Angle-resolved inverse photoemission from the Ag(100) surface

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Angle-resolved inverse-photoemission spectra from Ag(100) have been measured. The results are compared with the predictions of bulk band-structure theory and a free-electron model. The latter gives good agreement for the structure with a final state near the Fermi energy. Band theory is needed for the structure 17 eV above the Fermi energy. This structure is very nondispersive, indicating the existence of a very flat band throughout the ΓXUL plane.

INTRODUCTION

In the past ten years, inverse photoemission has been shown to be a good tool for investigating the unoccupied electronic states in a manner complementary to photoemission, which provides information about the occupied electronic states. However, inverse photoemission has much lower overall resolution than photoemission. It is an interesting problem to examine high-energy electronic states with inverse photoemission. Lifetime broadening by the imaginary part of the self-energy is very large (~ 2 eV around 17 eV above the Fermi energy for the *s-p* conduction bands of the noble metals[1]) so that the information obtainable about the higher states is limited. In this paper we report angle-resolved inverse photoemission spectra from Ag(100) measured up to 30 eV above the Fermi energy along the $\bar{\Gamma}$-$\bar{X}$ direction of the (100)-surface Brillouin zone. Two bulk-related structures and one surface-related structure were observed.

EXPERIMENT

In inverse photoemission the emitted ultraviolet photons are detected when low-energy electrons bombard the sample. Our photon detector consists of an electron multiplier with CuBe cathode and dynodes and a CaF_2 entrance window. It is similar to one previously described.[2] Its count rate is lower than that of the Geiger-Müller type but it is much easier to operate in a vacuum chamber and it has almost the same energy resolution as Geiger-Müller detector. Its full width at half maximum is 0.6 eV, centered on 9.7 eV. The electron gun is a custom-designed one[3] with an osmium-coated BaO cathode for minimal thermal energy width of the emitted electrons. The electron current is 3 μA at 7 eV with $\sim 3°$ spread in angle. The detector and electron gun are at a fixed angle of 45°. The incidence angle of the electron beam was varied by rotating the sample. The sample was cleaned by Ar-ion sputtering under 5×10^{-5} Torr. After sputtering the sample was annealed at 400 °C for 5–10 min. We used low-energy electron diffraction (LEED) to confirm surface order. Surface cleanliness was checked by Auger-electron spectroscopy, using the LEED optics as a retarding-field analyzer. The base pressure in the chamber was at most 2×10^{-10} Torr during the measurements.

In Fig. 1 we show a set of spectra from Ag(100) obtained for different angles of incidence in the ΓXUL plane. Peak $B1$, near the Fermi energy, was assigned previously[4] to a bulk-band-derived feature, and $S1$ to a surface-state feature.

Around 17 eV there is a very broad, nondispersive peak. According to band calculations[5] there is a very flat band around 17 eV above E_F which remains flat throughout the ΓXUL plane. Photoemission[6] and thermomodulation[7] experiments also show the existence of such a flat band at 17.5 eV above E_F. The latter measurements indicate, at least for Au, a lifetime for this band longer than that of the nearly-free-electron band just below it.[1] The lower energy resolution of inverse photoemission precludes us from seeing such lifetime effects.

This flat band could produce two nondispersive features in the spectrum. One could occur if this band were the initial states for the inverse photoemission. The other is if it were the final states. However, we do not see this feature appearing as the initial state in our spectra. This may be explained by the fact that electrons captured in this band decay dominantly by inelastic electron-electron scattering events, i.e., the dipole matrix element for transitions to states 9.7 eV lower in energy is small. (Such final states exist in the band structure.) The background of the inverse photoemission spectrum increases above 7–8 eV, indicating that there is an increase in inelastic decay for states 17–18 eV above the Fermi energy. Peak $B2$ is associated with the flat band as the final states.

Theoretical structure plots were calculated with a free-electron model and with a first-principles band structure, using k-conserving optical transitions to identify the bulk-band-derived features. We discuss the former first. The dipole matrix elements vanish for the free-electron model, but with a weak pseudopotential with Fourier coefficients V_G at reciprocal-lattice vectors G, the dipole matrix elements do not vanish and can be calculated easily for regions near the zone boundaries, where the transitions are strongest.[8] These occur between bands which were degenerate at the zone boundary. The same formalism can be used for transitions between bands that are associated with different reciprocal-lattice vectors, in which case the dipole matrix elements are much smaller. The allowed final states from the free-electron calculation

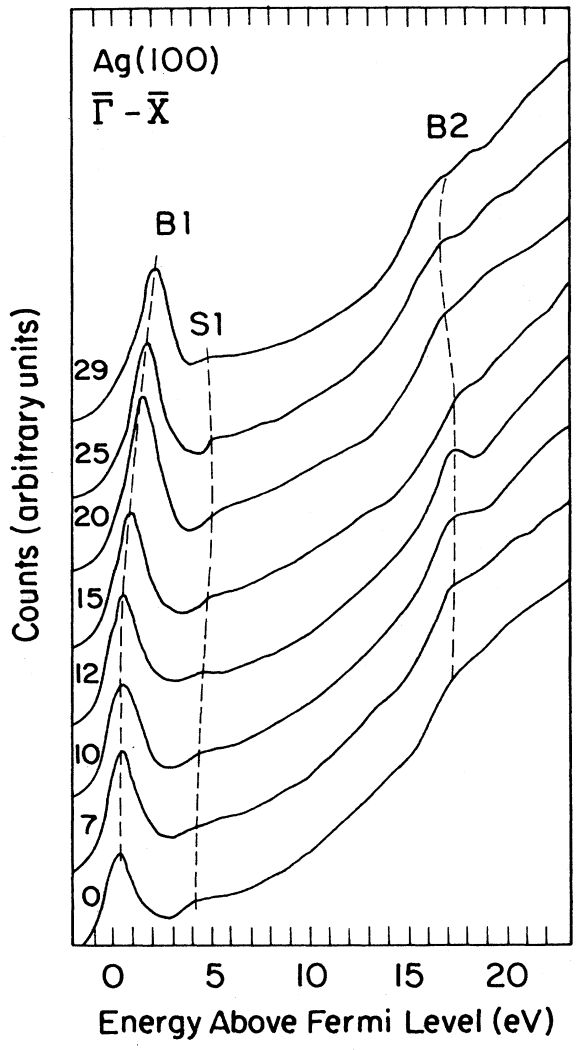

FIG. 1. Inverse photoemission spectra of Ag(100) in the isochromat mode at $\hbar\omega = 9.7$ eV along the $\bar{\Gamma}$-$\bar{X}$ symmetry line. The spectra are marked with the incidence angle of the electron in degrees. The energy scale is that of the final state.

(without calculating dipole matrix elements, see below) are shown in Fig. 2, along with the experimental results. The reciprocal-lattice vectors associated with the initial and final states are shown as labels.

This simple calculation gives a fairly good description of the spectra, especially for the structure near the Fermi energy. Although only one structure is found in the experiments, this simple model predicts many energetically possible transitions. However, only two spectral features are expected to have large oscillator strengths, those labeled (200,000) and (111,111). All others should be weak for reasons stated above. The second of these two transitions was not seen at the angles used, possibly because of large initial-state broadening and a larger background when the final-state energy is high at the small angles used. It should be easier to find at larger angles, but the small size of our sample precluded working at larger angles. Also the incoming electron can match the components of the plane wave $\exp[i(k+G_{200})]$ more effectively for the (100) face than it can match the components of $\exp[i(k+G_{111})]$. The incoming electrons in the ΓXUL plane do not scatter strongly with G vectors which are associated with parts outside the ΓXUL plane as observed for other materials and various faces.[9,10] This effect also leads to an emphasis on the transition labeled (200,000) in Fig. 2(a). Although the free-electron model shows some possible inverse photoemission transitions around 17 eV, their dipole matrix elements should be small, as described above. A flat band at this energy is not present in the free-electron model. It results from the crystal potential and a more realistic calculation is needed to describe the structure around 17 eV.

We used the linearized augmented-plane-wave (LAPW) method with a relativistic self-consistent potential[11] to calculate the bands up to 30 eV above the Fermi energy. Two energy windows were used to cover this large energy range. Instrumental broadening effects were included by finding all k-conserving transitions within a window of ± 0.3 eV around 9.7 eV. Because the calculation is based on the ground state, but the measurements involve the excited states, the neglected self energy may be an important factor in comparing experiment with theory. The self-energy gives a lifetime broadening as large as 2 eV around 17 eV above the Fermi energy, at least in the free-electron-like bands.[1] Although it is difficult to assign one-to-one band pairs to this peak because other bands are involved and the self-energy is very large, the existence of the nondispersive peak $B2$ throughout various angles indicates that it is related to that flat band. A high density of states at 17 eV in the two-dimensional density of states also supports this connection. This high density of states means that no matter where the wave vector of the incident electron lies in the ΓXUL plane, there is an initial state because of the large energy broadening of the nearly-free-electron bands so far above the Fermi level, and there is a final state at the same wave vector because of the very flat band 17 eV above E_F. The peak is strong at 12°.

By treating the initial state as nearly-free-electron-like, we can calculate $k_\perp$ as well as $k_\parallel$. The k point approaches the zone boundary around 12°. The plane wave is perturbed increasingly as the band approaches the zone boundary so that the energy distribution of the joint density of states is increased and the intensity of spectra also can increase if we treat matrix elements as constant. This flat band has been found in other band calculations,[12–16] where it appears at about the same energy in Cu, Ag, and Au, although it is not very prominent (flat) in Cu. At the zone center, this band has f character, with p states mixing in away from the zone center. It is clearly not free-electron like, and some of its unusual properties are a result of this.[6,7]

In summary, there is a very nondispersive structure at 17 eV above the Fermi energy in inverse photoemission spectra along $\bar{\Gamma}$-$\bar{X}$. Direct interband transitions are responsible for the observation of this feature. First-principles band-structure calculations to high energies are needed to show this nondispersive feature.

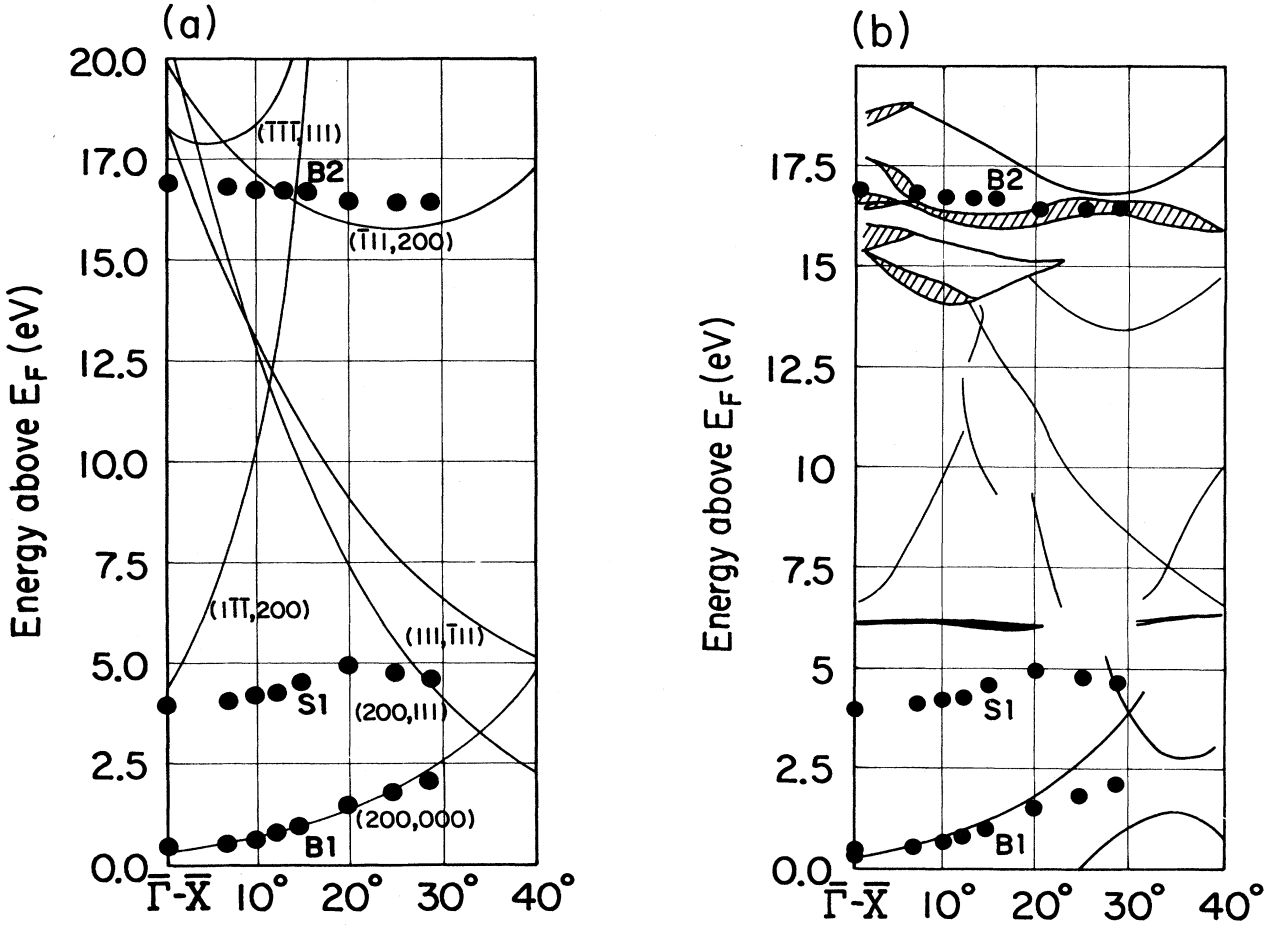

FIG. 2. Calculated structure plots for Ag(100). (a) was obtained from free electron bands, and only final states are displayed. The labels are the reciprocal-lattice vectors associated with the initial and final states of the k-conserving transitions. (b) is from a first-principles band structure. Matrix elements were not used. Dots on both plots are the experimental results. $S1$ is a surface-derived feature.

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