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Localized states at metal-metal interfaces: An inverse photoemission study of Pd/Nb(110)

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We present the results of experimental and theoretical investigations of the Pd/Nb(110) interface. In the experiment we identify an interface resonance which clearly displays the required two-dimensional character of such a state. We further show that it is derived from a surface resonance present on the bare niobium. The presence of the Pd overlayer serves to localize and increase the surface character of this state rather than quenching it. The theoretical calculations support the identification of this state as an interface state and further indicate that its intensity reflects the strength of the interface bond.

The study of metallic interfaces or thin films is an area of considerable interest, largely because of their unusual catalytic[1] and magnetic properties[2] which are associated with modifications in electronic structure.[3-5] One system that has received considerable attention has been the growth of Pd overlayers on the Nb(110) surface.[3] The initial motivation behind these studies was the observation that the hydrogen uptake rate, while relatively small for clean Nb(110), increases rapidly and approximately linearly with Pd coverages in excess of one monolayer.[6] In the region of one monolayer (or less) the photoemission spectra reveal a reduction in the density of states at the Fermi level[7] and indeed at this coverage the surface is observed to be relatively inert to the adsorption of carbon monoxide.[8] Studies at lower temperatures show that carbon monoxide can be weakly chemisorbed with a photoemission spectrum not unlike that of carbon monoxide adsorbed on a copper or silver surface.[9] A simple intuitive view of the lowered *d* bands for the monolayer coverage would be that the states are occupied Nb—Pd bonding states coming from the hybridization of the *d* bands at the interface. Further studies of the photoemission cross-sectional behavior[7] confirmed both Nb and Pd components in the bands and indicate them to be d_{xz} and d_{yz} in character. It is the unoccupied states which are of concern here. We present the results of an inverse photoemission study of the Pd/Nb(110) system which represents one of the first studies of unoccupied levels localized at a metal-metal interface. We are able to demonstrate that the predominant unoccupied orbital involved in the interface bond is derived from a Nb surface resonant state. We show that the Nb band, which shows substantial three-dimensional dispersion for the bare Nb becomes much more two dimensional, localizing in the interface upon the adsorption of Pd. We further find that unlike earlier photoemission[10] studies of the occupied levels, we are able to observe changes in the interface bonding as indicated by shifts in the binding energy of the interface state. While the presence of the interface state, and indications of its character, are clearly established by the experiment, these results have been augmented by a set of band theory calculations for a slab of Nb(110) with and without a commensurate adlayer of Pd as well as bulk multilayers of Pd-Nb having the Nb(110) layer spacing. The calculated results are in accord with the experimental data and their interpretation. Further, calculations done for other Nb interfaces suggest that the strength of the interface state may correlate with the strength of the bonding between the unlike atom layers at the interface.

There are at least two types of states localized at a metallic surface or interface. Tamm states involve levels pulled off from the edge of a band gap reflecting the change in the atomic potentials at the interface. The occupied interface state observed[4] for Cu adsorbed on Ru(0001) would seem to be of this type. The interface states encountered here are of the $n=0$ or crystal derived resonance states[11] type, which occur even in the absence of a gap and are the result of the change in scattering of bulk and evanescent Bloch states due to the presence of an interface, including the solid vacuum. It should be noted that conventional surface states are usually destroyed upon the introduction of an adsorbate. Here they become enhanced and even more localized at the interface between adsorbate and substrate. Such localized states obviously will be important to the transport properties across the interface, as well as the bonding of impurities (adsorbates) at both the interface and surface.

The experimental arrangement has been described in detail elsewhere.[12] Briefly, the apparatus consists of a custom-built electron source and grating spectrometer designed to detect photons in the range 10–30 eV. The overall energy resolution is typically 0.3 eV and in the present series of experiments each spectrum was acquired in 15–20 min. The (110) orientation was prepared by recrystallizing Nb foil, 0.005 in. thick, with repeated anneals to 2000 °C. Sample cleanliness and orientation were monitored by Auger electron spectroscopy and low-energy electron diffraction (LEED), respectively. Pd overlayers were deposited by evaporation from a tungsten wire boat heated to ≈1300 °C. A quartz crystal was installed to monitor the growth of the overlayers, and this was compared with both Auger electron spectroscopy and the variation in the secondary electron current measured at the sample as a result of the incident electron beam used for inverse photoemission.

The slab calculations were done employing the full-potential linearized-augmented-plane-wave (FLAPW) method[13] while the various bulk multilayer calculations were done employing muffin-tin potentials and the linearized augmented Slater-type orbital method[14] (LASTO). These local-density-theory self-consistent total-energy methods have been documented elsewhere[13,14] and this will not be repeated here.

As Pd is deposited, it firstly grows epitaxially on the Nb(110) substrate until a coverage of slightly less than a monolayer.[10] At this point it is thought that regions of Pd undergo a first-order phase transition and there is coexistence between the epitaxial Pd and Pd in the fcc(111) structure. This transition is marked by sharp changes in the LEED pattern but no marked changes have been noted in photoemission spectra. The multilayer calculations provide a measure of the energetics of varying the thickness of the commensurate Pd layer. They indicate a binding of $\sim -\frac{3}{8}$ eV per Nb-Pd pair in the interface and a distortion energy of $\sim +0.25$ eV per Pd atom in a lattice constrained to be commensurate with Nb(110). Thus at 1.5 layer coverage these bulk terms (note there are surface terms as well) indicate a net zero binding, a circumstance encouraging the Pd overlayer to reorganize into an energetically more favorable lattice.

In Fig. 1 we show the inverse photoemission spectra recorded as the Pd overlayers are deposited. There is both a shifting and a variation in the intensity of the peak labeled *A*. Studies of the clean surface indicate that this peak corresponds to transitions into the Σ_1 band going from $\Gamma_{25'}$ to $N_{1'}$. This band has d_{xz}, d_{yz} character at the center of the zone and p_z character at the N point. It should be noted that these band features lie in the *hollow* of the density of states characteristic of the bulk bcc transition-metal band structure. The intensity of peak *A* goes through a maximum when the Pd coverage is equal to one monolayer, an indication that it is associated with the interface. Also observe that as the Pd coverage increases up to approximately a monolayer the level slowly moves further from the Fermi level, its binding energy changing from 1.1 to 1.6 eV with respect to the Fermi level. With the growth of the second monolayer this interface feature moves back towards the Fermi level, its final binding energy being 1.35 eV with respect to the Fermi level.

In Fig. 2 are shown inverse photoemission spectra recorded from the Pd monolayer coverage, compared to the clean Nb spectra at the same incident electron ener-

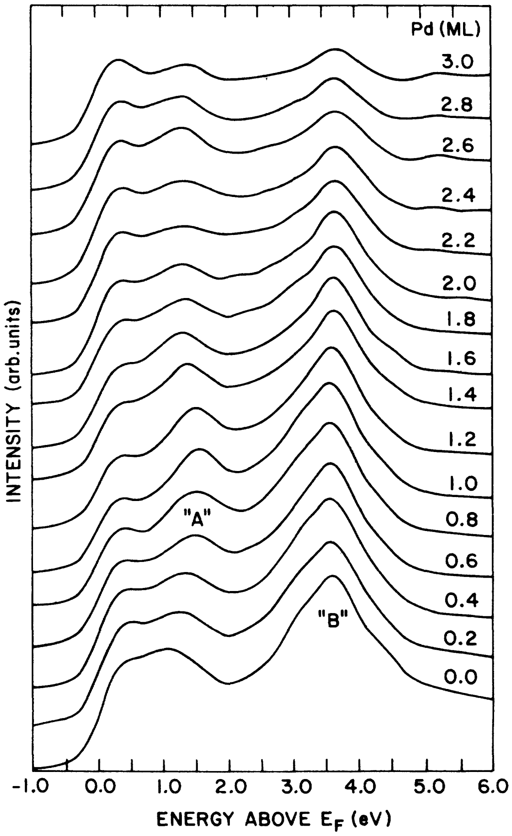

FIG. 1. Inverse photoemission spectra recorded for an electron beam normally incident on a clean Nb surface and the same surface with different coverages of Pd. The electron beam energy is 16.85 eV with respect to the Fermi level. Two different Nb *d*-band features are labeled *A* and *B*.

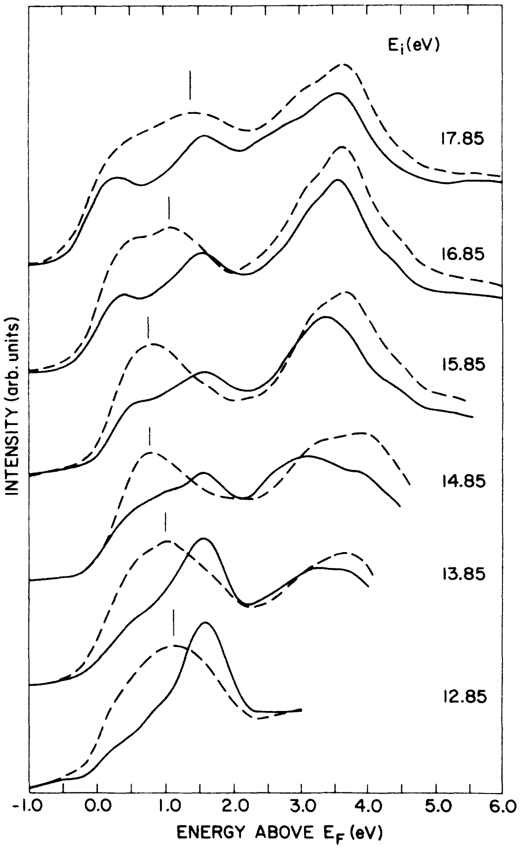

FIG. 2. Inverse photoemission spectra recorded from the clean Nb(110) surface (dashed spectra) and the Nb surface with a monolayer of Pd (solid line spectra). The normally incident electron beam energy with respect to the Fermi level is indicated.

gies, the variation in incident energy corresponding to a variation in the probed state's momentum perpendicular to the surface, $k_\perp$. We see from the figure that the Nb A band, which was identified as a Σ_1, shows dispersion with $k_\perp$ for the clean Nb but is replaced by a peak showing little or no dispersion for the interface. This clearly demonstrates the evolution from a three-dimensional-like band into a state with two-dimensional character appropriate for an interface state. Further, examination shows that the intensity of this "interface state" increases at points in $k_\perp$ at which the Σ_1 band of the substrate Nb comes closest to it in binding energy. Similar observations have previously been made in both photoemission[15,16] and inverse photoemission studies[17] of the intensity of crystal-derived surface states. This intensity variation in momentum space is thought to be a reflection of the localization of the state in real space. Indeed, the present experimental observations indicate that the state is not entirely localized at the interface but decays away from the interface.

Calculated local densities of states for three of the atomic sites are plotted in Fig. 3 for the Nb(110) slab, the Pd/Nb(110) slab, and a Pd_3Nb_3 multilayer. These densities of states were obtained for the electronic charge within atomic spheres of radii ~2.5 a.u., thus the interstitial charge has been left out of the accounting. The plot at the lower left-hand corner corresponds to the density of states appropriate to bulk Nb. Note the characteristic bcc hollow ~1 eV above the Fermi level which contrasts with the $\rho(\varepsilon)$ for most of the other Nb sites which are represented. In the case of Nb(110) both the surface Nb and the subsurface Nb layer, s-1, show substantial peaking at ~1 eV while the Pd and s-1 Nb, involved in the interface of Pd/Nb(110), show similar peaking at several tenths of an eV higher in energy. This shift is in the same direction as that of the peak A in the experiment (see Fig. 1). The peaking is almost undiscernable for the Nb once removed from the interface, the s-2 site; thus we are involved with a set of states almost entirely localized at the interface accounting for the lack of $k_\perp$ dispersion seen in the experiment. Inspection of the bare Nb $\rho(\varepsilon)$ suggests that these states fall off much more slowly in the absence of the interface, behavior characteristic of a surface resonance decaying into the bulk. The $\rho(\varepsilon)$ for the bulk Pd_3Nb_3 multilayer show a double-peaked feature at ~1 eV above the Fermi level and this is likely associated with interference effects between adjacent interfaces. Given that the slab results were obtained with full potentials and the bulk multilayer with muffin-tin potentials using different computational machinery, it is remarkable how similar the $\rho(\varepsilon)$ are.

In addition to the localization of the states involved in the peak at 1–1.5 eV, there are two other visible effects associated with bonding at the interface. First, the high Pd-like $\rho(\varepsilon)$ is pushed down below and away from the Fermi level, much as it is whenever Pd is involved in alloy compound formation. Secondly, there is a depletion in the interface Nb site $\rho(\varepsilon)$ in the same region, 0–2 eV below the Fermi level. Inspection of the multilayer results suggest that this Nb depletion is associated not so much with the Nb levels following the lowering of the bands for Pd as with an actual loss of several tenths of d-like electronic charge at the Nb site. Thus a bonding-antibonding situa-

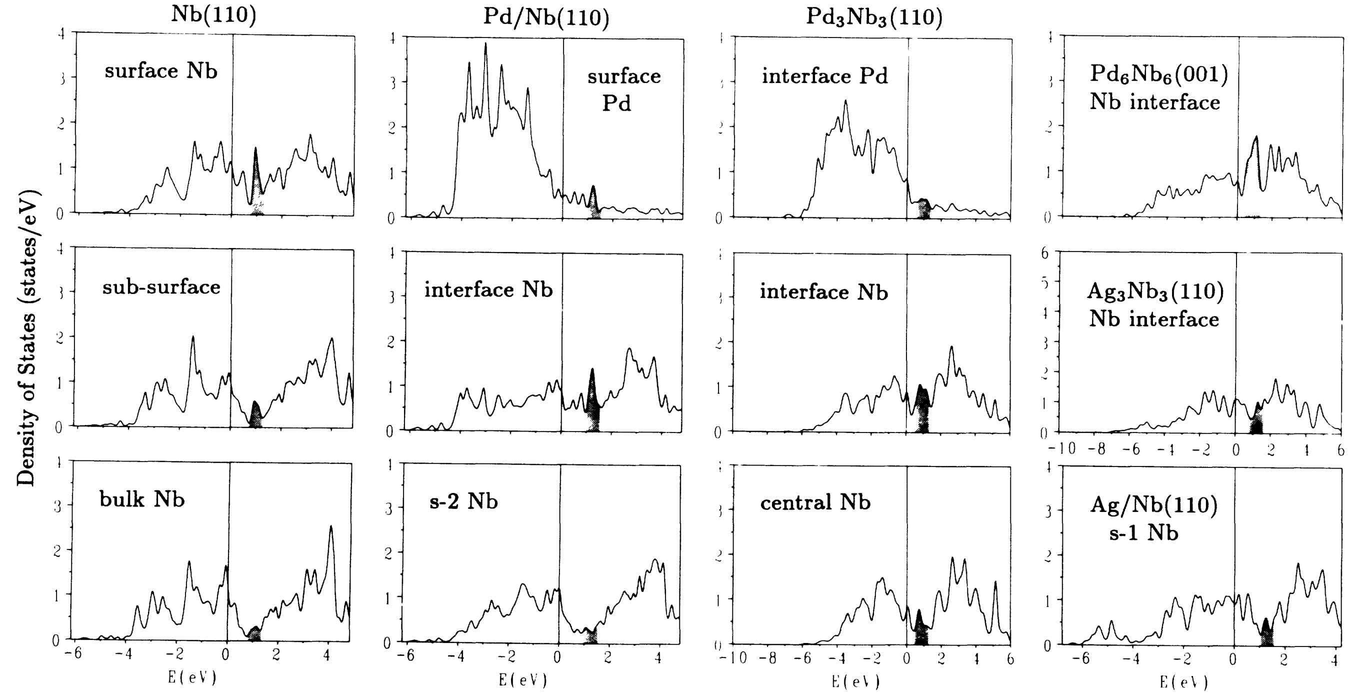

FIG. 3. Calculated local density of states at various sites (left to right) for the Nb(110) surface, for the commensurate Pd/Nb(110) surface, for the bulk Pd_3Nb_3 (110) multilayer, and for the $Pd_6Nb_6(001)$ and $Ag_3Nb_3(110)$ bulk multilayers and commensurate Ag/Nb(110) surface. The shaded regions delinate the positions of the surface and interface peaks in the various calculations.

tion seems to have arisen with Pd wave function character pushed deeper and Nb's up and above the Fermi level.

The right-hand column of Fig. 3 indicates the local density of states for the interface Nb site for a multilayer of Pd/Nb(100) and for both an adsorbed layer of Ag and a multilayer of Ag/Nb(110). The Pd-Nb interface bonding energy for Pd/Nb(100) is calculated to be about -0.8 to -0.9 eV per Nb-Pd pair or more than twice that at the (110) surface. The interface state associated with this increased binding is a far more pronounced feature of the density of states. In contrast, the bulk phase diagram for Ag-Nb displays neither compounds nor any miscibility and the calculated Ag/Nb interface energy is calculated to be nonbinding as is required by this phase behavior. Attending this is the disappearance of the interface peak. Thus it appears that in these systems, the stronger the interface bonding, the more enhanced is the interface state.

In summary, it has already been established[11] that there will be resonance states which are localized to some degree at the surface of a pure metal and which may or may not be occupied. This has been observed for bare Nb(110) and while concentrated close to the surface, they ar sufficiently delocalized so that there is some $k_\perp$ dispersion. The new information presented here is that such resonance states may actually sharpen up, becoming much more localized and chemically shifted at an interface involving active bonding between the two atomic species rather than being quenched as is generally the case for conventional surface states. The experiments indicate this for a surface adlayer, in this case Pd/Nb(110), and the calculations suggest that this occurs at the interface of a bulk multilayer as well.

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[1] J. W. A. Sachtler, J. P. Biberian, and G. A. Somorjai, Surf. Sci. **110**, 43 (1981).

[2] B. T. Jonker, K. H. Walker, E. Kisker, G. A. Prinz, and C. Carbone, Phys. Rev. Lett. **57**, 142 (1986).

[3] M. Strongin, M. El-Batanouny, and M. Pick, Phys. Rev. B **23**, 3126 (1980).

[4] J. E. Houston, C. H. F. Peden, P. J. Feibelman, and D. R. Hamann, Phys. Rev. Lett. **56**, 375 (1986).

[5] S. Xinyin, D. J. Frankel, J. C. Hermanson, G. J. Lapeyre, and R. J. Smith, Phys. Rev. B **32**, 2120 (1985).

[6] M. A. Pick, J. W. Davenport, M. Strongin, and G. J. Dienes, Phys. Rev. Lett. **43**, 286 (1979).

[7] M. El-Batanouny, M. Strongin, and G. P. Williams, Phys. Rev. B **27**, 4580 (1983).

[8] M. W. Ruckman and M. Strongin, Phys. Rev. B **29**, 7105 (1984).

[9] M. W. Ruckman, P. D. Johnson, and M. Strongin, Phys. Rev. B **31**, 3405 (1985).

[10] M. Sagurton, M. Strongin, F. Jona, and J. Colbert, Phys. Rev. B **28**, 4075 (1983).

[11] M. Weinert, S. L. Hulbert, and P. D. Johnson, Phys. Rev. Lett. **55**, 2055 (1985).

[12] P. D. Johnson, S. L. Hulbert, R. F. Garrett, and M. R. Howells, Rev. Sci. Instrum. **57**, 1324 (1986).

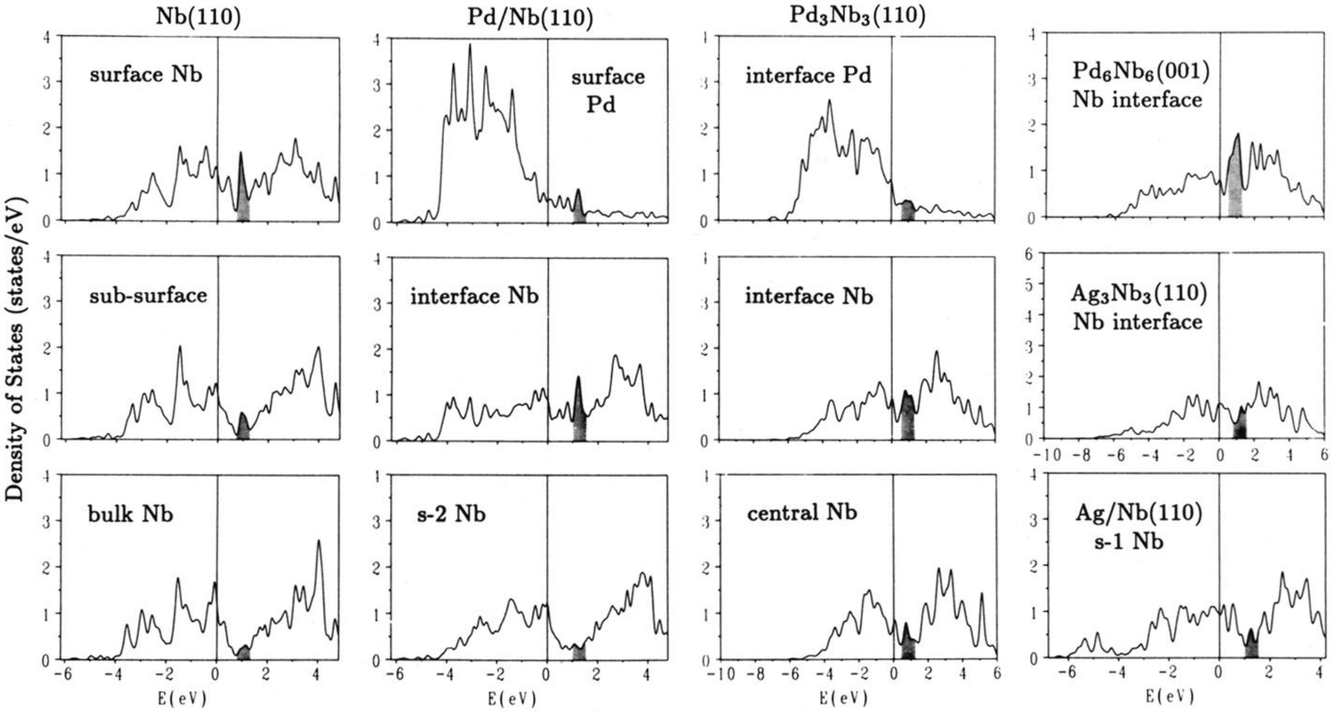
[13] E. Wimmer, H. Krakauer, M. Weinert, and A. J. Freeman, Phys. Rev. B **24**, 864 (1981).

[14] R. E. Watson, M. Weinert, and J. W. Davenport, Phys. Rev. B **35**, 9284 (1987) and references therein.

[15] S. G. Louie, P. Thiry, R. Pinchaux, Y. Petroff, D. Chandesis, and J. Lecante, Phys. Rev. Lett. **44**, 549 (1980).

[16] S. D. Kevan, N. G. Stoffel, and N. V. Smith, Phys. Rev. B **31**, 1788 (1985).

[17] S. L. Hulbert, P. D. Johnson, and R. F. Garret, Phys. Rev. B **33**, 7326 (1986).



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