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Qualitative determination of band occupancies and their correlation to chemisorption

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It is well known that Fano resonances occur at core thresholds in materials such as Ni and Pt. This is due to the high density of local final states just above the Fermi level caused by the incomplete *d*-band occupancy. Turning this argument around, we have used the presence or absence of a Fano resonance to infer information about the completeness of the *d*-band occupancy. As a prototype system we studied Pd overlayers on Nb(110), since previous work indicated that two phases of differing *d*-band counts exist. The present work confirms this and establishes the feasibility of this type of spectroscopy for studying band occupancies.

I. INTRODUCTION

It is now established[1–7] that Fano[8] resonances may be observed at core thresholds by studying valence photoemission. The resonances have been seen in materials such as Ni, Pt, Yb, and MoS_2 which have a high density of final states near the Fermi level E_F. In this paper we propose the idea of turning this type of study around to use resonance spectroscopy to deduce information about the local density of states near E_F by studying valence photoemission behavior in the vicinity of core thresholds. If feasible, the technique affords an opportunity to examine densities of states in the inaccessible region betwen E_F and the vacuum level. In addition it may be possible in alloys to study local site densities of states selected on the basis of the chosen core level.

As a prototype system for this study we selected Pd overlayers on Nb(110). This system was chosen because a series of previous experiments[9,10] showed that two phases of Pd overlayers exist on a Nb(110) surface which photoemission data suggested had different band occupancies.

II. FANO RESONANCES AS OBSERVED IN PHOTOEMISSION

A typical Fano interaction, which we consider here, can be accounted for as follows: From an atomic point of view, the ground state of a transition metal can be considered as a coherent superposition of two configurations $np^6nd^{m-1}(n+1)s^1$ and np^6nd^m which produce the appropriate *d*-hold count, whereas a noble metal has the configuration $np^6nd^{10}(n+1)s^1$. The process responsible for the Fano resonance involves the configuration $np^6nd^{m-1}(n+1)s^1$ and thus should be absent in a noble metal. This process can be described as

$$np^6nd^{m-1}(n+1)s^1+\hbar\omega\rightarrow np^5nd^m(n+1)s^1\ ,$$

which through a Coulomb interaction hybridizes with a continuum to produce

$$np^5nd^m(n+1)s^1\rightarrow np^6md^{m-2}(n+1)s^1+\cdots\ ,$$

where the ellipsis represents an unbound electron, and results in a coherent interference which is manifested as an asymmetric resonance line around the *np* core-level threshold. Thus, we expect that the strength of this type of Fano resonance will depend on the extent of the $np^6nd^{m-1}(n+1)s^1$ configuration in the ground state, which should, in other words, reflect the density of *d*-hole states above E_F. For example in Ni and Pt (Refs. 1 and 5) there are strong effects at the $3p$ and $4f$ thresholds, respectively, as measured by the $3d$ and $4d$ partial cross sections. In both materials the *d*-band occupancy is such that there is a high density of *d* holes in a very narrow energy range near E_F. In the rare earths and in the layered material MoS_2 similar effects have been reported.[4,6,7] In the case of Yb (Ref. 3) a stronger resonance has been observed for an oxidized than for a clean surface due to final-state hole effects. The technique for studying these resonances in this way can thus provide information about final-state hole densities in the neighborhood of the Fermi level and hence give band occupancy information. At present, since the shapes and strengths of the resonances are not well known, this data is only qualitative.

III. THE Pd-Nb SYSTEM

As mentioned in the introduction we have chosen to apply this technique to the study of Pd overlayers on Nb(110). This system was selected since it has already been studied in some detail[9] and has the interesting property that two overlayer structures of Pd exist, namely a commensurate phase called (110)* and an incommensurate (111) phase which were suspected of having different *d* band occupancies from the photoemission data[10] (see below). The two phases exhibit markedly different chemisorption behavior. For example, the (111) Pd overlayer is believed to dissociate molecular hydrogen impinging on the surface while the (110)* does not. This would account for the dramatic increase which is observed regarding the rate of hydrogen uptake of the system. Deuss and Van der Avoird[11] have considered dissociative chemisorption of H_2 and Ni and Cu, where the *d*-band occupancies are markedly different. Their calculations point towards a correlation between the existence of an activation barrier for dissociation and the *d*-band occupancy. It is of considerable interest then to determine whether, for example, the Pd(111) overlayer has a significantly different band occupancy or more holes near E_F than the (110)* overlayer.

It is worth remarking in the central context that when Pd overlayers are put down on Nb an alloy is created whose bands are formed by hybridization from both the Nb and Pd valence electrons. Our work showed, however, that despite this one can, from the multiplicity of valence emission peaks, determine which ones have predominantly Pd 4*d* and which Nb 4*d* character. This determination is based on the behavior of the photoemission cross sections of the peak over the photon energy range 20–100 eV. For example, the Nb 4*d* peaks undergo a large resonance at the Nb 3*p* threshold at ~31 eV and a Cooper minimum towards 100 eV, while the Pd 4*d* cross sections are monotonically decreasing throughout this range with a resonance at ~51 eV.

Recent photoemission energy-distribution curves[10] (EDC's) indicate major changes in the occupied valence-band density of states between Pd(110)* and Pd(111) overlayers, which are reproduced in Fig. 1. This shows photoemitted electron energy-distribution curves at $\hbar\omega = 90$ eV. The spectra are normalized to the incident photon flux and it can be seen that the Pd 4*d* emission is much stronger than the Nb 4*d* substrate emission (dotted curve) due to the photoexcitation cross-section effects just discussed. Thus, the figure highlights changes in those bands which have Pd 4*d* character. We can see clearly that for the (110)* overlayer (solid curve) the Pd 4*d* band appears to be deeper and to have an edge at ~1.5 eV below E_F. In fact, scanning the two-dimensional Brillouin zone of the corresponding (110) bcc mesh indicated that the Pd *d* band was about 1 eV below E_F. The *d* band for the (111) phase (dashed curve) lies shallower with its edge crossing E_F similar to the structure of bulk Pd(111). The (110)* and (111) phases thus appear to resemble noble and transition metals, respectively, in that in the Pd(110)* case there appears to be a full band occupancy (a *d*-band count of 10), whereas in the Pd(111) case the band occupancy appears to be incomplete.

IV. EXPERIMENTAL ASPECTS

In this paper we directly address this band occupancy question using photoelectron spectroscopy in

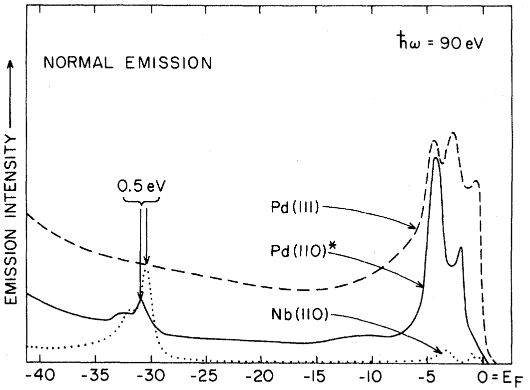

FIG. 1. Normal photoemission spectral energy-distribution curves at $\hbar\omega = 90$ eV for Pd(111) and (110)* overlayers on Nb(110). The emission from the Nb(110) substrate is also shown. Nb 4*p* core-level shifts can be seen for the Pd(110)* overlayer.

the constant initial-energy spectral (CIS) mode. In this, the electrons photoemitted by the sample from an initial energy $-E_i$ at a photon energy $\hbar\omega$ are collected by the analyzer at a pass energy $E_P = \hbar\omega + E_i - W$, where W is the work function. The spectra are generated by synchronously scanning E_P and $\hbar\omega$, thus keeping $-E_i$ fixed. Each spectrum therefore represents the excitation probability versus $\hbar\omega$ for states of a particular initial energy $-E_i$. These are usually rather smooth functions of $\hbar\omega$ except at small $\hbar\omega$ values due to final-state effects. At core thresholds, however, as discussed earlier, configuration interactions can markedly change the valence-emission spectrum superimposing a Fano profile on the smooth background. The strength of this configuration interaction depends primarily on the number of hole states available for the core level to be excited into, and how localized in energy the states are. In the case of the transition metals such as Pd, we expect the hole states to be localized and the interaction term to be large. The results obtained on Ni and Pt (Ref. 1) confirm this. Studying CIS spectra in the vicinity of core thresholds, then, can provide a direct qualitative method for estimating the band occupancies by being sensitive to the number of holes near E_F.

To obtain CIS data a continuum excitation source is required. The data presented here were taken at the University of Wisconsin synchrotron radiation center using radiation from the Tantalus I 240-MeV electron storage ring. The radiation was monochromatized using a double-grating toroidal grating monochromator with a 15° angle of incidence at the grating. A refocusing mirror brought the radiation in to the center of a Vacuum Generators double-axis ADES 400 photoelectron spectrometer system. Also incorporated in the experimental chamber were a low-energy electron diffraction (LEED) system and an Auger analysis facility. The photoemitted electrons were collected at normal emission. Previous work on Ni confirmed essentially no differences between angle integrated and normal-emission resonant effects.[12]

The experiment consisted then of measuring the variation of valence-band cross section with photon energy in the vicinity of the Pd 4p thresholds at 51.0 and 55.4 eV. These values were determined in this work from the energy-distribution curves.

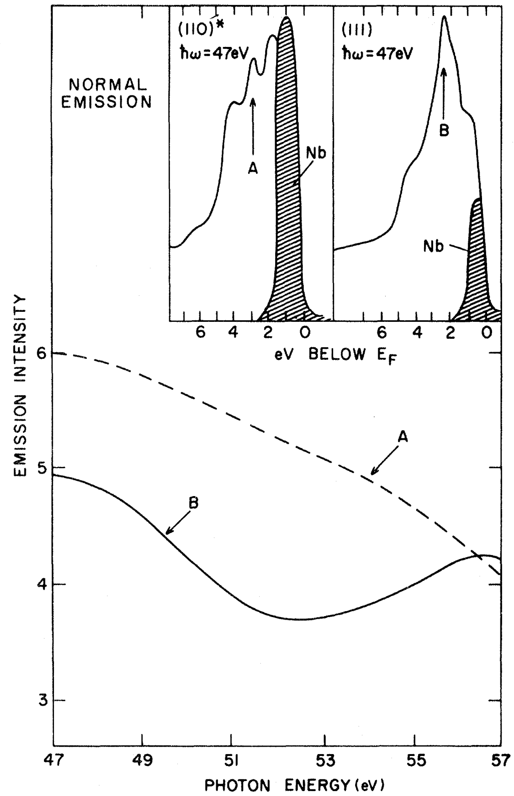

FIG. 2. Constant initial-energy spectra (CIS) for Pd(110)* (*A*) and Pd(111) (*B*) overlayers on a Nb(110) substrate. The inset shows EDC's for the two systems at a photon energy of 47 eV in which the peaks chosen for the CIS plots are identified. The shaded area in the EDC's indicates emission of Nb 4d character.

The incoherent decay (NVV Auger) generated a peak at a kinetic energy of 40 eV and approximately 15 eV wide. The width of the Auger peak reflects the bandlike nature of the process,[13] since it comprises the superposition of a pair of self-convoluted densities of occupied Pd d states each 10 eV wide (occupied Pd d bandwidth ~5 eV), separated by 4 eV (the separation of the 4$p_{1/2}$ and 4$p_{3/2}$ Pd core levels). Because of the Coulomb effects its apparent binding energy at the 4p threshold was 7 eV, thus ruling out any possibility of interference with the CIS data presented here.

V. RESULTS AND DISCUSSION

CIS data from the two overlayer structures (110)* and (111) are shown in Fig. 2 in the photon energy range 47–57 eV. In the inset we show EDC's taken at a photon energy of 47 eV for the (110)* and (111) Pd overlayer structures. We have identified the peaks which were selected for the CIS plots. Thus, the (110)* CIS plot labeled *A* shows the emission intensity as a function of photon energy of peak *A* which is at about 2.8-eV binding energy in the EDC. Similarly the (111) CIS plot labeled *B* shows the emission intensity versus photon energy for the -2.2-eV binding-energy peak in the EDC.

Peaks *A* and *B* were chosen on the basis that they had some Pd character. This was established in two ways. First, as discussed in Sec. III, it was possible to identify peaks whose cross sections as a function of photon energy resembled those of pure Pd and was very different from those of pure Nb.[14] Second, it can be seen from Fig. 1 that there is substantial emission at the binding energies corresponding to peaks *A* and *B* for both the (110)* and (111) overlayers at 90-eV photon energy where the Nb emission is very weak. Estimates of the percentage of Pd character of peaks *A* and *B* based on comparisons with pure Nb spectra are difficult to establish accurately, but are in the region of 30%.

In Fig. 2 we observe a pronounced dip for peak *B* which spans about 7 eV around the 4*p* core-level threshold. We attribute this behavior to an interference effect of the type discussed earlier. The difference in behavior between peaks *A* and *B* is caused by a change in the unoccupied density of states. The strength of the dip for peak *B* (around 20%) suggests its origin is *d* holes just above the Fermi level. *p*-*d* transitions have been observed previously to give stronger interferences[1] than *p*-*s* transitions.[15] The EDC's of Fig. 1 also suggest changes in the 4*d* band. If a resonance involving *p*-*s* transitions existed, it would also be seen for peak *A*. None was observed above the 5% noise level, however.

A quantitative analysis of the *d*-band count is not possible for several reasons. First, the shape of the resonance may be influenced by "band"[16] and lifetime[17] effects. In addition, the shape of the interference of peak *B* is not accurately known since some of the intensity into the peak comes from the Nb component. Finally, the close proximity of the $4p_{1/2}$ and $4p_{3/2}$ core levels (3.5 eV apart) also distorts the resonance line shape by superposition. Indeed, due to the lifetime broadening of the 4*p* levels, they were not resolved at all in the CIS data.

There is some evidence that the configuration interaction was sharper for thin Pd(111) overlayers than for bulk Pd(11). This could be due to the longer lifetime of the 4*p* hole in the thin overlayer, or the broadening of the unoccupied bands with increasing overlayer thickness.

The contrasting behavior in the photon-energy dependence of the Pd *d* states around the Pd 4*p* core threshold is thus a direct manifestation of the presence, on the one hand, of a coherent decay process in the (111) structure and, on the other hand, its absence in the (110)* structure. As mentioned previously this coherent decay process is due to the photoexcitation of the core electron into a *d* hole followed by Coulomb scattering of the two *d* electrons to fill the core hole, together with the production of an unbound electron. This in turn coherently mixed with the alternative channel of direct photoexcitation of a *d* electron to an unbound state. Both processes lead to a single *d* hole in the final state. The extent of observability of such a process is, therefore, directly dependent on the density of states of the *d* holes right above E_F. Accordingly, we find that the *d* band occupancy in the Pd(111) structure is lower than in the Pd(110)* structure.

Finally, and for the sake of completeness, we shall briefly discuss the effect of the Pd(110) overlayer on the Nb 4*p* levels which lie at 30.4- and 32.1-eV binding energies in pure Nb. These levels are observed to undergo a shift of about 0.5 eV to higher binding energies (Fig. 1) when the Nb(110) surface is covered with commensurate (110)* Pd overlayers. This shift toward higher binding energies may indicate a charge transfer from Nb sites to Pd sites which would be consistent with increased band occupancy in Pd(110)* over that of Pd(111).

VI. SUMMARY

In conclusion we have demonstrated the potential of using resonant photoemission in the CIS mode to yield qualitative information about band occupancies by applying it to the Pd-Nb overlayer system where the *d*-band occupancy is different in two observed structural phases. Four pieces of evidence support each other in concluding that the Pd(110) overlayer structure has almost full *d*-band occupancy. They are (1) photoemission EDC's taken between 16–100 eV which show a Pd *d*-band complex about 1.5 eV below E_F, (b) the fact that Pd(110) fails to dissociate H_2, while Pd(111) exhibits a sticking coefficient of 1, (c) the Nb 4*p* level shift indicating charge transfer from Nb to Pd site, and (d) no observable configuration interaction interference being seen within experimental uncertainties around the 4*p* threshold of Pd for the (110)* phase.

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