

Electronic surface states of submonolayer Cs films on W (110) and (100) faces

G. V. Benemanskaya and M. N. Lapushkin

A. F. Ioffe Physicotechnical Institute, Academy of Sciences of the USSR, Leningrad

(Submitted 30 March 1987)

Pis'ma Zh. Eksp. Teor. Fiz. **45**, No. 9, 423-425 (10 May 1987)

The formation of induced electronic surface states has been observed in submonolayer films of Cs on the (110) and (100) faces of a W single crystal. The formation of induced intrinsic surface states and the modification of these states are studied by analyzing the concentration dependence of the emission of electrons during excitation by polarized laser light.

The intrinsic surface states of the faces of a W single crystal have been studied in some detail by photoemission spectroscopy.¹⁻³ A question which remains unclear, however, is how the spectrum of surface states of tungsten and other metal crystals changes as a result of adsorption or the formation at the surface of foreign films. The behavior of the spectrum of intrinsic surface states of W (100) during the deposition of a cesium coating was first studied in Ref. 3. It was found that with increasing degree of submonolayer coverage, θ ($\theta < 1$), the peak corresponding to the surface state of the substrate with an energy $E = 0.3$ eV below the Fermi level E_F shifts in a linear fashion toward larger binding energies. The position of the peak stabilizes at $\theta \approx 0.6$ and corresponds to $E = 1.3$ eV. No evidence of new energy states is seen in the spectrum.

We have observed a surface electron emission at $\theta > 0.5$ in the W(100)-Cs system and at $\theta > 0.6$ in the W(110)-Cs system. This emission intensifies by more than an order of magnitude as the coverage is increased to a monolayer. These results are evidence of the formation of adsorption-induced surface states, which contribute substantially to the local state density near E_F . The behavior of the emission from the intrinsic surface states of the substrate at low degrees of coverage agrees with the results of Ref. 3.

In the present experiments we studied the photoemission of electrons from surface states of the W(110)-Cs and W(100)-Cs systems by a method involving recording the polarization dependence of the photoemission current.⁴ We recorded concentration curves of the photoemission $I_s(\theta)$ and $I_p(\theta)$, respectively, for *s*- and *p*-polarized light. The emission was excited by focused laser light at various wavelengths: 4416 Å (2.81 eV), 4579 Å (2.71 eV), 6328 Å (1.96 eV), and 6764 Å (1.84 eV). The laser beam was incident on the crystal at an angle of 45°. The measurements were carried out in high vacuum ($P \sim 10^{-10}$ torr).

The photoemission in the case of the *s* polarization of the exciting laser lines corresponds to a threshold emission from the substrate.⁴ The $I_s(\theta)$ curve for each system is shaped by the corresponding curve of the work function,⁵ $\phi(\theta)$. In the case of *p* excitation, the photoemission curves $I_p(\theta)$ are quite different from that of the bulk emission $I_s(\theta)$, containing an additional component $I_{\perp}(\theta)$, which is an emission

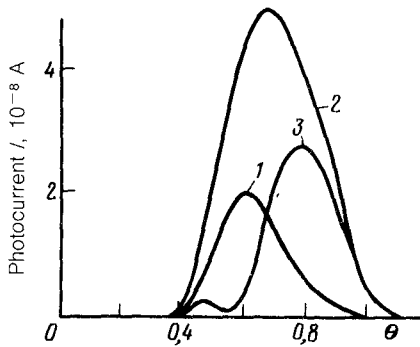


FIG. 1. Photoemission curves $I(\theta)$ of the W(110) system during excitation at $h\nu = 1.96$ eV. 1— $I_s(\theta)$; 2— $I_p(\theta)$; 3— $I_{\perp}(\theta) = I_p(\theta) - \alpha \cdot I_s(\theta)$, with $\alpha = 2$.

from surface states: $I_p(\theta) = I_{\perp}(\theta) + \alpha \cdot I_s(\theta)$, where the coefficient α depends on the optical constants of the substrate.⁴ For tungsten we have $1 < \alpha < 2$.

Studies of the changes induced in the energy structure of a surface by an adsorbed film in photoemission spectroscopy are usually carried out by the method of difference spectra. This approach is illustrated by Fig. 1, where the surface photoemission $I_{\perp}(\theta)$ is singled out for the W(110)-Cs system. At coverages $0.45 < \theta < 0.50$ the surface emission decreases with increasing θ by a factor of several units, reaching a minimum value at $\theta \sim 0.5$. A further increase in θ results in a pronounced intensification of the surface emission.

In our case, however, the difference-curve method is not sufficiently informative for a study of the polarization dependence $I(\theta)$, since the $I_p(\theta)$ curve is affected substantially by not only the change in the local state density but also the change in $\phi(\theta)$. We accordingly turn to the ratio $I_p(\theta)/I_s(\theta) = I_{\perp}(\theta)/I_s(\theta) + \alpha$, which corresponds to a surface emission normalized to the emission from the volume of the substrate and thereby eliminates an explicit effect of a change in the work functions with increasing θ .

Figure 2 shows the results of this analysis of the experimental curves. The intensity of the surface emission typically varies in a nonmonotonic way as the submonolayer film becomes denser. The initial decay of the emission intensity from the surface states agrees well with the data of Ref. 3. At coverages above half a monolayer, we observe a sharp increase in the intensity of the surface emission in both systems; this intensification is seen most vividly during excitation of the emission in the immediate vicinity of the threshold. This result is evidence of a narrow energy band, with a width ~ 0.3 eV, below E_F in which the local density of induced surface states increases sharply. The variation in the shape of the $I_p(\theta)/I_s(\theta)$ curves with the energy of the exciting light reflects the spectral variation of the surface photoemission.

For the two systems which we studied there exists a clearly defined coverage interval in which the surface emission reaches a minimum intensity (Fig. 2). This coverage interval corresponds to the minimum value of the work function for each of the systems studied. At coverages corresponding to ϕ_{\min} , we find essentially no spectral dependence of the surface emission.

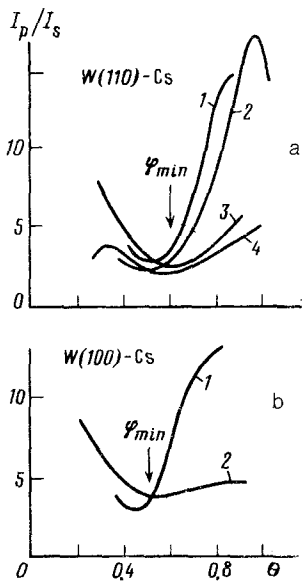


FIG. 2. Concentration dependence of the surface photoemission normalized to the emission from the volume, $I_p(\theta)/I_s(\theta) = I_1(\theta)/I_s(\theta) + \alpha$, for two systems. a: W(110)-Cs at several excitation energies. 1—1.84 eV; 2—1.96 eV; 3—2.71 eV; 4—2.81 eV. b: W(100). 1—1.96 eV; 2—2.81 eV.

These results thus reveal a modification of the surface-state spectrum near E_F , which is evidence of a change in the electronic structure of the faces of pure tungsten and the formation of two-dimensional induced electronic surface states in the Cs film. A theoretical analysis shows that during the adsorption of Cs on W(110), the band of valence electronic states of the adsorbate lies near E_F , and its filling increases with increasing θ (Ref. 6). In this connection, it might be suggested that the increase in the local density of surface states, which is observed during adsorption, stems from the formation of a two-dimensional band of 6s-6p valence states of Cs.

Induced surface states have previously been observed^{4,7} in research on threshold photoemission. The use of high-energy excitation sources was apparently the reason why electronic surface states induced by Cs adsorption could not be observed in Ref. 3. This suggestion is supported by the spectral variation of the emission from the induced surface states at $\theta \sim 1$ (Fig. 2), which exhibits a tendency toward a decrease in the emission quantum yield with increasing excitation energy.

¹S. L. Seng, J. E. Inglesfield, D. A. King, and C. Somerton, J. Phys. C14, 3099 (1981).

²M. W. Holmes, D. A. King, and J. E. Inglesfield, Surf. Sci. 89, 133 (1979).

³P. Soukiasian, R. Riwan, J. Lecante, E. Wimmer, S. R. Chubb, and A. J. Freeman, Phys. Rev. B 31, 4911 (1985).

⁴G. V. Benemanskaya and M. N. Lapushkin, Pis'ma Zh. Eksp. Teor. Fiz. 41, 432 (1985) [JETP Lett. 41, 531 (1985)].

⁵V. S. Fomenko, Émissionnyye svoïstva materialov (Emission Properties of Materials), Kiev, 1981.

⁶K. F. Wojciechowski, Surf. Sci. 55, 246 (1976).

⁷S. A. Lindgren and L. Wallden, Solid State Commun. 28, 283 (1978).

Translated by Dave Parsons