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Three Surface Resonances on the (100) Face of W and Mo: An Angle-Resolved Synchrotron Photoemission Study

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We have studied the surface resonances on Mo(100) and W(100) with angle-resolved, $\hbar\omega$-dependent photoemission using synchrotron radiation. For normal emission, two resonances are seen. They are located 0.3 and 3.3 (0.4 and 4.2) eV below E_F for Mo (W). The high-lying resonance remains symmetric and narrow for all photon energies used. Its intensity peaks at $\hbar\omega = 15$ and 30 (14 and 29) eV for Mo (W). For $\theta \geq 2°$, a second high-lying resonance appears a few tenths of an eV below the first one. Many-body phenomena are not required to explain the data.

To explain the surface resonances observed in our field-emission measurements[1] of Mo(100), we have recently presented a parametrized linear-combination-of-atomic-orbitals calculation[1,2] of the $\vec{k}_{\parallel}$- and orbital-resolved surface local density of states. We noted that this calculation could also serve as a theoretical basis for most of the previous angle-resolved photoemission studies of this resonance feature on W(100).[3] However, recent photoemission studies of this resonance on both W(100)[4,5] and Mo(100)[6] seem to have generated considerable confusion and debate regarding the origin and characteristics of these surface resonances as well as the applicability[6] of our tight-binding Green's-function calculation.[1]

In this Letter, we report on angle-resolved photon-energy–dependent photoemission studies of W(100) and Mo(100) using synchrotron radiation. Our results on both metals are in sharp contrast to the previous reports by Egelhoff, Linnett, and Perry,[4] by Feuerbacher and Willis,[5] and by Noguera *et al.*[6]; and, considering the simplicity of the model, in amazingly good agreement with our calculation.[1] First, we find that for normal emission, the well-known high-lying resonance[7,8] remains symmetric and sharp for $\hbar\omega$ between 10 and 40 eV. The peak width of this resonance is nearly identical with the width observed in a field-emission energy distribution.[1,7,8] Second, we find that, for emission angles θ greater than 2°, a second high-lying surface resonance appears just a few tenths of an eV below the first one, as predicted in our previous paper.[1] Third, our measurements confirm the existence of a low-lying surface resonance on both metal surfaces.[1,9,10] Fourth, the overall dispersion of these resonances within the surface Brillouin sone (SBZ) is compatible with our $\vec{k}_{\parallel}$-resolved calculation.[1,2] Fifth, we find that it is not necessary to invoke many-body phenomena to explain the photoemission from these resonances.

Angle-resolved photoemission spectra were obtained at the 240-MeV storage ring at the Synchrotron Radiation Center of the University of Wisconsin using the same analyzer as recently used by Allyn, Gustafsson, and Plummer.[11,12] The analyzer has an acceptance of $\pm 2°$ and is independently rotatable around two orthogonal axes.[12] Its resolution is ≥ 0.12 eV.

In order for us to identify a peak in a photoemission energy distribution as a surface state/resonance, we feel that four criteria have to be fulfilled: (1) It should be sensitive to contamination. (2) Its energy position should be independent of the photon energy. (3) It should be consistent with (our) angle-integrated photoemission results.[9] (4) It should be consistent with (our)

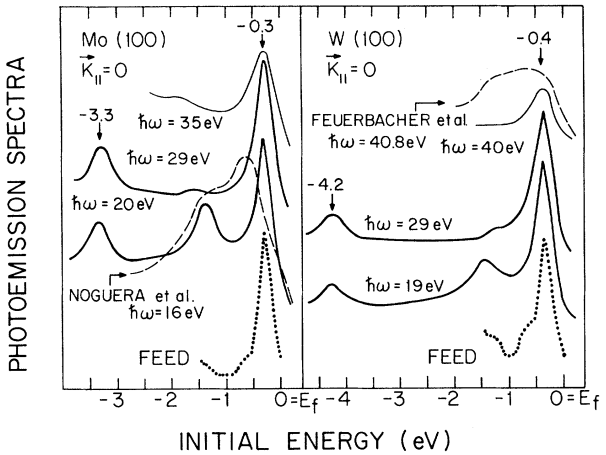

FIG. 1. Angle-resolved photoemission spectra of Mo(100) and W(100) at $\theta = 0°$ (normal exit) with use of synchrotron radiation. The angle of incidence was 45° (p-polarization). Dotted lines are the enhancement factors of the field-emission spectra of Mo(100) and W(100). The two peaks indicated by the arrows are the high-lying and low-lying resonances. Dashed lines are some earlier photoemission data from Refs. 5 and 6.

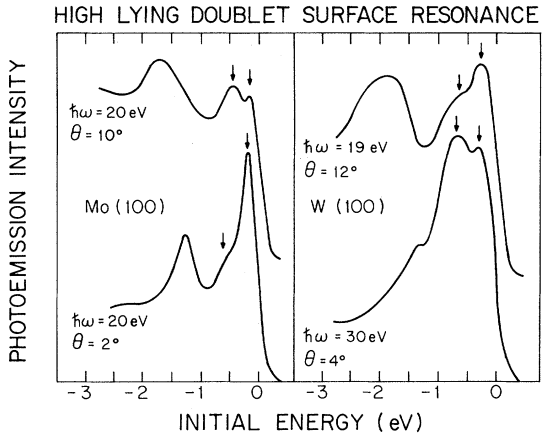

FIG. 2. Angle-resolved photoemission spectra of Mo(100) and W(100) for $\vec{k}_{\parallel} \neq 0$. The p-polarized light was incident at 45°. θ is the collection angle measured from the normal. All data refer to the plane perpendicular to the plane of incidence. The two peaks indicated by the arrows are the two high-lying resonances.

calculation.

For normal emission, the high-lying resonance[13] is a symmetric sharp peak for all the photon energies used. Figure 1 shows this fact for several photon energies. We find that not only the peak shape remains symmetric, but also that the peak width remains quite small (≤ 0.5 eV) for all photon energies between 10 and 40 eV.[14] At $\hbar\omega = 20$ eV, the peak width of this resonance [0.25 (0.4) eV for Mo (W)] is nearly identical with the width observed in a field-emission spectrum (0.2 eV for Mo[1] and 0.35 eV for W[8]). There is thus no discrepancy[5,6] as far as the peak width is concerned between the normal photoemission data and field emission (Fig. 1). Our results are in sharp contrast to the reports by Feuerbacher and Willis[5] and by Noguera *et al.*[6] concerning either the peak shape or the peak width.

For emission angles greater than 2°, we find that a second high-lying resonance appears just a few tenths of an eV below the first one (Fig. 2). The energy splitting of these two resonances is about 0.3 (0.5) eV for Mo (W). We wish to stress that the observation of the second high-lying resonance is extremely sensitive to the detection angle. We find that, in order to observe a single symmetric surface resonance, the detector has to be aligned with the normal to within 1°. An analyzer with a larger acceptance than ours, or an incorrectly aligned one, would thus give an asymmetric peak shape. As the photon energy increases, the analyzer will integrate over states of larger $\vec{k}_{\parallel}$. The apparent peak width should then increase with such an analyzer. Even for an angle as small as 2° off the normal, the second resonance appears as a shoulder.[15] As the angle increases, the second resonance increases its intensity, and the first resonance decreases its intensity. Around $k_{\parallel} = 0.3$ Å^{-1}, the second resonance has a higher amplitude than the first one. These observations suggest that the asymmetric broad peak at $\theta = 0°$ as reported by others[5,6] is due to neither time-dependent relaxation[5] nor d-band–edge effects,[6] but rather to differences in analyzer resolution and/or alignment.

The existence of these double high-lying resonances at $\theta \geq 2°$ has indeed been predicted in our previous paper (see Fig. 5 of Ref. 1). However, our calculation, as well as other nonrelativistic calculations,[16] cannot explain the existence of a single symmetric high-lying resonance in the normal direction for unrelaxed surfaces.[17] This fact suggests that the single high-lying surface resonance may be due to relativistic effects.[18] We believe that our calculation is applicable to finite $\vec{k}_{\parallel}$ since the relativistic and nonrelativistic band structures do not differ very much at these finite-$\vec{k}_{\parallel}$ points.

The photoionization cross section[19] of this single high-lying surface resonance (at $\vec{k}_{\parallel} = 0$) is a strong function of photon energy. It exhibits peaks at 14, 29 (15, 30, and 38) eV for W (Mo)

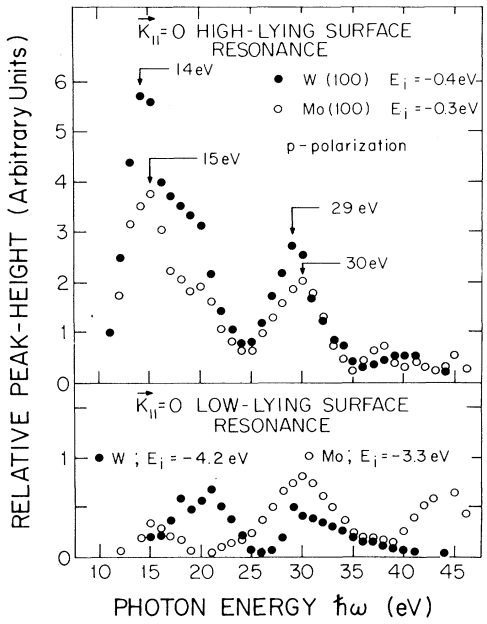

FIG. 3. The photoionization cross section of the high-lying and low-lying resonances at $\vec{k}_{\parallel} = 0$ as a function of photon energy.

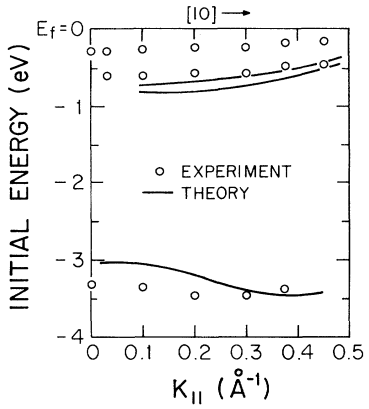

FIG. 4. The dispersion of the three resonances as a function of $k_{\parallel}$ along the [10] direction of Mo(100).

(Fig. 3). (We will refer to these peaks as "photoresonances".) Considering the differences in collection geometry, our results are in satisfactory agreement with the early data by Waclawski and Plummer.[20] The spectra of secondary electrons obtained at higher photon energies show structure at kinetic energies corresponding to the structure in the cross section for the high-lying resonance at $\theta = 0°$. We believe hence that this structure in the cross section of the resonance is due to final-state effects.

Our observations of these $\hbar\omega$-dependent photoionization cross sections are in direct conflict with the report by Egelhoff, Linnett, and Perry[4] who have suggested that excitation from this resonance will be quenched by plasma interaction when the photon energy is above the plasma energy (about 23 eV for W).

In addition to these high-lying surface resonances, we have also confirmed the existence[1,9,10] of a low-lying surface resonance on both metals. In the normal direction, this low-lying resonance is located at 3.3 (4.2) eV below E_F for Mo (W) (see Fig. 1).

The dispersion of these resonances is compatible with our calculation (Fig. 4). The agreement between our nonrelativistic calculation and experiment suggests that many-body phenomena are not involved in photoemission from these resonances, as has been previously suggested,[5] and that relativistic effects are not important for the interpretation of these resonances except close to $\bar{\Gamma}$.

Theoretically, our calculation[1,2] shows the origin of these surface resonances at finite $\vec{k}_{\parallel}$ to be as follows: (1) The high-lying double surface resonances, existing primarily in the region 0.1 Å^{-1} $< k_{\parallel} <$ 0.6 Å^{-1} of the SBZ, is made up of d_{zx}, $d_{x^2-y^2}$, and s orbitals[21]; and is located inside a hybridization gap which is related to the crossover of Δ_2 and Δ_5 bands at $\bar{\Gamma}$. (2) The low-lying surface resonance, existing mainly in the region $k_{\parallel} < 0.5$ Å^{-1} of the SBZ, is composed of d_{z^2}, s, and p_z orbitals; and is located inside the sp-d hybridization gap.[22]

In summary, two conclusions are reported: (1) For normal emission ($\theta = 0$), there are two occupied resonances. The high-lying resonance remains symmetric for all the photon energies used. Its peak width is nearly identical with the width observed in a field-emission spectrum. Its existence may be due to relativistic effects. Moreover, many-body phenomena are not important, since there is no evidence for time-dependent relaxation or plasma interaction. (2) For $\theta \geq 2°$, there are three occupied resonances, namely two high-lying resonances and one low-lying resonance. Their existence can be well explained by our nonrelativistic $\vec{k}_{\parallel}$-resolved calculation.[1,2] The agreement between theory and experiment suggests that relativistic effects may not be important for the interpretation of these resonances except close to $\bar{\Gamma}$.

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[14]The monochromator was operated with constant wavelength resolution. This explains the slight increase in width of the higher-photon-energy spectrum.

[15]The data tend to suggest that the second resonance disappears and does not merge into the first resonance as θ goes to zero.

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[21]One can most probably not extrapolate this orbital decomposition to $\vec{k}_{\parallel}=0$. As J. Hermanson [Solid State Commun. 22, 9 (1977)], has pointed out the angle-of-incidence dependence of the $\vec{k}_{\parallel}=0$ structure would be inconsistent with such a symmetry.

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