Discrete Valence-Electron States in Thin Metal Overlayers on a Metal

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We have measured photoelectron energy spectra from thin Na and Ba overlayers on Cu(111). The spectra show extremely narrow adsorbate-induced peaks, much narrower than observed for any other adsorbate system. These features arise from electrons trapped in the potential well between the vacuum barrier and the Cu(111) surface which has a high electron reflectivity for energies within the band gap producing the necks of the Cu Fermi surface.

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For zero parallel wave vector, a thin film of free-electron-like metal bounded by vacuum has discrete electron energy levels with energies given by $E=\pi^2\hbar^2n^2/2ma^2$ if we assume unrealistic infinite barriers and a thickness of a. In contrast there will be a continuum of energies for the electrons if the film is placed on a metal substrate such that the electrons are able to move across the interface between substrate and adsorbate. For several systems studied, the electrons in the overlayer form an electron gas, which already at around full monolayer coverage has a density and a vacuum barrier similar to that of a thick sample of the overlayer metal.[1-4] Na adsorbed on Cu(100) provides an example of this behavior. At around full monolayer coverage the photoemission spectrum, which is due to the surface photoelectric effect, is similar to that obtained for thick Na films.[4]

For free-electron metals adsorbed on Cu(111) the overall properties of the overlayer are similar to that for Cu(100). There is, however, one important difference. For electrons in the overlayer with energies and wave vectors within the necks of the Cu Fermi surface, the substrate erects a barrier which, as will be discussed further below, is not, for these electrons, drastically different from the vacuum barrier. For this range of energies and $k_{\parallel}$ values there is thus a chance of observing states having discrete energies. The purpose of the present Letter is to point out that such states can be and, indeed, have already been observed.

In our early work on Na-covered Cu(111) we observed a narrow peak close below the Fermi edge in photoemission spectra recorded in the normal direction at around full monolayer thickness of Na.[5] This peak was poorly understood with regard to both the ejection mechanism and the states involved. The later breakthrough in the understanding of the surface photoelectric effect,[4,6,7] the recent calculations of electronic structure of monolayer films of free-electron-like metals,[8,9] the calculations of energies for states in the image-potential region of low-index Cu surfaces,[10,11] together with the present data on Ba-covered Cu[111] provide a framework for understanding of the narrow emission peaks observed for Ba and Na overlayers. Of particular interest with the Ba adsorbate is that, in contrast to Na, distinct new structure is observed in the photoemission spectra when the layer thickness is increased beyond the monolayer stage.

Ba is evaporated onto the Cu(111) crystal from a heated boron nitride crucible. The photoelectron energy spectra reveal a Ba-coverage dependence for the work function similar to that typical of alkali-metal adsorbates. After an initial decrease from a value of 4.9 eV for Cu(111) to a value of around 2.1 eV, the work function increases to 2.7 eV as the Ba deposition continues. To estimate the amount of adsorbed metal we observe the LEED pattern and monitor the work-function change, which, as for alkali metals, is expected to saturate at around full monolayer coverage. At somewhat less than full monolayer coverage there appear diffraction spots characteristic of a $p(2\times2)$ Ba overlayer. At high monolayer coverages a narrow emission peak appears at the Fermi edge (Fig. 1). The peak reaches maximum intensity at around full monolayer coverage. Up to this evaporation time, the spectra are similar enough to those obtained for Na on Cu(111) that it would be difficult to note a difference. As the Ba evap-

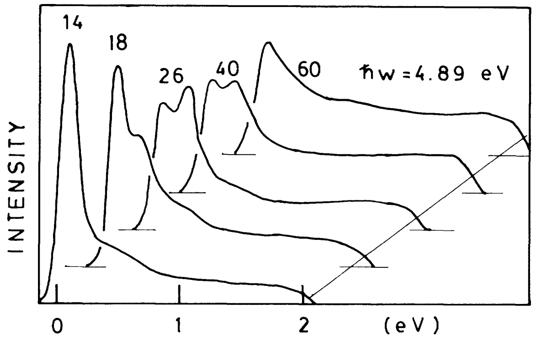

FIG. 1. Photoelectron energy spectra, recorded in the normal direction, of Cu(111) covered by different amounts of Ba. The Ba evaporation times in minutes are given in the diagram and correspond to coverages ranging from approximately one to five atomic layers of Ba.

oration is continued the peak at the Fermi edge begins to lose some of its intensity as a second narrow peak appears at 0.2 eV higher binding energy. No second narrow peak was observed for Na. As the Ba evaporation is continued further the second peak gains in strength, its intensity reaching a maximum after an evaporation time corresponding to somewhat more than two full atomic layers. When additional Ba is deposited the doublet becomes gradually smeared out (Fig. 1).

Spectra recorded at different polar emission angles show that the narrow peaks may be observed only for small $k_{\parallel}$ values. This is as expected if it is the Cu band gap at L which is responsible for the well-defined energy of the states. The neck radius of the Cu Fermi surface is 0.27 Å^{-1}.[12] Over the limited range of $k_{\parallel}$ values where the doublet is well resolved, the dispersion is free-electron-like for the band which produces the peak at around 0.3 eV below the Fermi edge in emission spectra recorded along the normal direction of the sample (Fig. 2). During the dispersion measurements the energy analyzer was set to a somewhat higher resolution than used to record the spectra shown in Fig. 1. Even for these spectra, however, the peak widths are dominated by the experimental resolution. The lifetime broadening is therefore less than 100 meV. As far as we know, adsorbate-related structure as narrow as this has not been observed previously.

To explain why the narrow states appear we consider the electronic structure of a monolayer of Na or Ba bounded by vacuum. The energy bands for such films have recently been calculated.[8,9] Na has a simpler electronic structure and the experiment results obtained can be accounted for in more detail for this case. When the film is placed on Cu(111), one of the vacuum barriers is, in the energy range of interest, replaced by the barrier produced by the Cu conduction band gap at the L point in the Brillouin zone. To find the influence of this barrier change on the electronic structure we consider the difference in phase change between the two barriers. In Fig. 3 are shown the phase change in the L gap,[10] ϕ_C, and that produced by the Na-vacuum barrier, ϕ_B. ϕ_B is obtained by use of the phase shift of the image potential,[10,13,14]

$$\frac{\phi_B}{\pi}=\left(\frac{3.4\ \text{eV}}{E-E_v}\right)^{1/2}-1,$$

down to the Fermi energy and continuation of this smoothly to the value of $-\pi$ at the bottom of the Na well, 6 eV below the vacuum level, E_v.

For a film with a vacuum on both sides, bound states appear when $\phi_B+\phi_D=\pi n$, where n is an integer and $\phi_D=ka$ is the phase change across the assumed flat region of length a of the well. For the overlayer on Cu(111) the condition becomes $(\phi_C+\phi_B)/2+\phi_D=n\pi$. One notes that the interface barrier phase change is not very different from that of the vacuum barrier in the energy range of interest (Fig. 3). There will thus be only a moderate change of the electron energies when a monolayer thin Na film is transferred from vacuum to a

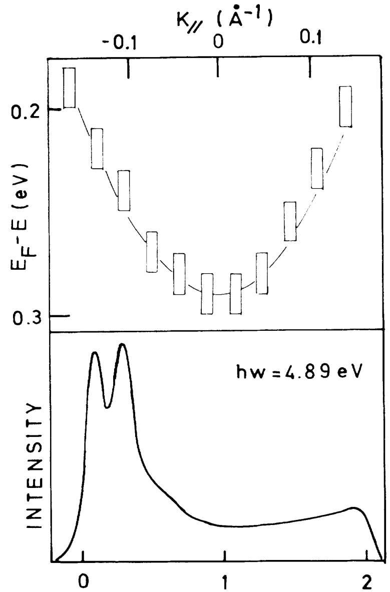

FIG. 2. Photoelectron energy spectrum recorded in the normal direction for Cu(111) covered by approximately two atomic layers of Ba (lower panel) and the dispersion of the band producing the peak at around 0.3 eV below the Fermi edge (upper panel). The solid line is a free-electron parabola.

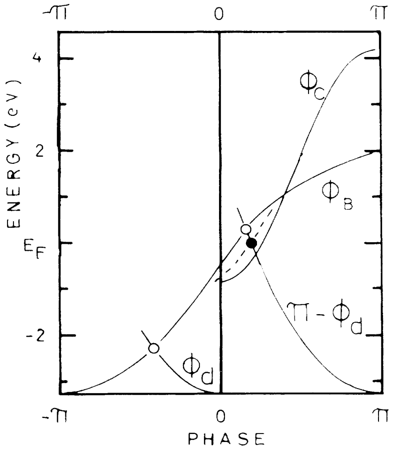

FIG. 3. Phase shifts vs electron energy for the Na-vacuum barrier potential (ϕ_B), for the Cu band gap at L (ϕ_C), and for the phase change across the Na layer (ϕ_D). The intersections indicated by open circles give the electron energies for a Na monolayer in vacuum while the intersection indicated by the filled circle gives the discrete electron energy for a Na monolayer on Cu(111). The dashed curve represents $(\phi_B+\phi_C)/2$ relevant for the adsorbed monolayer.

Cu(111) surface. To proceed we choose $a = 2.7$ Å, which should be compared with the smallest interlayer spacing of 3.0 Å for bulk Na. The exact value chosen for a is of no great importance for the present purpose. That the ϕ_B and ϕ_D values used here are reasonable is demonstrated by the fact that we obtain energy values (see Fig. 3) not far from those obtained by a full calculation of the electronic structure for a Na monolayer.[8] Of particular present interest is the shift in energy obtained for the state close above E_F when the film is taken from vacuum and placed on this substrate. The energies are given by the intersection of the curves for ϕ_B and $\pi - \phi_D$ for the monolayer in vacuum and between the curves for $(\phi_B + \phi_C)/2$ and $\pi - \phi_D$ for the adsorbed layer. The state shifts downward in energy by around 0.2 eV when one vacuum barrier is replaced by the interface barrier. We associate this state with the narrow peak observed at the Fermi edge in photoemission spectra from Na-covered Cu(111)[5] at full monolayer coverage.

Once this interpretation of the peak is made we can proceed to make a more detailed comparison with the theoretical results obtained for the Na monolayer in vacuum. The experimental peak is very close to the Fermi edge. The 0.2-eV difference obtained from Fig. 3, between the energies for the adsorbed monolayer and the monolayer in vacuum, means that for the latter the energy is 0.2 eV above E_F. This is the energy of the state provided that the work function is 2.75 eV which is the experimental value for the adsorbed monolayer and the value used to draw the barrier phase shift in Fig. 3. According to Wimmer's calculation,[8] however, a Na monolayer has a work-function value of 3.1 eV. If we were to use this value a diagram similar to that of Fig. 3 would give an energy of 0.5 eV above E_F, which is quite close to the energy, 0.65 eV, calculated by Wimmer. The present narrow emission peak observed for metal monolayers on metals thus allows predictions to be made regarding the electronic structure of monolayers in vacuum.

Cu(111) has a well-known surface state 0.4 eV below E_F. The phase condition satisfied by this state is $\phi_B + \phi_C = 0$. At only around 0.3 eV higher energy, the condition $\phi_B + \phi_C + 2\phi_D = 2\pi$ is satisfied for Cu(111) covered by a full Na monolayer. The extra 2π phase change for the overlayer system is mainly due to the phase change $2\phi_D$. For any close-packed alkali-metal monolayer, $2\phi_D$ will be somewhat less than 2π. This can be understood from the fact that in bulk alkali metal an electron at E_F is close to the nearest Brillouin-zone boundary if the electron propagates in a direction perpendicular to the close-packed planes. The second contribution to the extra phase change is due to the lower work function of the alkali-metal–covered surface. Using the expression for ϕ_B, one finds that for energies near E_F the phase shift ϕ_B is around 0.25π bigger for Na-covered Cu(111) than for clean Cu(111).

It is interesting to note that if the same phase-shift analysis is made for Na films two or more atomic layers thick, one finds that the corresponding state will be shifted to higher energies. This explains why the narrow peak observed for the Na monolayer fades away as the Na deposition is continued. This occurs both for experiments where the substrate is held at liquid-nitrogen temperature and at room temperature. The room-temperature data are, however, of less interest in this respect since the film thickness is not homogeneous when the evaporation is continued beyond the first monolayer.[15] A well-defined thickness is evidently necessary if the energy is to be well defined. The present results for Ba show that in this case one can obtain at least the two-atomic-layer stage with sufficient thickness homogeneity.

The electronic structure calculated for a Ba monolayer[9] shows that for $k_\parallel = 0$ there are two states in the energy range of interest near E_F. One of these has an energy very close to E_F while the second state has an energy at about 0.3 eV above E_F. There is an admixture of d character, and the energy bands, especially the lower one, are flatter than the corresponding band for Na. We associate the peak at the Fermi edge observed for a full Ba monolayer with the state calculated to fall at E_F. Unfortunately there are no calculations of the electronic structure for Ba films two atomic layers thick. One expects, however, that the two states near E_F will split and form four states for the duolayer. The fact that we observe a doublet means that two of these states are filled.

One observation which at first glance appears to be in conflict with the calculated band structure of the Ba film is the free-electron-like dispersion of the band which at $k_\parallel = 0$ has its energy 0.3 eV below E_F. Firstly, one should note, however, that the measured range of $k_\parallel$ values covers only a small fraction of the Brillouin zone. Secondly, the dispersion will be affected by the Cu as well as the Ba potential. Since the band mass is small for the band describing the dispersion across the necks of the Cu Fermi surface and for the Cu(111) surface state found in this neck, one would expect the Cu potential to reduce the mass of the Ba electrons as the Ba film is placed on the Cu(111) substrate. Thirdly, lacking calculations for a duolayer we have compared the dispersion measured for a double layer with the calculation for a monolayer.

In conclusion we find that filled states with discrete energies can be found in thin metal overlayers on a metal. For nearly-free-electron-like overlayers, the spectrum of states for layers of different thickness can be accounted for in simple terms with use of the phase shifts of the vacuum and interface barriers.

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