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High-resolution inverse-photoemission study of the Pd(111) surface

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We present high-resolution inverse-photoemission spectra for the clean Pd(111) surface. For what we believe to be the first time we clearly resolve the anticipated Shockley state at the bottom of the $L_{2'}L_1$ band gap. This state is found to have a binding energy of 1.3 eV above the Fermi level and an effective mass of approximately $0.3m_e$. We further observe the $n=1$ image state and find that it has a binding energy of 0.5 eV with respect to the vacuum level and an effective mass of $1.0m_e$. Comparison with the phase model shows good agreement with these measured binding energies. We find that these measurements indicate that the image plane is close to the jellium edge.

INTRODUCTION

It is well established from photoemission studies[1] that the (111) surfaces of all the noble metals support a Shockley-type surface state at the bottom of the $L_{2'}L_1$ s-p band gap. In all cases it is found that these states have binding energies close to the Fermi level and that, near the center of the zone, they disperse towards the vacuum level with effective masses of approximately $0.5m_e$. The recent observation of image states,[2-4] a new class of surface state derived from the long-range image potential, has led to a renewed interest in the factors that determine the binding energies of surface states in general. Indeed, it has been demonstrated that a one-dimensional model originally developed to determine the binding energies of the image states[5] may be extended to account for the binding energies of the crystal-derived (Shockley) states.[6] It has further been demonstrated that measurements of the binding energies of these states in principle yield information about the position of the image plane.[7]

The situation on the (111) planes of the transition metals is less clear. A photoemission study on Ni(111) by Himpsel and Eastman[8] identified an occupied surface state of the appropriate symmetry at the center of the zone. They further found that this state showed photoemission cross-section behavior similar to that of the surface state at the center of the zone on Cu(111). However, on moving away from the center of the zone the state was observed to disperse to higher binding energies, unusual behavior for a free-electron-like state.

An inverse photoemission[9] study of this same surface identified an unoccupied surface resonance which dispersed to higher binding energy on approaching the center of the zone but which was not observed at the center of the zone. The authors of the latter paper, Borstel *et al.*, attributed the lack of observation at the center of the zone to the fact that only one Shockley state may exist at the center of the zone and this allowed state they identified with the occupied state observed in the earlier photoemission study.[8] Further, using the one-step model of photoemission developed by Pendry,[10] Borstel *et al.*[9] were able to generate both the dispersion of the occupied surface state and the unoccupied surface resonance. We note, however, that an earlier theoretical study,[11] using the same model, predicted that the Shockley state would be unoccupied at the center of the zone of the three transition-metal (111) surfaces, Ni, Pd, and Pt. Indeed, an unoccupied Shockley-type surface state has been predicted in a first-principles calculation of the Pd(111) surface by Louie.[12] This latter calculation has been shown to be relatively accurate in its description of the occupied surface states on this surface.[13]

Two early inverse photoemission studies of the Pd(111) surface by one of the present authors[14,15] have been inconclusive. The first study[15] was later found to be troubled by angular resolution. The subsequent study,[14] whilst withdrawing the earlier assignment of surface state, was still unable to conclusively associate the observed structure with bulk-derived features. Consequently, it was suggested that the attempt to fit the dispersion of the observed peak to the bulk band structure was complicated by the presence of a surface feature.

Finally we note that on both Ni(111) and Pd(111), image states have been observed in the $L_{2'}L_1$ band gap in the different inverse photoemission studies.

In this paper we report the first inverse photoemission study to our knowledge of the Pd(111) surface with higher resolution. We are clearly able to show that this surface supports a surface state at the bottom of the $L_{2'}L_1$ gap. We are further able to demonstrate that the same one-dimensional models applied to the surface states on noble metals also apply to this transition-metal surface.

EXPERIMENTAL PROCEDURE

The present inverse photoemission study was carried out on an experimental apparatus described in detail elsewhere.[16] This system consists of a grating spectrometer allowing detection of photons in the range 10–30 eV with a resolving power of approximately 75. Electrons are obtained from a source having an energy spread of approximately 275 meV (Ref. 17) and the incident beam allows a momentum resolution of 0.1 Å^{-1}. Inverse photoemission spectra are recorded as a function of incident electron beam energy for different angles of incidence.

The palladium crystal was the same one that we have used in our two earlier studies[14,15] and again we note that it was oriented in the (111) direction to within 1°. Standard cleaning procedures included cycles of argon bombardment and annealing at approximately 800 °C. Low-energy electron diffraction and Auger electron spectroscopy were used to monitor surface order and cleanliness.

EXPERIMENTAL RESULTS

Figure 1 shows inverse photoemission spectra recorded from the clean Pd(111) surface as a function of electron beam energy, defined with respect to the Fermi level. The peak immediately above the Fermi level we identify as associated with the unoccupied *d* band, as in our earlier studies.

Two other features are clearly observed which show no dispersion as the incident beam energy is changed. These features at 1.3 eV above the Fermi level and 0.50 eV below the vacuum level are identified as surface states, the higher binding-energy state being the anticipated Shockley- or crystal-derived state and the state near the vacuum level being the image state derived from the long-range image potential.

In Fig. 2 we show inverse photoemission spectra recorded as a function of the angle of incidence of the electron beam for an incident beam energy of 16.85 eV. It will be seen that both features disperse upwards away from the Fermi level and least-squares fitting produces effective masses equal to approximately $0.35m_e$ for the Shockley state and $1.0m_e$ for the image state. We believe that the dispersion of the surface state is influenced by interaction with the bulk band edge, which lies 1.0 eV above E_F at the center of the zone and disperses in the $\overline{\Gamma}\,\overline{K}$ direction with an effective mass of approximately $0.3m_e$.[14]

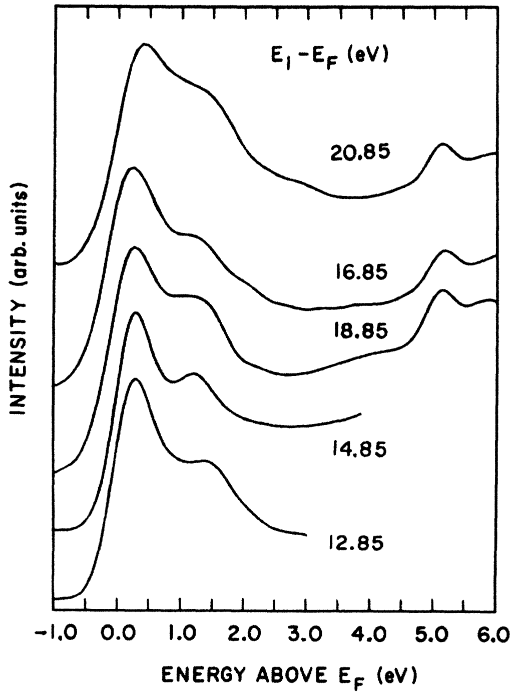

FIG. 1. Inverse photoemission spectra recorded from the Pd(111) surface as a function of incident electron beam energy with respect to Fermi level E_F.

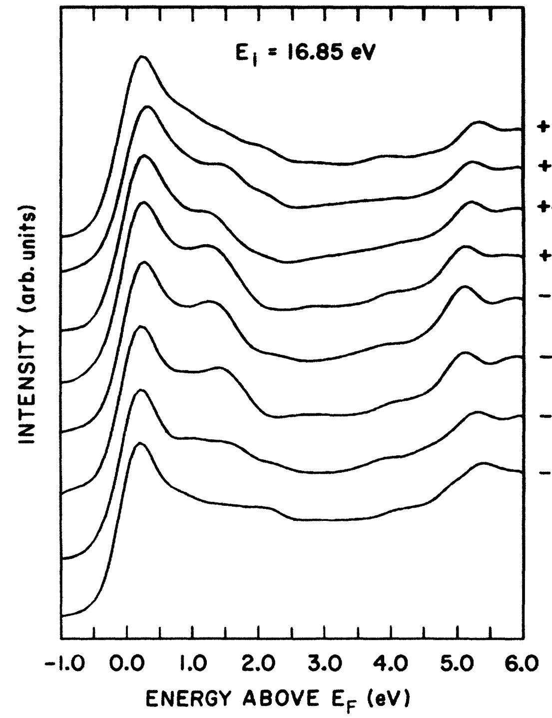

FIG. 2. Inverse photoemission spectra recorded as a function of angle of incidence defined with respect to the surface normal. The incident electron beam energy is 16.85 eV with respect to the Fermi level E_F.

DISCUSSION

It has been shown elsewhere[6,7] that simple one-dimensional models may be used to give a reasonable quantitative measurement of the binding energies of surface states. We briefly review those models.

In the bulk band gaps, opened up by the periodic crystal potential, electronic states may exist at the surface with complex momentum; divergences prohibit these states from existing in the bulk. Thus, there exists within the band gaps a complex band structure. The exact location of the surface state on the complex bands is determined by the matching conditions at the solid-vacuum interface.

Traditionally the solid-vacuum interface has been represented in simple models by a step potential.[18] With the observation of surface states derived from the long-range image potential and the subsequent observation that for a given metal there exists a crystallographic dependence on their binding energies,[6] it became clear that the step potential should be replaced by the image potential.

It was realized that a simple multiple-scattering formalism could be used to give a quantitative measure of the binding energies. In this phase model, an electron is pictured as being trapped between the bulk crystal potential and the image potential barrier. If ϕ_c is the phase change on reflection from the crystal and ϕ_B is image barrier phase change, then stationary states exist for energies such that the total phase change

$$\phi=\phi_c+\phi_B=2\pi n \ , \tag{1}$$

where n is an integer. For $n \geq 1$, the phase model predicts bound states near the vacuum level corresponding to the image states; in addition, "$n=0$" states are predicted several eV below the vacuum level that can be identified with the standard Shockley- or crystal-derived surface states. In a subsequent paper,[7] it was demonstrated that the image states and crystal-derived states are related in a simple manner: The binding energy of surface states is a multibranch function of the position of the image plane. Then for a given image plane position, a whole series of states, including both the $n=0$ crystal-derived and $n \geq 1$ image states, are predicted. Since the position of the image plane is related to the response of the electron density at the surface, the measurement of the binding energy of the image states gives, in principle, information about both the electron density at a surface and the position of the image plane. However, since the electron density at a surface is sensitive to details of the surface potential, it may not be possible to extract model-independent values of the image plane position.

In Fig. 3(a) we show the results of applying the phase-analysis method to the Pd(111) surface. The edges of the band gap are fitted to the experimental results of Himpsel and Eastman.[19] From the figure it will be seen that the model predicts a binding energy of 1.28 eV above the Fermi level for the $n=0$ crystal-derived state and 0.56 eV below the vacuum level for the $n=1$ image state. Reference to the experimental results in Fig. 2 shows good agreement between the model and experiment; the measured binding energies being 1.3 eV above the Fermi level for the crystal-derived state and 0.50 eV below the vacuum level for the image state.

In Fig. 3(b) we show the binding energy of the surface states as a function of the image plane position for Pd(111) determined using the wave-function matching method.[7] The binding energy ε_b is related to the parameter κ by the expression

$$\varepsilon_b=\frac{0.85}{\kappa^2} \ . \tag{2}$$

In our earlier applications to the noble metals, the potential in the plateau region was approximated by subtracting the potential producing the band gap from the inner potential. This produced a value characteristic of the potential found both in first-principles surface calculations and for a saturated potential. However, for Pd(111) this method produces a potential in the plateau region which is quite small (-2 eV). Using such a value, the image plane for an $n=1$ binding energy of 0.52 eV is 0.22 a.u. outside the crystal edge and the $n=0$ crystal-derived state occurs at a binding energy 2.4 eV above E_F independent of the image plane position. Using a more reasonable value for the plateau region we obtain [(Fig. 3(b)] binding energies of 0.52 eV ($n=1$), 0.17 eV ($n=2$), and $E_F+1.37$ eV ($n=0$) for an image plane near the

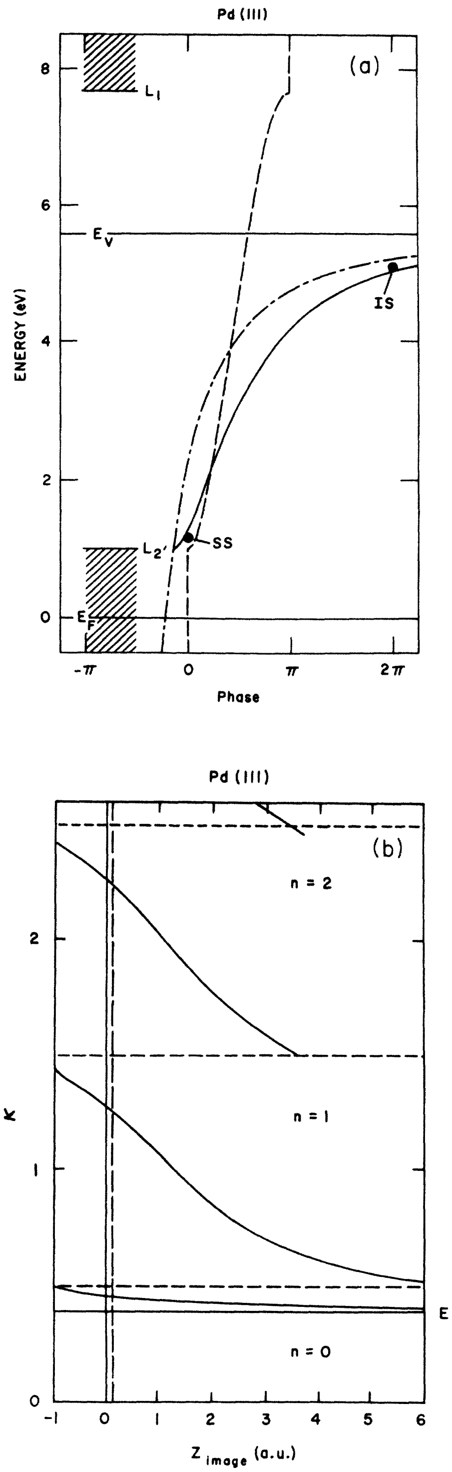

FIG. 3. (a) Phase-analysis method applied to the Pd(111) surface; long-dashed–short-dashed, phase ϕ_B; long-dashed line, phase ϕ_c; solid line, total phase ϕ as defined in the text. The experimentally observed binding energies of the $n=0$ surface state and the $n=1$ image state are indicated by SS and IS, respectively. (b) Result of applying wave-function matching to the Pd(111) surface. The image plane position is defined with respect to the jellium edge and the appropriate image plane is indicated by the vertical dashed line. The parameter κ is defined in the text.

crystal edge. While the exact value of the plateau region influences the binding energy of the $n=0$ state and the position of the image plane, the *existence* of the $n=0$ state is independent of these details. A related point concerns the use of the simple Goodwin[18] form for the bulk wave function. There is experimental evidence[20] that the Goodwin decay length in some cases may be too large. Decreasing the decay length causes the image plane to move out from the crystal edge. Even with such changes, we find that the image plane for Pd(111) is closer to the crystal edge than for Ag(111) consistent with the fact that the atomic density for Pd is more compact than for Ag.

We note that our method places the image plane considerably closer to the jellium edge than either the model of Lang and Kohn[21] or indeed typical values derived from studies of inert-gas adsorption.[22] However, we note that a recent jellium calculation using a nonlocal exchange-correlation potential[23] and a further attempt to fit the experimental observations of the core-level observed in inert-gas physisorption[22] both suggest that the image plane is closer to the jellium edge than originally proposed by Lang and Kohn.

CONCLUSIONS

In conclusion we have clearly demonstrated that the transition-metal Pd(111) surface supports a Shockley-type surface state, as do the noble-metal surfaces. The phase model is again found to be capable of making quantitative predictions of the binding energies of both this state and the $n=1$ image state. As on the (111) planes of the noble metals we find that the binding energies of these states indicate that the image plane is close to the jellium edge, even though the image state has a binding energy characteristic of the binding energies of the image states on the (001) surface of the noble metals.

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