

# Surface photoemission spectra of the Ba–W(110) system

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The energy spectrum of surface states in the Ba–W(110) system has been studied for the first time through measurements of spectra of the threshold photoemission with *s*- and *p*-polarized excited light. Two surface states induced by a submonolayer Ba film were observed near the Fermi level.

As an interface forms between a metal substrate and a film, the redistribution of the electron density in the joining region occurs primarily by virtue of valence electrons of the adatoms and surface states of the substrate. For this reason, we would expect the primary changes in the energy spectrum of the surface states, such as the shift and disappearance of intrinsic surface states of the substrate and the formation of new states induced by the film, to occur near the Fermi level  $E_F$ . Indeed, experiments on metal single crystals with submonolayer coatings of alkali metals<sup>1–3</sup> have shown that a single induced surface state, with a binding energy of 0.1–0.3 eV, forms for each of the adsorbates.

A method of optical spectroscopy of the threshold photoemission current was proposed in Ref. 2 for seeking and studying surface states near  $E_F$ . That method is far more sensitive in the detection of surface states than the customary methods of photoemission spectroscopy during high-energy x-ray and UV excitations. One feature of this new method is that one can spectrally select photoemission from surface states, which may be more intense than emission from the interior by more than an order of magnitude.

This letter reports the first study of the surface photoemission of the Ba–W(110) system over a wide range of submonolayer coverages  $\theta$  (a monolayer corresponds to the value  $\theta = 1$ ). The spectrum of surface states observed near the Fermi level has a complex structure, including one intrinsic surface state of the substrate and two surface states induced by the barium coating.

The experiments were carried out in ultrahigh vacuum, at  $P \sim 1 \times 10^{-10}$  torr. Atomically pure Ba was deposited on a clean surface of a W(110) single crystal to various surface concentrations. The degree of coverage was in the interval  $0.2 \leq \theta \leq 1.0$ . The conditions for preparing the surface of the sample and for determining the degree of submonolayer coverage by Ba are described in Ref. 4. Polarized monochromatic light ( $\Delta\lambda = 4$  nm) was incident on the crystal at an angle  $\gamma = 45^\circ$ . We recorded spectra of the integrated threshold photoemission current  $I_s(\lambda)$  and  $I_p(\lambda)$  for respectively *s*- and *p*-polarized exciting light, using the method of Ref. 2.

Figure 1 shows experimental spectra  $I_s(\lambda)$  and  $I_p(\lambda)$  for a submonolayer cover-

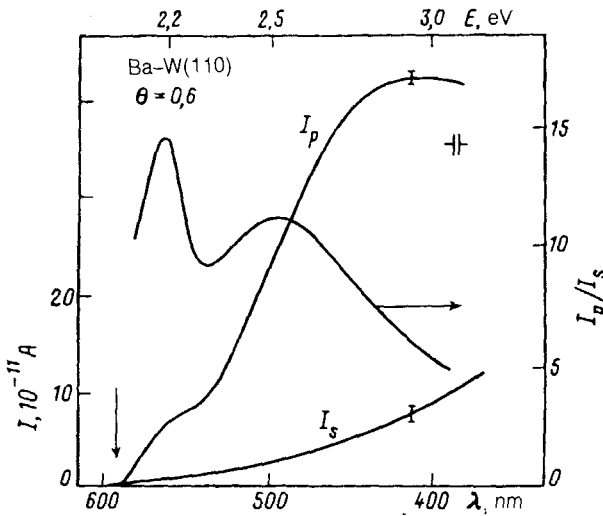


FIG. 1. Spectra of the photoemission current,  $I_s(\lambda)$  and  $I_p(\lambda)$ , during excitation by  $s$ - and  $p$ -polarized light, respectively, along with a spectrum of the surface photoemission  $I_p/I_s$  of the Ba-W(110) system in the case of a submonolayer coating,  $\theta = 0.6$ . The arrow shows the red boundary for the photoelectric effect.

age  $\theta = 0.60$ . The arrow marks the red boundary for the photoelectric effect, which corresponds to the position of the Fermi level in the case of metals. The photoemission  $I_s(h\nu)$  can be described quite accurately by the standard Fowler law<sup>5</sup>  $I \propto (h\nu - \phi)^2$ , where  $\phi$  is the work function ( $\phi = E_F - E_{\text{vac}}$ ; here  $E_{\text{vac}} = 0$ , and the positive direction of the energy axis is toward the valence band). This photoemission is associated with the excitation of bulk electronic states in the periodic potential of the lattice. For the case of the  $p$ -polarized light, the spectrum  $I_p(h\nu)$  is a superposition of bulk and surface photoemission, which is associated with the excitation of surface electronic states by the normal component of the electric vector of the  $p$ -polarized light.<sup>2</sup> As was shown in Ref. 2, a joint study of  $I_p(h\nu)$  and  $I_s(h\nu)$  reveals the spectrum of the surface photoemission, which is equal to the ratio  $I_p/I_s$ . In the case of a coverage  $\theta = 0.60$ , the surface-photoemission spectrum has two peaks, at  $h\nu_{\text{max}} = 2.17$  eV and  $h\nu_{\text{max}} = 2.50$  eV. Theoretical predictions show that the position of the peak in the  $I_p/I_s$  spectrum coincides quite accurately (within  $\sim 0.03$  eV) with the energy position (with respect to the vacuum level) of the peak in the local density of states in the surface band. It is thus a simple matter to determine the binding energy of the surface band:  $E = h\nu_{\text{max}} - E_F$ . For the given Ba coverage, there are two surface bands, with binding energies  $E_B = 0.09$  and  $E_C = 0.42$  eV.

A study of the surface-photoemission spectrum of the Ba-W(110) system over a wide range of submonolayer coverages reveals different stages in the formation and modification of the surface bands. Figure 2 shows that in the case of a thin coating ( $\theta < 0.40$ ) there is a peak  $A$  which corresponds to photoemission from intrinsic surface states of W(110). The behavior of this peak with increasing  $\theta$  correlates well with the data of Ref. 2 on the increase in the binding energy of an intrinsic surface state of

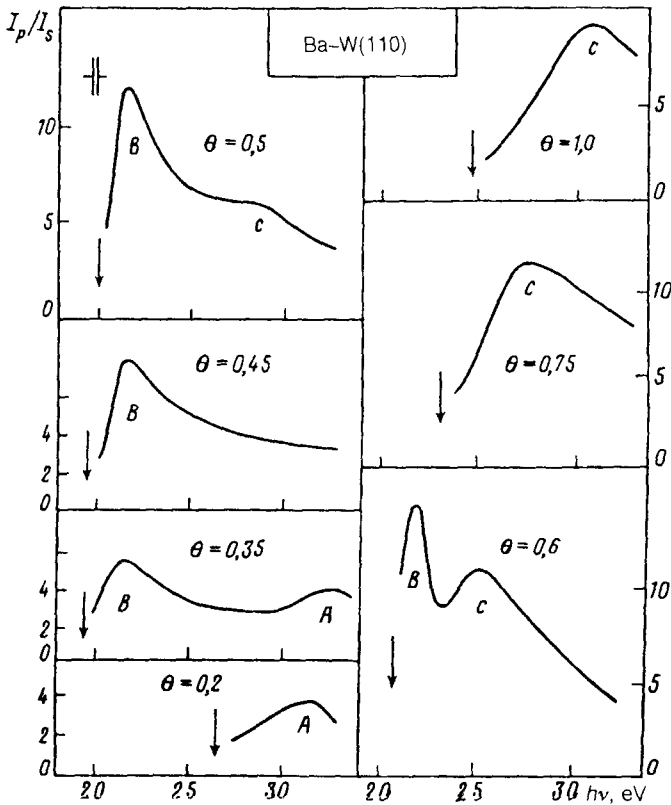


FIG. 2. Spectra of the surface photoemission  $I_p/I_s$  of the Ba-W(110) system for various submonolayer Ba coverages. The arrows show the values of the work function  $\phi$ .

W(110) upon the adsorption of Cs. An increase in the surface concentration of Ba gives rise to a peak *B* in the immediate vicinity of  $E_F$ . The interval in which this surface state exists is  $0.30 < \theta < 0.65$ . At  $\theta > 0.65$ , surface band *B* intersects the Fermi level and becomes inactive in the photoemission. The most interesting case is in the interval of coverages  $0.50 \leq \theta \leq 0.65$ , in which two peaks, *B* and *C*, are seen simultaneously in the surface-photoemission spectrum. These peaks correspond to two induced surface bands. With a further increase in the degree of coverage ( $\theta > 0.70$ ), a single surface band remains in the spectrum. Its binding energy increases to the value  $E_C = 0.75$  eV at a monolayer coverage.

These results thus demonstrate the complex evolution of the spectrum of surface states in an interval of submonolayer barium coatings. These results provide evidence that several excited *s-p-d*-electronic states of the Ba adatom participate in forming the interface. The modification of the surface-photoemission spectrum indicates large changes in the local density of surface states as the barium film grows. In particular, there is a sharp increase in the local density of surface states near the Fermi level at the

value  $\theta = 0.60$ , and there is an equally sharp decrease at barium coverages close to a monolayer.

A two-band structure of induced surface states has been detected for the first time at submonolayer Ba coverages. Corresponding studies<sup>1-3</sup> involving the adsorption of alkali metals show that only a single filled surface band forms at submonolayer coverages. Calculations of the local density of electronic states of the Ba-W(110) system for  $\theta = 0.4-0.8$  (Ref. 4), for a Ba monolayer on W(100) (Ref. 6), and for an isolated Ba monolayer (Ref. 7) indicate that there is again a single peak in the density of *ds*-hybridized states. The binding energy of this band has been found to be  $E \sim 0.8$  eV. This figure agrees well with the result we found on band C ( $\theta = 1$ ). A theory for the threshold photoemission incorporating the surface band shows that the shape of the peak in the surface photoemission  $I_p/I_s$ , especially the shape of the high-energy decay, contains information on the nature of the hybridization of surface states.<sup>2</sup> Since the shape of peak C in the spectrum (Fig. 2) varies only slightly with the degree of coverage, it can be suggested that the hybridization of this band remains a *ds* hybridization over the entire range of submonolayer coverages in which it is observed. The qualitative difference between the high-energy decays of peaks B and C in the experimental spectra (Fig. 2) indicates that there is a difference in the nature of the hybridization of the corresponding bands. On the basis of the electronic structure of the adsorbed barium atoms, we believe that a *dp* hybridization is most likely for band B.

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