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Oscillatory photoemission cross section for simple-metal quantum wells

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A strong, oscillatory photon energy dependence is observed for the intensity of photoemission peaks due to quantum-well states in Na overlayers on Cu(111). The measurements are made at low photon energies ($h\nu < 8$ eV) with Na films, which are between four and eight atomic layers thick. The intensity oscillations are ascribed to the interference between the contributions to the outgoing wave associated with the two tails of a quantum-well state.

Photoemission is an old method, and it has been realized for a long time that the emission is due in part to the surface and in part to the bulk. Each of the two components has been studied in some detail,[1] but the interference between them largely remains to be investigated and utilized as a probe of the electronic structure. Here we report on strongly oscillatory emission intensities for ultrathin overlayers ascribed to an interference between the waves from the front and back sides of the film. The intensity variations are observed at low photon energies ($h\nu < 8$ eV) for quantum-well-type states in ultrathin films of Na on Cu(111). In previous work, line-shape changes in the spectrum of Na(110) were successfully explained in terms of interference between the bulk and surface although, as pointed out by the authors, some uncertainty about the interpretation remains due to uncertainty about the sign of the contribution from the bulk.[2] One advantage of using thin films as samples is that individual states may be probed over a range of photon energies. Another is that by changing the film thickness the distance can be varied between the surface barrier and the substrate surface region, which, we believe, are the two main contributors to the emission intensity in the range of photon energies investigated. Oscillatory cross sections due to the periodic bulk potential have previously been observed for *s,p* surface states on noble metals.[1,3,4] Since the spatial period of the bulk potential is one interlayer distance, the oscillatory period of the cross section is typically an order of magnitude larger than in the present case when the interfering parts of the wave function may be separated by several interplanar distances.

Angle resolved photoelectron energy spectra (recorded at BL52, MAX-lab., Lund) are obtained along the surface normal from Na-covered Cu(111), cooled to 170 K during Na evaporation and measurement. The light is p polarized and the incidence angle is 50°. As discussed previously, the films consist of a stack of close-packed Na layers with an interplanar distance of around 3.1 Å.[5] The discrete states are formed by Na valence electrons confined to the overlayer due to a substrate band gap ranging from 0.8 eV below to 4.2 eV above E_F in the direction normal to the surface. In previous work, discrete states have been observed for one-, two-, and three-atomic-layer-thick Na films on Cu(111).[6,7] In the present work we observe quantum-well states for a larger range of thicknesses. The perpendicular wave vector k_i for initial states in a film with thickness d can be estimated quite well from the phase condition $\Phi_B + \Phi_C + 2k_i d = 2\pi m$, $m = 0, 1, 2, \ldots$, assuming a constant potential in the film.[6] Φ_B and Φ_C are the phase shifts at the vacuum barrier and at the overlayer/substrate interface, respectively, and m is a quantum number. For the states discussed below, $m = N - 1$, if N is the number of atomic layers. One thus obtains $k_i = \pi(N-1)/aN - (\Phi_B + \Phi_C)/2aN$, where a is the thickness of one layer of Na atoms. In the energy range of interest the sum of the barrier phase shifts is small, and the wave vector as well as the energy of the state will increase as the film is made thicker.[6]

The first member of the $m = N - 1$ series of states to appear as Na is evaporated onto the crystal is the $N = 4$, $m = 3$ state which has an energy of 0.75 eV below E_F and falls just above the low-energy edge of the substrate band gap (Fig. 1). The intensity of the emission peak falls off with increasing photon energy, and the workable range of photon energies is limited to below around 8 eV. Of main interest at present is that the emission peak is suppressed for photon energies around 6 eV. When more than four layers of Na are deposited, the spectra show more than

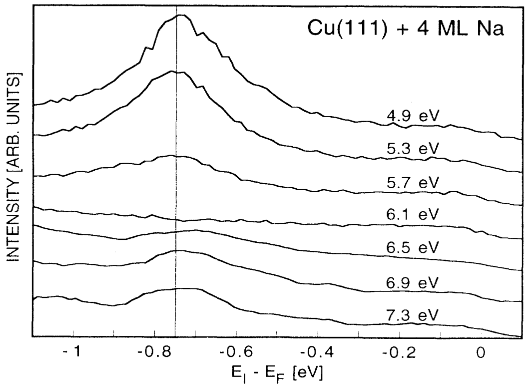

FIG. 1. Photoemission spectra recorded at different photon energies and along the surface normal from Cu(111) covered by 4 ML of Na.

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one $m=N-1$ quantum-well state, demonstrating that the film thickness is not homogeneous but well defined over large enough areas that states with well-defined energy can form. An example of this is given by the spectra shown in Fig. 2. These are obtained at a nominal thickness of 6 ML, but states characteristic of 5- as well as of 7-ML-thick parts of the film are also observed. As the films are made thicker, the energies of the states for N and $N+1$ thick parts come closer. Since we are interested in resolving individual states, we have made the present observations for nominal thicknesses below 8 ML (although this is not an experimental limit for resolving the states). The nominal thickness is obtained from the evaporation time, using as a reference the time required to form one full atomic layer of Na which is characterized by strong photoemission from the $m=N=1$ quantum-well state.

Plotted against the photon energy, the relative intensities of the three peaks shown in Fig. 2 vary as depicted in Fig. 3. The relative intensities are obtained by assuming that the three intensities add up to the same value independent of the photon energy. The relative intensities plotted in Fig. 3 are for a nominal thickness of 6 ML. Measurements for films with a nominal thickness between 5 and 7 ML show that the intensity variations discussed below are characteristic of a certain state independent of the nominal thickness. The intensity variation observed for the $N=6$, $m=5$ state for a film with a nominal thickness of 6 ML is thus very similar to that obtained with a nominal thickness of 7 ML regarding the positions of maxima and minima.

To explain the results, we consider the matrix element M for photoemission from a thin film. Our primary objective is to account for the intensity extrema observed for photon energies between 6 and 8 eV, and it then appears sufficient to use the expression for M when the spatial variation of the incident field is neglected. As discussed by Feibelman[8] this variation contributes strongly to the emission for photon energies below the plasmon energy (5.7 eV for Na). With a constant field, M is proportional to $\int_{-\infty}^{\infty}\Psi^{>}dV/dz\,\Psi_i dz$, where $\Psi^{>}$ represents an incoming wave, V the potential, and Ψ_i the initial state.[9] The origin of the intensity oscillations is evident even if a further simplification is made by approximating the overlayer potential with a finite square well. For such a well M is proportional to $(1\mp e^{ikd})(1\pm re^{ikd})^{-1}$, where $r=(k-q)/(k+q)$ is the reflectivity at the barriers, and k and q are the wave vectors of the final state inside and outside the well, respectively.[9] The upper (lower) sign is for even (odd) initial states.

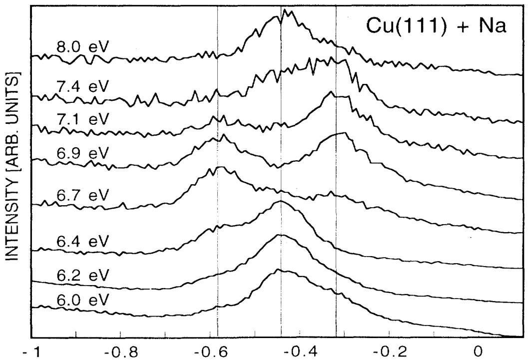

FIG. 2. Photoemission spectra recorded at different photon energies along the surface normal from Cu(111) covered with a Na film having an average thickness of 6 ML. The three peaks are due to quantum-well states characteristic of 5- (the peak at $E-E_F=-0.58$ eV), 6- (-0.44 eV), and 7-ML-thick (-0.32 eV) parts of the film.

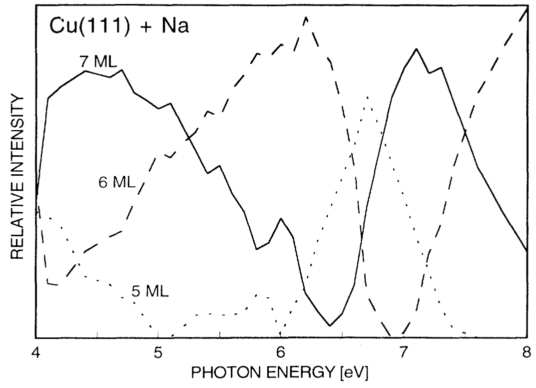

FIG. 3. Photon energy dependence of the relative intensities of peaks due to quantum-well states observed for Cu(111) with a nominal Na coverage of 6 ML.

Characteristic of the finite square well are intensity oscillations proportional to $|M|^2$ which are out of phase for even and odd states. For our asymmetric overlayer well there will be a similar distinct difference between quantum-well states with equal and opposite signs for the values $\psi_i(0)$ and $\psi_i(d)$ of the wave function at the interfaces. For the overlayer states the relative sign is given by the quantum number m, since m is the number of nodes in the film. With $m=N-1$ for the states observed, the signs of $\psi_i(0)$ and $\psi_i(d)$ are the same if N is odd and different if N is an even number. One thus expects the intensity oscillations to be out of phase for even and odd values of N. This behavior is observed. As an example, there is an intensity minimum for $N=6$ (at $h\nu=6.9$ eV; Fig. 3), which falls between intensity maxima for $N=5$ (at $h\nu=6.7$ eV) and $N=7$ (at $h\nu=7.15$). The agreement between expectation and observation on this point is a main reason for ascribing the intensity oscillations to an interference between the photoelectron waves from the front and back sides of the film.

If the positions of maxima and minima are calculated from the square-well model, one finds that the energies come in the correct sequence but are spread over a wider range than observed. While the observed energies plotted in Fig. 4 are spread over a range of 1.5 eV (between 5.3 eV at $N=4$ and 6.8 eV at $N=7$), this range is 3 eV for the estimated values. There are several reasons for the discrepancy. For the overlayer well the matrix element M for photoemission includes contributions not only

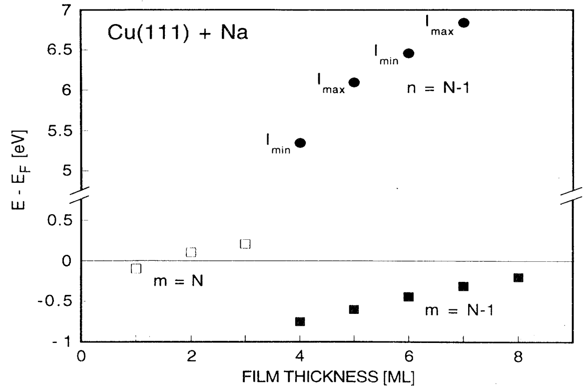

FIG. 4. Energy vs thickness in units of atomic Na layers, N, for quantum-well states with quantum number $m=N$ (open squares) and $m=N-1$ (filled squares) in Na films on Cu(111), and final-state energies for intensity maxima (minima) observed for the emission from quantum-well states obtained when N is an odd (even) number.

from the potential steps at the front and back interfaces, M_1 and M_2, but also from the potential in the interior of the film, M_3, and from the substrate bulk potential, M_4. In the case of a free-electron-like metal such as Na, M_3 is expected to be small, especially at photon energies which do not satisfy the condition for direct optical transitions in Na. With photon energies in the range 6–8 eV the selection rule picks out initial Na states with smaller wave vectors than the k_i values of the present quantum-well states. For the photoelectron wave from the back side of the film given by M_2+M_4, the dominating contribution is probably due to M_4. The Cu(111) surface state 0.4 eV below E_F has a tail similar to the quantum-well states, and for this the observed interferences have been assigned to the bulk part of the potential.[1,3,4] If M_4 dominates, there will be an additional phase change ϕ added to the phase change kd of the photoelectron wave across the overlayer. This additional phase change (which depends on the initial- as well as final-state energy) together with the asymmetry of the overlayer well, which gives different electron reflectivities at the interfaces, will affect the oscillatory behavior of the intensity. Close above the high-energy edge of the Cu band gap 4.2 eV above E_F, the reflectivity is high for electrons incident on the substrate, while the reflectivity at the vacuum barrier for an electron approaching it from the interior is expected to be insignificant.[10] If the reflectivity at the substrate surface, r, is taken into account, one finds that M is proportional to $(1\pm e^{-i(kd+\phi)})-r(1\pm e^{i(kd-\phi)})$. Furthermore one may note that self-energy corrections are expected to be important in the measured range of final energies. The theoretical estimates made for the self-energy corrections suggest that these would reduce the energy spread discussed above by 0.5 eV.[11]

In conclusion, we observe an oscillatory photoemission intensity for Na overlayer states. The intensity variation is ascribed to the interference between emission from the two sides of the film. As predicted for even and odd states in a finite square well, the intensities from the overlayer are different for states with even and odd numbers of nodes in the film. On a relative energy scale the shift with changing thickness or photon energy of maxima and minima in I-$h\nu$ spectra can be explained in terms of the phase change for the photoelectron wave as it traverses the film. Our results show that photoelectron interferences in solids can be observed even when the interfering parts of the wave function are separated by several interatomic distances. Finally we note that oscillations characteristic of a well-defined thickness may be observed for a sample which is homogeneously thick only patchwise.

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