuttenmaer, H. E. Elsayed-Ali, R. J. D. Miller, J. Cao, Y. Gao, and D. A. Mantell, J. Chem. Phys. **102**, 8606 (1995).
- ²³D. W. Juenker, J. Appl. Phys. **28**, 1398 (1957).