Relationship between Electronic Structure and Hydrogen-Uptake Kinetics

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Striking changes have been observed in the photoemission energy-distribution curves from two phases of Pd overlayers on (110) Nb surfaces. In the commensurate (110) phase the Pd 4*d* band is found to have an edge about 1.5 eV below E_F , similar to that of a noble metal. When the transition to the incommensurate Pd(111) phase occurs, the Pd 4*d* bands broaden and cross the Fermi level. As the density of Pd 4*d* states increases near E_F , a dramatic increase in the hydrogen-uptake rate through the Pd is observed.

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Recently it was reported that a few layers of Pd dramatically increase the rate of uptake of hydrogen into bulk niobium¹ and, in fact, the process of hydrogen dissociation becomes so efficient that it is estimated that in the composite system every hydrogen molecule that hits the surface dissociates and is absorbed in the bulk. Further $work^2$ showed that up to about one monolayer, Pd on the niobium (110) surface grows in a commensurate 1×1 Pd structure which we call Pd*(110) and in this structure no increase of hydrogen-uptake rates above that seen in pure Nb was observed. Additional deposition leads to the appearance of low-energy electron-diffraction spots characteristic of the Pd(111) fcc mesh, together with satellite patterns which result from multiple scatter ing^3 between the underlying (110) structure and the Pd(111) structure. We interpret this as evidence for a structural phase transition in the Pd overlayer after about one-monolayer coverage,² or possibly the growth of the Pd(111) structure in a second layer. The appearance of the Pd(111)signature is accompanied by a dramatic increase in the hydrogen-uptake rate² by the bulk sample, which approaches unit sticking coefficient as the Pd(111) layer thickness increases to a few layers.

This system provides, then, an excellent prototype for studying how subtle changes in crystal structure influence physical phenomena such as hydrogen uptake, presumably through the changes in electronic structure which can be crucial to hydrogen dissociation and chemisorption. The importance of electronic effects is demonstrated by the simple result that the hydrogen-uptake rate increases as the Pd structure becomes more dense. To understand the electronic structure in the two phases we have carried out angle-resolved photoemission studies which we report here. The photoemission measurements were done in ultrahigh vacuum (10^{-10} Torr) , with light from a gasdischarge lamp [(HeI 21.2 eV) and (NeI 16.8 eV)] and from synchrotron radiation at the University of Wisconsin storage ring. The analyzer used was a Vacuum Generators spherical condenser with energy resolution of 0.1 eV and an electron acceptance cone of 4° . When the gas-discharge lamp was used the working pressure was 2×10^{-9} Torr. The substrate was a 0.001-in. Nb foil which was cleaned by resistive heating to about 2100 °C and was found to recrystallize with large (110) crystallites. The sample-cleaning technique that was used prevented the incorporation of azimuthal rotation. Auger-electron spectroscopy was used to provide a reliable calibration of coverage and thickness of Pd. Full details of the sample preparation and characterization are contained in Ref. 2.

In Fig. 1 we compare normally emitted photoelectron energy-distribution curves (EDC's) for a Pd(111) overlayer, curve A, and a Pd*(110) overlayer, curve B. The spectra were taken at a photon energy of 90 eV, where the Pd 4d cross section is high relative to the Nb 4d cross section. Curve C shows emission from a Nb (110) surface normalized to curves A and B, which indicates how weak the Nb 4d-band emission is, relative to the Pd 4d-band emission at this photon energy.

A comparison of curves A and B shows very striking differences in the emission near the Fermi level. The 4*d*-band emission in Pd*(110) is narrower and deeper than that for Pd(111). The



FIG. 1. Normal-photoemission spectra at $\hbar\omega = 90$ eV: Curve A, a Pd(111) overlayer on Nb(110); curve B, a Pd*(110) overlayer on Nb(110); and curve C, Nb(110). The insets show schematically the hydrogen-uptake curves where the change in resistance (ΔR) of the Nb foil is plotted against time. Hydrogen uptake is measured by the change in the resistance of the Nb foil with hydrogen bulk concentration.

data suggest, in fact, that the Pd 4*d*-band density of states is low near $E_{\rm F}$ for the Pd*(110) overlayer. Further data taken at various angles away from normal emission support this conclusion. One is indeed tempted to remark that the Pd*(110) overlayer partial 4*d* density of states is similar to that of a noble metal such as silver which also has a low 4*d*-band density close to $E_{\rm F}$.

In Fig. 2, spectra A-D show the evolution of the electronic structure of the Pd-Nb system as a function of coverage at a photon energy of $\hbar\omega$ = 21.2 eV where the Nb 4d and Pd 4d cross sections are similar. Also shown, as an inset, are curves representing the hydrogen uptake of the various samples, which demonstrate that the increase in the rate of hydrogen coincides with the structural change from Pd*(110) to Pd(111). The Pd(111) spectra exhibit the double-peaked structure reported previously by several groups.⁴⁻⁶ From this data we draw two conclusions. First, at low coverages a peak develops at -3 eV which



FIG. 2. Normal-photoemission spectra at $\hbar\omega = 21.2$ eV: Curve A, a Pd(111) overlayer on Nb(110); curve B, a Pd overlayer on Nb(110) at the Pd(111) to Pd*(110) transition; curve C, a Pd*(110) overlayer on Nb(110); and curve D, Nb(110). The insets show schematically the hydrogen-uptake curves where the change in the resistance (ΔR) of the Nb foil is plotted against time. Hydrogen uptake is measured by the change in the resistance of the Nb foil with hydrogen bulk concentration.

continually shifts to lower binding energies as the coverage is increased, reaching -2.4 eV at a commensurate monolayer. To establish the character of this peak we investigated its photon-energy-dependent cross section, which exhibits some similarity to that of the d band in pure Nb. This, together with the fact that Nb has no structure at -2.4 eV, suggests that the peak can be attributed to a Nb-Pd d resonance comprising contributions from both alloy constituents. This conclusion is further supported by the fact that this peak is the first to appear with Pd coverage and may be responsible for the bonding. The second conclusion drawn from Fig. 2 is that the total density of states near the Fermi level is low for the $Pd^*(110)$ overlayer. The emission strength at -0.4 eV is attributed to emission from the Nb substrate for the following reasons: (a) its photon-energy dependence strongly follows that of the Nb *d* band; (b) its angular dependence is similar to that of a Nb(110) peak located also at -0.4eV; and (c) it is attenuated as the Pd coverage is increased in the first monolayer. Furthermore, it is more strongly attenuated at $\hbar\omega = 50$ eV, where the mean free path is very short, than at $\hbar\omega = 21.2$ eV. Such a trend is consistent with subsurface emission.

Changes in work function are not revealed by the spectra in Figs. 1 and 2. In fact, the growth of the $Pd^{*}(110)$ overlayer does not significantly change the work function from that of the Nb(110)substrate. However, once the structural transition starts, the work function changes continuously upwards towards the value of 5.6 eV for pure Pd. The effect of hydrogen exposure on the electronic structures of Pd*(110) and Pd(111) phases is also different. In the $Pd^{*}(110)$ phase, no change is observed in either the work function or the photoemission intensity of the corresponding EDC's when the surface is exposed to hydrogen. On the other hand, exposure of the Pd(111) phase to hydrogen leads to a noticeable reduction in the photoemission intensity near $E_{\rm F}$ together with a decrease in the work function of about 0.2 eV. This is somewhat surprising since hydrogen usually increases the Pd work function.⁷ However, no characteristic hydrogen-induced peaks were detected in the angle-resolved EDC's.

The comparison, then, of the electronic structures of the Pd*(110) and Pd(111) phases reveals the following. (1) In the Pd*(110) phase the Pd 4d bands are ~4-eV wide with an edge at -1.5 eVand a low density of states near E_F similar to that of a noble metal. (2) The electronic structure of Pd(111) is similar to that of the normal transition metal for which E_F crosses the *d*-band complex at a high density of *d*-derived states. (3) The growth of the Pd*(110) phase does not significantly change the work function from that of a clean Nb value; however, once the structural transition starts, the work function changes continuously towards a Pd value of about 5.6 eV.

The low hydrogen-uptake rate into the Nb substrate bulk associated with the Pd*(110) surface phase is believed to be a manifestation of the failure of this surface to dissociate hydrogen. This view is motivated by the surprising similarity between the electronic structure of Pd*(110) and that of noble metals such as Cu,⁸ where the lowlying d states are not capable of interacting effectively with the incoming hydrogen molecule to completely remove the activation barrier, and consequently, hydrogen does not dissociate at room temperature. Further evidence for this picture is the absence of any hydrogen-induced changes in the electronic structure of $Pd^*(110)$ (both in the density of states and work function), as well as the absence of any evidence of the presence of atomic hydrogen on that surface in electron-stimulated desorption.⁹ On the other hand, in the Pd(111) phase, where the relevant *d* levels lie close to E_F , their attractive interaction with the hydrogen molecule is effective enough to completely remove the activation barrier and hydrogen readily dissociates.

Thus, an explanation for the observed differences in hydrogen-uptake rates might be the fact that the *d* band is shallower in Pd(111) than in $Pd^{*}(110)$.

Note that on the clean $Pd^*(110)$ surface we argue that the low hydrogen-uptake rate is due to a low dissociation rate. In contrast, on the clean Nb(110) surface we contend that dissociation is initially rapid until the strongly chemisorbed hydrogen limits further dissociation of the incoming H₂ molecules and slows up the uptake process.

In summary, we have found that when Pd is adsorbed on the Nb(110) surface it initially prefers to assume a commensurate structure with the Nb surface where the interaction between the Pd overlayer and the neighboring Nb atoms tends to push the bulk of the Pd 4d bands about 1.5 eV below $E_{\rm F}$. However, when coverages start to exceed a monolayer of this structure, the Pd overlayer becomes unstable and transforms to its more close-packed fcc (111) mesh, thus increasing the d-band width to about 4.5 eV. It was also found that these changes in the electronic structure of the Pd overlayer have dramatic effects on its interaction with hydrogen.

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Positron Annihilation in Graphite Intercalation Compounds

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Graphite intercalation compounds have been studied by positron annihilation experiments. In donor compounds, a highly inhomogeneous charge distribution is detected by Coulomb repulsion of the positrons from the intercalant. In acceptor compounds, however, quasifree positron-anion systems are formed within the intercalant. This is used to identify the anionic species.

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Graphite intercalation compounds (GIC's) have been studied for more than fifty years.¹ It is known that they form ordered sequences of graphite and intercalated layers.² In many cases, they exist in different "stages," where the stage n is determined by the number of carbon planes between two successive intercalated layers. In the past few years, GIC's have attracted increased interest because of possible applications in electrical conduction, catalysis, electrochemical systems, and other fields.^{3,4} Simultaneously, scientific interest has been stimulated, particularly in the field of electronic properties of these compounds.^{3,4} One area of interest concerns the local charge distribution in GIC's. Whereas earlier experiments were interpreted by a homogeneous charge distribution,⁵ recently Pietronero et al.⁶ have shown theoretically that the intercalant layer is screened nonhomogeneously according to a power law. The experiments which have been carried out so far have only revealed a distinction between the bounding graphite layers next to the intercalant and the other interior graphite layers.⁷⁻⁹ Another area of interest deals with the identification of the intercalant species within the graphite sublattice. In particular, the location and the amount of charge in the intercalant layers have been subject to discussions.¹⁰⁻¹⁵

In the present paper we report the first results of positron annihilation experiments obtained with donor- and acceptor-intercalated graphite. The effects are much larger than those normally encountered with use of the positron as a solidstate probe and there is a pronounced difference between the behavior of donor and acceptor compounds. The probability for an annihilation process with a pair momentum p_z perpendicular to the quanta emission is described by the 2γ angular correlation distribution (ACD), $N(\theta)$, where $\theta = p_z / m_0 c$. The quantity $N(\theta)$ depends on the Fourier transform of the electron-positron wavefunction product.¹⁶ In most applications of ACD, the primary aim is to investigate the electronic structure of solids. In many cases it is sufficient to approximate the positron wave function by a plane wave with wave vector $k_+ \simeq 0$. In the present experiments, however, the surprisingly pro-