Electronic properties of Nb and H-treated Nb surfaces

Bo-Shung Fang, C. A. Ballentine, and J. L. Erskine
Department of Physics, University of Texas, Austin, Texas 78712
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Clean Nb and H-treated Nb surfaces are studied using angle-resolved photoemission. Intrinsic surface states and hydrogen-induced states are characterized along the $\bar{\Gamma}$-$\bar{X}$ direction of the two-dimensional Brillouin zone. Hydrogen-induced states exhibit reversible temperature-dependent effects providing direct experimental evidence of the self-trapped surface states which have been proposed to account for novel properties associated with hydrogen uptake by Nb.

The interaction of hydrogen with metals is an important topic because of the technological importance of metal-hydrogen systems (embrittlement, catalysis, and hydrogen storage), and because hydrogen-metal systems serve as prototypes for studying chemical and physical processes at metal surfaces. Chemisorption at a surface is characterized by the heat of adsorption ($E_{\rm ads}$), while the corresponding parameter which governs bulk absorption is the heat of solution ($\Delta\bar{H}^{\infty}$). For most metal-hydrogen systems, $E_{\rm ads} > \Delta\bar{H}^{\infty}$, which favors a high concentration of hydrogen at the surface.

A systematic experimental investigation[1] of the bonding of hydrogen to the (111) surface of three column-10 transition metals (Ni, Pd, Pt) has established a systematic trend in the behavior of the surface hydrogen bond even though the properties of hydrogen in the bulk is quite different. (Specifically, $\Delta\bar{H}^{\infty}$ is positive for Pd, negative for Ni, and more negative for Pt.) An irreversible temperature-induced conversion of the low-temperature ($T \sim 100$ K) stabilized chemisorbed phase to a different phase is observed for all three metals. The conversion, which occurs at $T \sim 320$, 270, and 270 K for Ni, Pd, and Pt, respectively, is manifested by the disappearance of the hydrogen-induced bands and the reappearance of the intrinsic electronic surface states. Thermal desorption measurements have established that the conversion does not involve depletion of hydrogen from the crystal. The results are therefore interpreted to indicate phonon-assisted hydrogen migration to lower-energy octahedral sites under the surface plane (corresponding to the location of hydrogen atoms in the metal hydride). Related calculations[2] which address subsurface occupation and order-disorder transitions for H on Pd(111) predict that hydrogen atoms locate in subsurface octahedral sites at submonolayer coverage. At monolayer coverages where a $(\sqrt{3}\times\sqrt{3})R\,30°$ structure exists, a lower-energy configuration is predicted in which $\frac{1}{3}$ of the H atoms are moved to surface tetrahedral sites. Direct and unambiguous experimental results supporting these predictions for Pd(111) are not yet available.

The group VB metals (V, Nb, Ta) also appear to exhibit some rather unusual properties in relation to their interaction with hydrogen. Considerable attention[3-8] has been directed towards elucidating the role of the surface in accounting for these properties. Several experimental[3,9] and theoretical[5,6] studies have concluded that Nb surfaces also exhibit a strongly bound subsurface state of hydrogen. The striking difference between the novel thermally activated state in Nb and the corresponding state in the three transition metals is that in Nb the state occupancy is a reversible function of temperature. Lagos and Schuller[5] have calculated the energy of solution for hydrogen as a function of depth for Nb(110) and Pd(111) in an attempt to account for the unusual uptake kinetics associated with Nb surfaces. The results (summarized in Table I) predict a deep subsurface bonding well for hydrogen at Nb(110) but not for Pd(111), in apparent disagreement with the recently reported[2] embedded-atom calculations for the H/Pd(111) system. An important aspect of kinetic models that includes the "subsurface bonding" is that these states act as a barrier or valve allowing reversible diffusion of hydrogen into the bulk above a system specific temperature.

Recent studies[9] of the H/Nb(100) system utilizing high-resolution electron-energy-loss spectroscopy (EELS) have yielded initial experimental evidence for subsurface

TABLE I. Heats of absorption and adsorption for hydrogen on selected metals. Upper and lower theoretical limits for the calculated values of $-[\Delta\bar{H}^{\infty}+\Delta_s(n)]$ are shown.

	$-E_{\rm ads}$ (eV)	$-\Delta\bar{H}^{\infty}$ (eV)	Layer	$-[\Delta\bar{H}^{\infty}+\Delta_s(n)]$ Upper limit	Lower limit
Ni[a]	0.50	−0.10			
Pt[a]	0.23	−0.26			
Pd[a]	0.45	0.20	(1)	0.337	0.253[b]
			(2)	0.234	0.0220
			(3)	0.212	0.208
Nb	0.55	0.36	(1)	0.808	0.562[c]
			(2)	0.461	0.427
			(3)	0.393	0.385
			(4)	0.374	0.371

[a]Reference 1.
[b]Octrahedral site in Pd(111) (Ref. 5).
[c]Tetrahedral site in Nb(110) (Ref. 5).

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sites and for the reversible temperature effects associated with them. The present paper reports a systematic study of the electronic properties of Nb surfaces and the hydrogen-niobium system using photoelectron emission spectroscopy which provides additional direct and unambiguous evidence for these novel subsurface states. Our experiments were performed at the Synchrotron Radiation Center in Stoughton, Wisconsin using the Seya-Namioka monochromator, and an angle-resolving photoelectron spectrometer described previously.[10] The single-crystal samples were prepared, as described previously,[9] and analyzed *in situ* by low-energy electron diffraction and Auger spectroscopy before performing photoemission experiments. The primary surface contaminant (found to be oxygen) was maintained below 1% of a monolayer by repeated cleaning during the experiments.

Figure 1 displays selected angle-resolved photoemission spectra taken along the $\bar{\Gamma}$-$\bar{X}$ symmetry line of the two-dimensional Brillouin zone for clean and hydrogen-treated Nb(100) surfaces. Hydrogen-induced peaks are denoted by lines labeled H; other peaks have been assigned to bulk states (Δ_1 and Δ_5) and surface resonance states ($\bar{\Delta}_1$). The prominent peak with binding energy of ≈ -2.4 eV persists after hydrogen doses, and also exhibits disperson with polar angle ($k_\parallel$) and photon energy ($k_\perp$). This peak is produced by direct transitions from the Δ_1 symmetry bulk band. A photon energy of 17 eV places the initial state at $k_\perp$ approximately half the distance between Γ and H of the three-dimensional Brillouin zone. In normal emission geometry and at $\hbar\omega = 17$ eV, the final band has Δ_5 symmetry[11] (dipole forbidden), and for $\theta = 0°$ (not shown) and $\theta = 12°$ in Fig. 1, the Δ_1 band is not observed, as expected. Off the symmetry line, direct transitions are allowed, and the Δ_1 band is observed. There is also evidence of a bulk Δ_5 band near E_F (-0.30 eV). Since the bulk band calculations place the Δ_5 band just above E_F at Γ, a small upward shift of E_F (approximately 0.3 eV for the calculations of Louie *et al.*[12]) is required to account for this interpretation. Such a shift is not inconsistent with observations of the

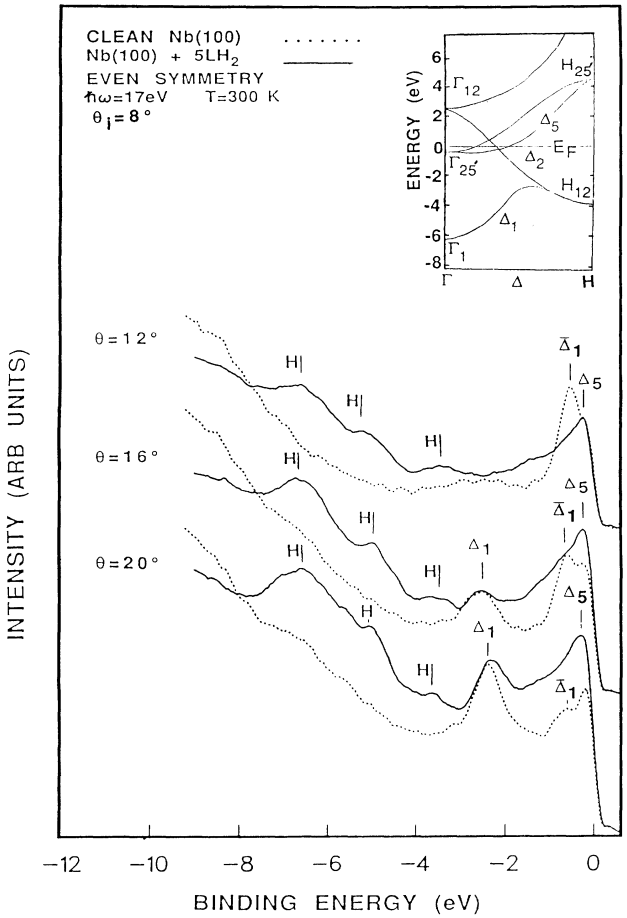

FIG. 1. Angle-resolved photoemission electron energy distribution curves for clean Nb(100) and hydrogen dosed Nb(100) surfaces. Lines labeled H represent hydrogen-induced peaks; peaks labeled Δ_1 and Δ_5 are produced by bulk states, peaks labeled $\bar{\Delta}_1$ are produced by surface resonances. Inset: bulk bands of Nb (Louie *et al.*, Ref. 11).

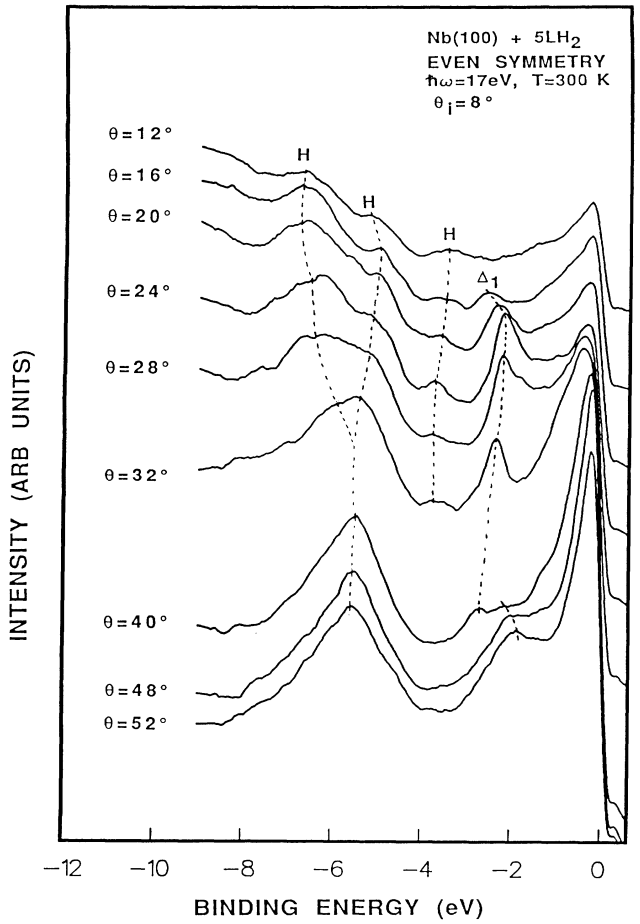

FIG. 2. Angular dependence of photoemission spectra along the $\bar{\Delta}$ line of the two-dimensional Brillouin zone. Dispersion of the $\bar{\Delta}_1$ band and hydrogen-induced bands is shown by dashed lines.

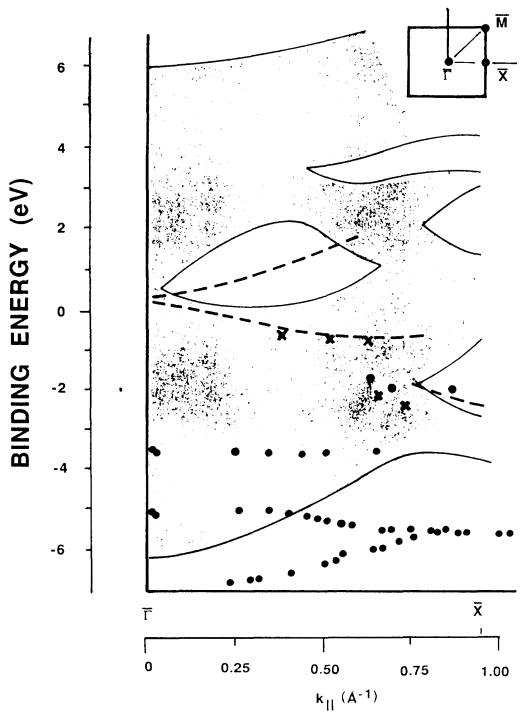

FIG. 3. Bulk bands of Nb projected onto the two-dimensional Brillouin zone along the $\bar{\Delta}$ direction. Dashed lines represent predicted surface resonances (Louie *et al.*, Ref. 11). Points represent experimental data for H dosed surfaces; crosses represent experimental data for clean surfaces.

binding energy of the Σ_1 band reported by Smith *et al.*,[13] and with our observations the two $\bar{\Delta}_1$ surface resonances. A slight upward shift of E_F is also required for these states to be occupied at $\bar{\Gamma}$.

Near E_F there is evidence of two surface sensitive peaks. A third peak near E_F that persists after hydrogen dosing is attributed to the bulk Δ_1 band. Photoemitted electrons were detected in the (010) plane which also contained the polarization vector of incident synchrotron radiation. In this configuration initial states having even symmetry ($\bar{\Delta}_1$) are probed. Figure 2 displays a more extensive series of angle-dependent spectra for hydrogen dosed Nb(100). These spectra show the $k_{||}$ dispersion of the hydrogen induced bands, and the Δ_5 and the Δ_1 bulk bands. Corresponding spectra for clean Nb (not shown) reproduce the Δ_1 peak behavior, and also establish the $k_{||}$ dispersion of the structure assigned to the $\bar{\Delta}_1$ surface resonance (binding energy ~ -0.6 eV). Three hydrogen-induced bands are shown. The first (at -3.5 eV) is weak and exhibits pronounced odd symmetry character as judged by the polarization dependence. The second hydrogen-induced band exhibits smaller dispersion (~ 0.5 eV) than that of the third band (dispersion ~ 1.2 eV). Both the second and third bands exhibit even symmetry.

Figure 3 displays the $\bar{\Delta}_1$ symmetry surface bands of Nb(100) calculated by Louie *et al.*[14] (dashed lines), and the projected bulk bands along $\bar{\Gamma}$-$\bar{X}$. Superimposed on the calculated results are our experimental data for the three hydrogen-induced bands and the $\bar{\Delta}_1$ surface resonance observed on the clean surface. There is also evidence in both our clean surface data, and the hydrogen covered surface data (refer to $\theta = 48°$ and 52° spectra of Fig. 2) for the surface state predicted to exist in the gap around $\bar{X}$. The hydrogen-induced bands on Nb(100) are similar to corresponding bands for other metal surfaces; i.e., the bonding states of chemisorbed hydrogen are observed at binding energies of approximately -8 eV at $\bar{\Gamma}$ and exhibit approximately 2 eV dispersion throughout the two-dimensional Brillouin zone.

Having accounted for the structures in the photoemission spectra, we now consider the temperature dependent of the spectra. Figure 4 displays photoemission spectra for clean and hydrogen treated Nb(100) as a function of temperature. The lower two curves correspond to (1) clean Nb prior to hydrogen dosing, and (2) the hydrogen dosed surface at room temperature. The next three curves illustrate the temperature dependence of the hydrogen-induced peak for two cycles of temperature variation. This data verifies the reversible temperature-dependent effect established by EELS experiments: cycling a hydrogen dosed Nb(100) crystal above $T = 200$ °C causes the hydrogen vibrational bands to van-

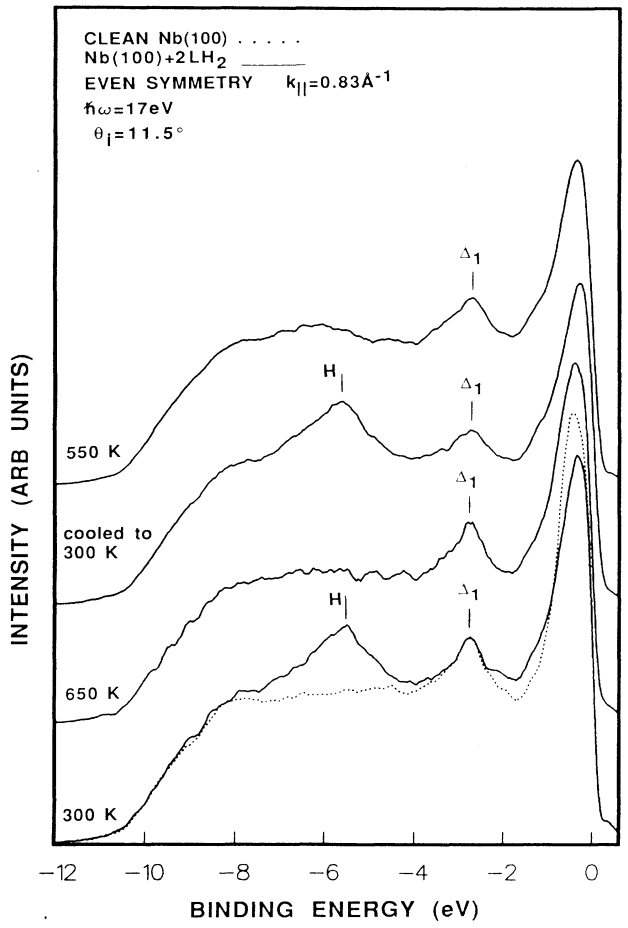

FIG. 4. Reversible temperature effect for the hydrogen-induced bands for hydrogen dosed Nb(100).

ish, but they return upon cooling below approximately 180 °C. Other data (not shown) indicates that all three hydrogen-induced peaks (in Fig. 1) exhibit the reversible temperature-dependent effect. The peak having binding energy of -3.5 eV appears to weaken and broaden slightly after cooling to room temperature.

The reversible temperature-dependent transformation between observable and nonobservable hydrogen sites at Nb(100) surfaces is consistent with a corresponding transformation reported by Nb(110).[3] In the case of Nb(100), the location of the observable states appears well established (indirectly) by EELS experiments. A conversion temperature of ~ 200 °C is consistent with the (lower limit) calculated estimates[5] of the well depth for the $n=1$ layer of Nb(110). The model calculation appears to be qualitatively accurate. Although the electronic properties of Nb appear to be well behaved in terms of first-principles predictions, and the properties of the hydrogen-induced bands are similar to what have been observed for other hydrogen-metal systems, the reversible temperature-dependent effects associated with the hydrogen Nb systems appear to be genuine, and represent a significant departure from the trends established for other similar systems.

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