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Spectroscopy of a surface of known geometry: Ti(0001)-N(1 × 1)

Peter J. Feibelman
Sandia Laboratories, Albuquerque, New Mexico 87185*

F. J. Himpsel
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

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In order to test the low-energy electron diffraction (LEED) "underlayer" geometry of the Ti(0001)-N(1 × 1) system we have carried out self-consistent electronic-structure calculations and a variety of ultraviolet-photoemission-spectroscopy measurements. The assumption of the Shih *et al.* underlayer geometry yields the correct N-2*p* level ordering at Γ and the correct directions of dispersion along Γ-*M*. The positions of these levels are calculated to within 0.7 eV. The Fermi-level surface state predicted earlier for clean Ti(0001) is observed experimentally and, as predicted by the present calculations, is not quenched as the N adlayer forms. This result indicates that the outer Ti layer screens the potential due to N quite effectively. A layer of H on the Ti(0001) surface is found to quench the Fermi-level surface state, as predicted in the overlayer calculations of Feibelman and Hamann.

I. INTRODUCTION

The key problem in surface science remains the determination of surface atomic arrangement. For some systems this problem has apparently been solved by comparison of low-energy electron diffraction (LEED) theoretical and experimental results.[1] But there are few cases in which a LEED structure determination has been tested by comparison of spectroscopic measurements and calculations.[2] In this paper the first results of such a test are presented, showing good agreement between a self-consistent electronic-structure calculation and ultraviolet-photoemission-spectroscopy (UPS) data for the Ti(0001)-N(1×1) adsorption system, whose "underlayer" geometry was quite convincingly determined in the LEED study of Shih *et al.*[3]

II. DESCRIPTION OF THE CALCULATIONS

From the theoretical point of view the Ti-N adsorption system is technically a particularly favorable one. Ti is nonmagnetic, which means that issues such as how to include somewhat itinerant somewhat localized spins into a band-structure calculation do not render the results ambiguous as they would for Ni,[4] for example. Correlation effects should also not be particularly large.[5] And finally, since the N overlayer is 1×1, the two-dimensional unit cell contains few enough atoms that the spectroscopic calculations can be performed without great difficulty.

As already noted, the Ti(0001)-N(1 × 1) system was found by Shih *et al.*[3] to adopt an underlayer geometry. The separation between the outer and next Ti(0001) planes which best fit the LEED data was expanded from the bulk value of 4.42 to 4.63 a.u., with the N atoms residing in the octahedral interstices halfway between the planes. Self-consistent linear combination of atomic orbitals calculations[6] for this surface geometry, were performed for 5-layer Ti films with an N underlayer beneath each film surface. By means described at length elsewhere,[6] the film was then stretched non-self-consistently to eleven layers of Ti (plus two of N), both in order to render negligible any splitting of surface or N-induced states due to interaction between the two film surfaces, and also to make it easier to identify which are the surface states. The results of the eleven-layer film calculations are presented in Figs. 1–3.

III. THEORETICAL RESULTS

In Figs. 1 and 2 layerwise local densities of states (LDOS's) are shown which were calculated via a Mulliken-type population analysis[7] for the Ti(0001)-N(1×1) system. The work function of the film is found to be 0.158 a.u. (4.3 eV), in reasonable agreement with the measured work function (cf. below) of 4.45 ± 0.1 eV. At −0.70 a.u. relative to the vacuum level and thus 14.8 eV below E_F we find the N-2*s* peak (Fig. 2), which on the N atom contains about 1.7 electrons. The fact that it does not contain two electrons is of course due to mixing with Ti orbitals. This hybridization is evidenced by the small peaks on the layer 1 and 2 Ti atoms at −0.70 a.u.

Centered at −0.186 a.u. (5.1 eV) relative to E_F is a three-peaked structure in the outer layer LDOS's. The outer two peaks are predominantly N $2p_x$-$2p_y$ in character and lie at −0.384 and −0.318 a.u. relative to the vacuum level. The central peak is pre-

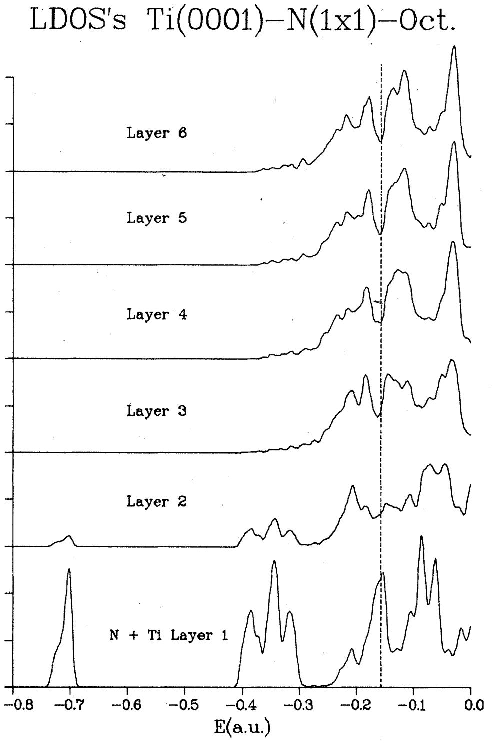

FIG. 1. Layerwise local densities of states for the Ti(0001)-N(1 ×1) adsorption system with the Ns occupying the octahedral interstices between the first and second Ti layers. The energy zero is the vacuum level, and the Fermi-energy indicated by the dashed line is at −0.158 eV.

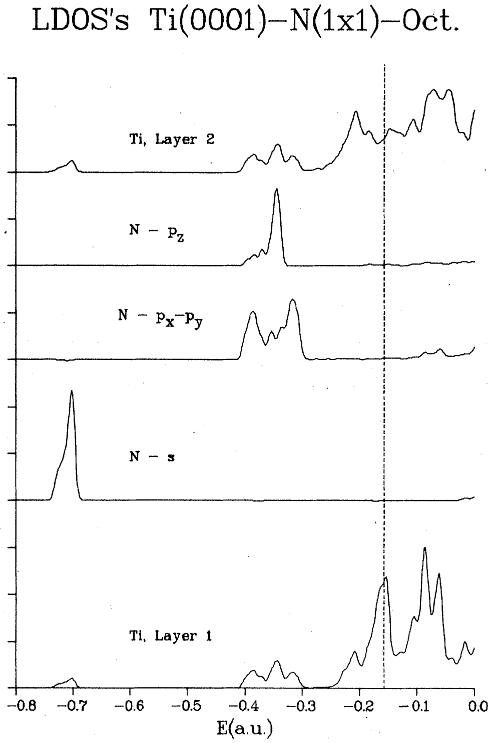

FIG. 2. Layerwise local densities of states for the outer layers of the Ti(0001)-N(1 ×1) adsorption system. The N LDOS's are decomposed into contributions from the $2s$, $2p_z$, and $2p_x$-$2p_y$ states.

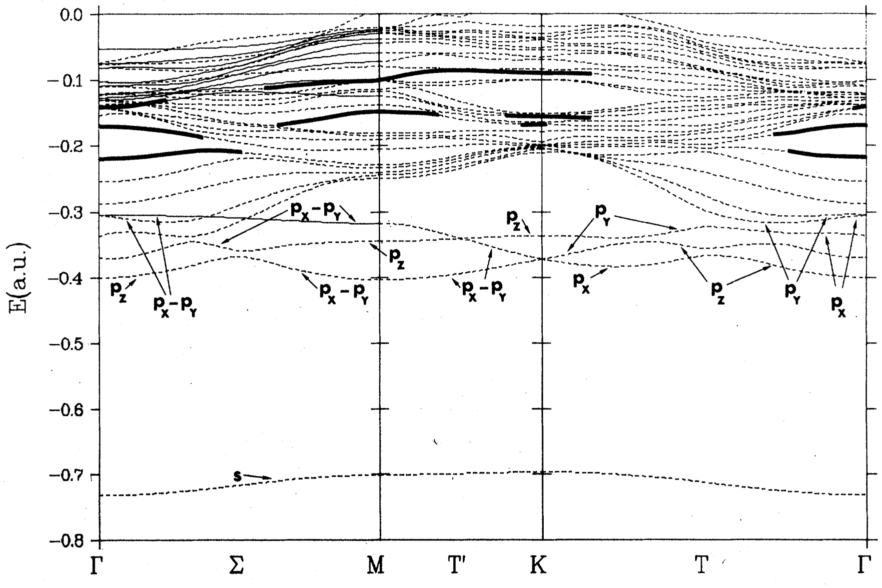

FIG. 3. Band structure of the Ti(0001)-N(1 ×1) film, showing the states which are even under reflection in the central plane. Heavy, solid lines indicate low-lying, Ti-derived, surface states and resonances. The labels s, p_x, p_y, and p_z indicate the orbital character of the N-derived states. The states which are even under reflection in the $(2\bar{1}\bar{1}0)$ mirror plane, along Γ-Σ-M, are indicated by a dashed line. The odd states are indicated by a solid line.

dominantly N $2p_z$, and lies at -0.344 a.u. Not surprisingly, since the N $2p$ states are closer to the Ti bands than the $2s$'s, they mix more strongly with them. Integration of the partial LDOS's shown in Fig. 2 reveals that the N-$2p_z$ peak contains 1.3 electrons on each N atom while the N-$2p_x$-p_y peaks contain 2.6. Thus the hybridization of the N and Ti orbitals leads to the calculation of a charge of $-0.6e$ for the N atom. For a similarly located H atom the charge is found to be $-0.4e$.[8] These results are consistent with the fact that N is somewhat more electronegative than H.[9]

Above the peaks associated with the N-$2p$ levels the spectrum is virtually purely Ti in nature. There is a strong surface state right at the Fermi level and coincident with the valley between the first major d-band peaks in the bulk Ti (or equivalently "layer 6") DOS. This surface peak is strongly reminiscent of what was found for clean Ti(0001) (Ref. 10) and suggests that strong as the potential associated with the N's may be, it is screened out over the distance between the underlayer N's and the Ti-vacuum selvedge region. The generality of this short-range screening phenomenon is indicated by similar behavior reported earlier[8] for a Ti(0001)-H(1×1) underlayer adsorption system.

The electronic structure of the Ti(0001)-N(1×1) can be understood in greater detail by examining the band-structure plot of Fig. 3. Let us focus first on the region of the N-$2p$ states. Near Γ the N-$2p$ levels and the lowest Ti s-d band overlap in energy. The N-$2p_z$ orbital at Γ is almost 0.1 a.u. lower than the two $2p_x$-$2p_y$ states, which are degenerate. Moving along Γ-Σ-M, which is a symmetry line in the surface Brillouin zone (SBZ), the degenerate $2p_x$-$2p_y$ pair splits into a state which is even under reflection in the (0001) surface's mirror plane and one which is odd. The odd state disperses downward very slightly from Γ to M. The even state disperses downward more rapidly. Each time it encounters another band there is a near crossing [prevented by the fact that the (0001) film has lower symmetry than a bulk hcp crystal, which allows states that would not mix in bulk to be mixed at the surface], and at each near crossing the orbital characters of the bands interchange. Thus, at M the even N-$2p_x$-$2p_y$ state is ~0.08 a.u. lower than the odd one, with the N-$2p_z$ state in between.

In the outer part of the SBZ the bands derived from the N-$2p$ levels become well-separated from, though still hybridized with the Ti d bands. In this region as well as along the Γ-T-K line the pattern of near band crossings with interchange of orbital character continues, as is indicated in the figure.

Above the N-$2p$ bands, as is seen in Fig. 2, the bands of the Ti(0001)-N(1×1) film are derived purely from the Ti orbitals. Surface-localized states (as recognized via a layerwise population analysis[7]) are weakly split off the band edges on either side of the s-d hybridization gap about Γ, and also off the bottom of the band of states odd under reflection in the $(2\bar{1}\bar{1}0)$ mirror plane. In addition there are strongly surface-localized, weakly dispersive, states near the Fermi energy (-0.158 a.u.), split off the top of the second d band into a wide gap about M, and near K. These states give rise to the large peak at the Fermi energy in the first layer Ti LDOS (Fig. 2). At the point K, the lower of the two surface-localized states is of P_3 symmetry and lies at the edge of a band of P_3 states. The upper state is of symmetry P_1-P_2 and lies in a large symmetry gap overlaying the P_3 band. These states are similar in all respects to the states which give rise to the Fermi-level surface-state peak in the outer layer LDOS of clean Ti(0001) (Ref. 10) and of Ti(0001)-H(1×1) in an underlayer adsorption geometry.[8]

Finally it should be noted that there is a surface resonance above E_F which is present over all the outer part of the SBZ. This state is not very strongly surface localized and so does not noticeably affect the outer layer Ti LDOS.

IV. EXPERIMENTAL

Angle-resolved and angle-integrated (1.8 sr) photoelectron spectroscopy using synchrotron radiation were combined with LEED and (photoexcited) Auger spectroscopy using a two chamber arrangement described in Ref. 11. The basic units are a toroidal grating monochromator (6 eV $< h\nu < 150$ eV), a display-type photoelectron spectrometer and a sample preparation chamber separable from the spectrometer. A Ti(0001) crystal was sputter cleaned with ~400-eV Ar$^+$ ions going through extensive heating cycles (up to ~800 °C) during sputtering. It was then transferred to the spectrometer chamber and annealed in a vacuum of ~4×10^{-11} Torr. To obtain an ordered 1×1 nitrogen layer, we proceeded similarly to Shih *et al.*[3] in their LEED work. Dosing the sample with nitrogen we found an increase of the N-$2p$ signal and of the mixed (Ti-$3p$, N-$2p$, Ti valence band) Auger peak ($E_{\rm kin}$ ~ 26 eV above E_F, labeled 23 in Ref. 3) up to 4-L exposure (1 L $=10^{-6}$ Torr/sec) where the signals saturated. The saturation exposure gave a clear 1×1 LEED pattern whereas higher doses (≤ 10 L) resulted in large background intensity. This is in qualitative agreement with the observations of Shih *et al.*[3]

V. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 4 shows an angle-integrated photoelectron spectrum [energy distribution curve (EDC)] of

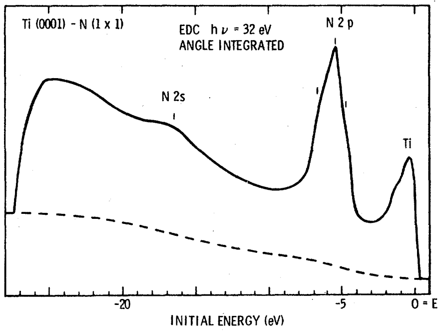

FIG. 4. Density of states type angle-integrated photoelectron spectrum (photon energy $h\nu = 32$ eV) for an ordered 1×1 nitrogen overlayer on Ti(0001). The dashed curve represents spectrometer background.

Ti(0001)-N(1×1) at a photon energy $h\nu = 32$ eV (just below the Ti-3p threshold). This spectrum is typical for high photon energies ($h\nu < 25$ eV) where the spectral shape does not depend much on $h\nu$, since the spectrometer angular acceptance averages over the whole Brillouin zone. Comparing to the calculated DOS's (Figs. 1 and 2) we easily identify the N-2s level (16.4 eV below E_F, ~3 eV full width at half maximum), the N-2p triplet ($4.7^{+0.4}_{-0.2}$ eV, 5.4 ± 0.1 eV, and $6.6^{+0.2}_{-0.4}$ eV below E_F) and the Ti valence band and surface states peaking at the Fermi level (E_F). The work function is measured to be 4.45 ± 0.1 eV from the width of the EDC for Ti(0001)-N(1×1). This is 0.15 eV lower than for the clean Ti(0001) surface. Notice that the triplet of 2p levels agrees in splittings to within 0.1 eV and in overall position to ~0.4 eV with the calculated 2p energies of 4.4, 5.1, and 6.2 eV. This agreement is as good as can be expected within the few tenths eV accuracy of calculations, but provides a less stringent test of the theory than the polarization and angle-resolved UPS (ARUPS) experiments discussed below. The disagreement between the calculated (14.7 eV) and the measured (16.4 eV) N-2s peak positions is an indication of the importance of including screening effects in a calculation of the ionization potential of this core-like level.

Figure 5 presents spectroscopic evidence that the nitrogen layer does not quench the intrinsic Ti(0001) surface states located mainly near E_F. Angle-integrated spectra are compared for clean Ti(0001), Ti(0001)-N(1×1), and an ordered Ti(0001)-H(1×1) structure which forms at 2-L hydrogen exposure (saturation).[12] Hydrogen quenches states within ~0.4 eV of the Fermi level whereas nitrogen appears to enhance those states. Calculations performed for clean Ti(0001)[10] and for various sites of H on Ti(0001) (Ref. 8) show that the high DOS near the Fermi level is due to intrinsic Ti(0001) surface states which are quenched if H sits above the Ti surface but are not much affected by a hydrogen underlayer. Comparing to our data this suggests that H forms an overlayer whereas N forms an underlayer in agreement with other spectroscopic data for H on Ti (Ref. 8) and LEED analysis for Ti(0001)-N(1×1) (Ref. 3).

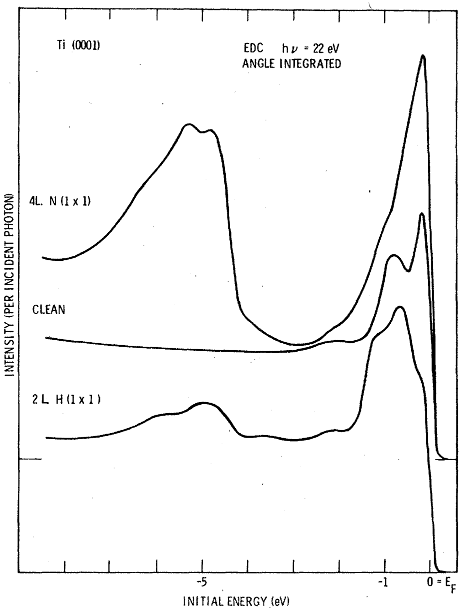

FIG. 5. Angle-integrated photoelectron spectra for clean Ti(0001), Ti(0001)-N (1×1), and Ti (0001)-H(1×1) (note zero offsets). Surface states within 0.4 eV of the Fermi level E_F are quenched by hydrogen but not by nitrogen. Also, the N 2p and H 1s levels are seen at ~ 5 eV below E_F.

Figure 6 shows how states of different symmetry can be identified via angle-resolved, polarization-dependent photoelectron spectroscopy. The spectra shown in this figure are taken for emission normal to the sample surface ($\delta\theta = 6°$ full angle), i.e., we are looking at the center of the surface Brillouin zone (Γ) which corresponds to $\vec{k}_{\parallel} = 0$. The symmetry group is C_{3v} which implies that Λ_1-symmetry (e.g., s, p_z, d_{z^2}) initial states can be seen with the electric field vector $\vec{E}$ perpendicular to the surface and Λ_3-symmetry (e.g., p_x, p_y) initial states are seen with $\vec{E}$ parallel to the surface (s polarization).[13] Using s polarized and mixed s,p-polarized light, we find one (doubly-degenerate) Λ_3 state at 4.7 eV below E_F which represents the N-2$p_{x,y}$ orbitals (see Fig. 6, full line). For finite $\vec{k}_{\parallel}$ along ΓM (not shown in the figures) this state is observed to disperse downwards in agreement with the calculation.[14] All other states have Λ_1 symmetry. The N-p_z states lie below the N-$p_{x,y}$ state at Γ and hybridize with the Ti-4s, 4p_z, 3d_{z^2} states having the same Λ_1 symmetry, i.e., they form a surface res-

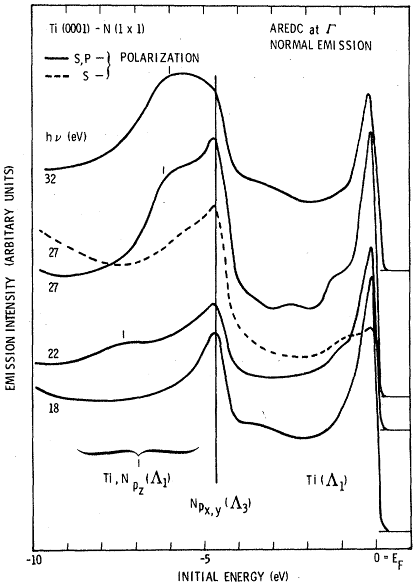

FIG. 6. Angle-resolved photoelectron spectra (normal emission) for Ti(0001)-N(1 ×1) for various photon energies $h\nu$ and polarizations. The Λ_3-symmetry N $2p_{x,y}$ states are excited in s polarization where the Λ_1-symmetry N-p_z and Ti states are forbidden. Tick marks show the dispersion of the hybridized N $2p_z$, Ti $4s4p$ states with $h\nu$. The Λ_3 state does not disperse with $h\nu$.

onance. This can be seen from their dispersion with $h\nu$ (i.e., varying $k_\perp$ of the final state) which would be absent for a true surface state (see, e.g., the Λ_3 state at -4.7 eV). The peak at E_F does not disperse with $h\nu$ (the shift downward at $h\nu = 32$ eV is due to degrading resolution). We identify this peak with the surface state at Γ (mostly Ti $3d_{z^2}$) calculated for both clean Ti(0001) (Ref. 10) and Ti(0001)-N(1×1) (see Fig. 3).

It is important to recognize that this ordering of the N-$2p_x$-p_z levels at Γ is not a foregone conclusion. For O on Al(111), for example, the O-$2p_x$-p_y levels lie deeper than the O $2p_z$.[15] Therefore, the fact that our calculation predicts the correct level ordering at Γ as well as the correct direction of dispersion of these levels along Γ-M represents qualitative confirmation of our choice of surface atomic geometry.

It is not clear, at this point, what is responsible for the 0.7 eV difference in the calculated (4.0 eV) and measured (4.7 eV) positions of the $2p_x$-p_y level at Γ. Further experiments to elucidate the systematics of the discrepancy throughout the SBZ would be useful in this regard.

VI. SUMMARY

Electronic structure calculations assuming the underlayer adsorption geometry of Shih *et al.*[3] for Ti(0001)-N(1×1) show quite reasonable agreement with UPS data. They predict the observed N level orderings at Γ and the directions of their dispersion along Γ-M. The predicted level positions agree to about 0.7 eV, and at this point it is not clear how seriously one should view this discrepancy. The calculated and measured work functions agree to within 0.15 eV.

On clean Ti(0001) we observe a surface state at the Fermi level as predicted in Ref. 10. This state is quenched if we add a monolayer of H but not if we form the N(1×1) adlayer. These results accord with the prediction that an underlayer of N [or H (Ref. 8)] should have little effect on this surface state while an overlayer should quench it, if we assume that H adsorbs in overlayer sites while N(1×1) structure corresponds to an underlayer.

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[1] F. Jona, J. Phys. C 11, 4271 (1978).

[2] J. R. Smith, F. J. Arlinghaus, and J. G. Gay, Solid State Commun. 24, 279 (1977); A. Liebsch, Phys. Rev. B 17, 1653 (1978); C. S. Wang and A. J. Freeman, Phys. Rev. B 19, 4930 (1979).

[3] H. D. Shih, F. Jona, D. W. Jepsen, and P. M. Marcus, Surf. Sci. 60, 445 (1976).

[4] V. Korenman, J. L. Murray, and R. E. Prange, Phys. Rev. B 16, 4032 (1977); 16, 4048 (1977); 16, 4058 (1977); J. Hubbard, Phys. Rev. B 19, 2626 (1979).

[5] Two hole interaction effects such as are thought to distort the photoemission spectrum of Ni [D. R. Penn, Phys. Rev. Lett. 42, 921 (1979)] should be small in Ti. See, e.g., N. D. Lang and A. R. Williams, Phys. Rev. B 20, 1369 (1979).

[6] The method is described in detail by P. J. Feibelman, J. A. Appelbaum, and D. R. Hamann, Phys. Rev. B 20, 1433 (1979) and J. A. Appelbaum and D. R. Hamann, Solid State Commun. 27, 881 (1978).

[7] See Ref. 6; also D. G. Dempsey and L. Kleinman, Phys.

Rev. B 16, 5356 (1977).

[8] P. J. Feibelman and D. R. Hamann, Phys. Rev. B 21, 1385 (1980).

[9] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, 1960), p. 90.

[10] P. J. Feibelman, J. A. Appelbaum, and D. R. Hamann, Phys. Rev. B 20, 1433 (1979).

[11] D. E. Eastman, J. J. Donelon, N. C. Hien, and F. J. Himpsel, Nucl. Instrum. Methods (in press).

[12] F. J. Himpsel *et al.*, report (unpublished).

[13] F. J. Himpsel and D. E. Eastman, Phys. Rev. B 20, 3217 (1979).

[14] This dispersion also suggests that the peak associated with the high-lying shoulder of the N-$2p$ triplet in Fig. 4 is somewhat lower than 4.7 eV below E_F.

[15] W. Eberhardt and F. J. Himpsel, Phys. Rev. Lett. 42, 1375 (1979).