UNCLASSIFIED

DTIC FILE COPY

(2)

AD-A207 846

IT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Unclassified	1b. RESTRICTIVE MARKINGS: None
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT: Unlimited
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S): AFOSR-86-0109	5. MONITORING ORGANIZATION REPORT NUMBER(S): AFOSR-TR- 89-0569
6a. NAME OF PERFORMING ORGANIZATION: The University of Texas Department of Physics; 6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION: Air Force Office of Scientific Research Chemical and Atmospheric Sciences
6c. ADDRESS (City, State, and ZIP Code): The University of Texas at Austin Department of Physics Austin, Texas 78712	7b. ADDRESS (City, State, and ZIP Code): Building 410 Bolling Air Force Base Washington, D.C. 20332-6448
8a. NAME OF FUNDING/SPONSORING ORGANIZATION: AFOSR; 8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER: AFOSR-86-0109
8c. ADDRESS (City, State, and ZIP Code): Building 410 Bolling AFB, DC 20332-6448	10. SOURCE OF FUNDING NUMBERS: PROGRAM ELEMENT NO. 61102F; PROJECT NO. 2303; TASK NO. A2; WORK UNIT ACCESSION NO.

11. TITLE (Include Security Classification)
Hydrogen adsorption at Nb(100): photoemission evidence of two-state exchange involving subsurface states

12. PERSONAL AUTHOR(S)
B.-S. Fang, C.A. Ballentine, and J.L. Erskine

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Technical Reprint	FROM 1 Ap.88 TO 30 Mar89	1989 April 14	8

16. SUPPLEMENTARY NOTATION
Surface Science Letters, 204, (1988), L713-L720

17. COSATI CODES		
FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
Surface Chemistry, Structure, and Electronics Properties, of Surfaces, Niobium, reprints. (mgm)

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Temperature dependent properties of electronic states resulting from hydrogen adsorption on Nb(100) surfaces have been studied by photoemission spectroscopy using synchrotron radiation. The most prominent hydrogen induced feature in photoemission spectra exhibits a temperature dependence that requires contributions from two distinct states. Analysis of the photon energy dependent cross section of the hydrogen induced features suggests that hydrogen chemisorption sites are located below the surface. These results have important consequences for kinetic models that attempt to account for hydorgen uptake by Nb.

(1)

DTIC ELECTE MAY 15 1989 S E

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS	Unclassified/Unlimited
22a. NAME OF RESPONSIBLE INDIVIDUAL: Lt. Col. Larry Burggraf	22b. TELEPHONE (Include Area Code): (202) 767-4960; 22c. OFFICE SYMBOL: AFOSR/NC

DD Form 1473, JUN 86 — Previous editions are obsolete. — SECURITY CLASSIFICATION OF THIS PAGE

89 5 11 041

Surface Science 204 (1988) L713–L720
North-Holland, Amsterdam

SURFACE SCIENCE LETTERS

AFOSR-TR- 89-0569

HYDROGEN ADSORPTION AT Nb(100): PHOTOEMISSION EVIDENCE OF TWO-STATE EXCHANGE INVOLVING SUBSURFACE STATES

B.-S. FANG, C.A. BALLENTINE and J.L. ERSKINE
Department of Physics, University of Texas, Austin, TX 78712, USA

Received 3 June 1988; accepted for publication 13 July 1988

Temperature dependent properties of electronic states resulting from hydrogen adsorption on Nb(100) surfaces have been studied by photoemission spectroscopy using synchrotron radiation. The most prominent hydrogen induced feature in photoemission spectra exhibits a temperature dependence that requires contributions from two distinct states. Analysis of the photon energy dependent cross section of the hydrogen induced features suggests that hydrogen chemisorption sites are located below the surface. These results have important consequences for kinetic models that attempt to account for hydrogen uptake by Nb.

Hydrogen metal systems have served as a prototype of studying chemical and physical processes at metal surfaces [1]. In group VB metals, Nb in particular, the extremely high mobility of hydrogen in the bulk has stimulated considerable interest in the role played by the surface in admitting hydrogen into the Nb lattice [2,3]. A number of theoretical [2–8] and experimental [9–13] studies have attempted to account for the novel kinetic properties associated with the transfer of hydrogen from the gas phase into the metal and vice versa. Early uptake kinetic studies of Nb hydrogen systems [2,9] appear to have established a correlation between the surface hydrogen coverage and the concentration of hydrogen in the bulk. However, attempts to reconcile hydrogen uptake data and surface coverage results within a kinetic model which assumed a dilute hydrogen phase on the surface in equilibrium with the concentration of hydrogen in the bulk were unsuccessful [2]. Specifically, rates of surface coverage determined by photoemission [10] were found to exceed rates that could be associated with bulk concentrations assuming that the dilute phase model described the surface and bulk "equilibrium" concentrations.

The failure of the dilute phase model to adequately account for uptake kinetics of hydrogen by Nb has lead to the suggestion of several alternate models. One model is based on the (ad hoc) assumption that two different hydrogen states exist at the surface [10]. The two-state exchange model requires both states to be strongly bound (because of the desorption tempera-

0039-6028/88/$03.50 © Elsevier Science Publishers B.V.
(North-Holland Physics Publishing Division)

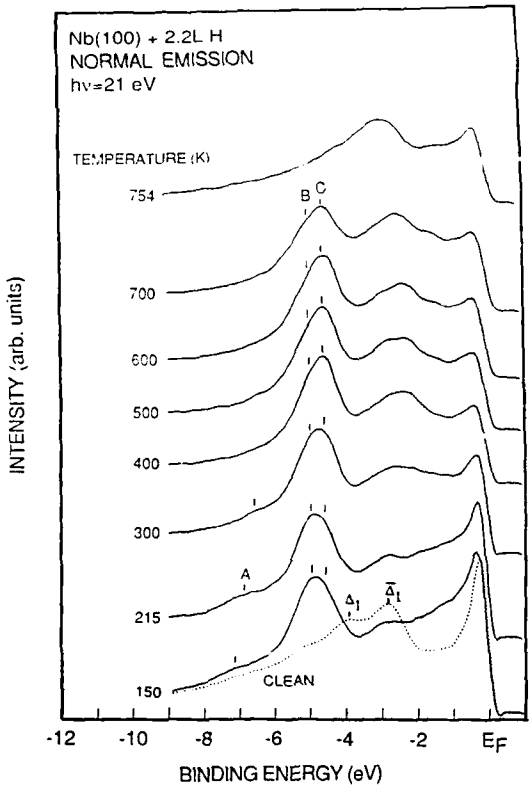
Approved for public release;
distribution unlimited.

ture for hydrogen of about 750 K) and the barrier for hydrogen exchange between the two states to be small to permit reversible exchange of hydrogen atoms at lower temperatures. Furthermore, the state that is populated at higher temperatures is required to have an undetectable photoemission cross section to account for the reversible appearance of hydrogen induced features in photoemission spectra as the temperature is cycled. The two-state model is decoupled from the bulk hydrogen concentration and is therefore capable of providing the saturation values of surface concentration at low exposures that are required to account for experimental uptake kinetics data. A second model based on the assumption that a thin hydride layer forms at the surface has also been proposed [11]. In this model, the probability that hydrogen dissociation occurs at the surface is controlled by the concentration of hydrogen in the surface hydride phase and the concentration of hydrogen at the metal surface. In order to achieve reasonable agreement with uptake kinetics data, the hydride model required an additional postulate related to the behavior of the precipitated hydride phase during heating.

None of the kinetic models for hydrogen uptake by Nb appear to be universally accepted, as indicated by recent papers expressing differing views [6,7]. In addition, most of the ad-hoc assumptions required to formulate microscopic mechanisms to account for hydrogen adsorption and uptake kinetics have not been explored experimentally in sufficient detail to validate them. The purpose of the present paper is to study selected microscopic physical properties of hydrogen on Nb(100) that underlie kinetic models. In particular, we address the location of the hydrogen atoms near the Nb surfaces, and the temperature dependencies associated the hydrogen induced electronic states.

Our experiments were performed at the Synchrotron Radiation Center, Stoughton, Wisconsin. The single crystal samples were prepared using conventional methods [12, 13], and characterized using Auger electron spectroscopy and low energy electron diffraction (LEED). Fig. 1 displays normal emission electron energy distribution curves (EDCs) for clean and hydrogen dosed Nb(100) surfaces at various temperatures. The overall energy resolution in our photoemission measurements is 0.25 eV. Hydrogen doses in our experiments were measured using a standard Varian nude ion gauge (corrected for hydrogen by multiplying the gauge reading by a factor of 2.2). Our previous photoemission studies [17] of clean Nb(100) have established the origin of peaks labeled Δ_1 and $\bar{\Delta}_1$ as a bulk state and a surface resonance state respectively. Features labeled A, B, and C originate from hydrogen induced states.

The primary hydrogen induced feature is labeled as though it consists of two distinct states. The strength of this feature diminishes as temperature is increased from 150 to 700 K, and the shape changes as the peak center moves from -5.1 to -4.6 eV binding energy. The peak vanishes irreversibly for



INSPECTED COPY

Accession For
NTIS GRA&I
DTIC TAB
Unannounced
Justification
By
Distribution/
Availability Codes
Dist | Avail and/or Special
A-1 | 20

Fig. 1. Normal emission photoemission EDCs for clean Nb(100) and hydrogen dosed Nb(100) as a function of temperature. Peaks labeled Δ_1 and ($\bar{\Delta}_1$) are produced by bulk and (surface) electronic states of Nb (ref. [15]). States labeled A, B, and C are induced by hydrogen adsorption.

temperature excursions beyond 750 K where hydrogen desorbs from the surface. Curve fitting techniques were used to separate the two temperature dependent contributions of peaks B and C. Several different background subtraction models were used, but the results, displayed in fig. 2, were found to be fairly insensitive to details of the assumed background.

Fig. 2 represents compelling experimental evidence that supports the two-state or multiple-state exchange model for uptake kinetics by Nb(100). Reversible exchange of hydrogen between states B and C and other states occurs in the temperature range $300 \leq T \leq 600$ K. For temperatures above 450 K, it is clear that both B and C states are depleted of hydrogen. The hydrogen migrates to other near-surface states that are not clearly manifested in photoemission EDCs or in vibrational spectra. It is also possible that the hydrogen enters the bulk Nb lattice, but the process is reversible. We have not investigated the reversibility of hydrogen exchange between states B and C below 300

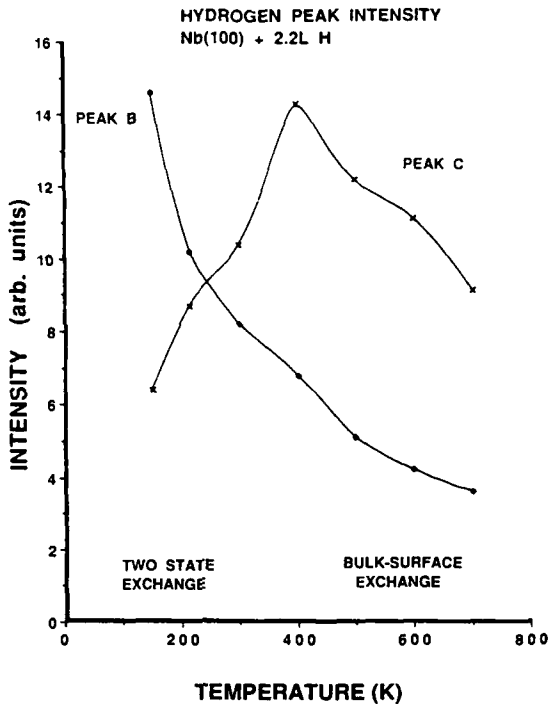


Fig. 2. Temperature dependence of the two peaks labeled B and C obtained by curve fitting of data displayed in fig. 1.

K. There is some evidence in our experimental data suggesting that the exchange between states B and C is not totally reversible in the lower temperature range (below 300 K). This behavior is similar to that observed for hydrogen chemisorption on (111) surfaces of Ni, Pd and Pt [14,15].

Our previous studies of hydrogen uptake by Nb(100) using electron energy loss spectroscopy (EELS) [12] have suggested that the hydrogen atoms, after dissociating at the surface, occupy tetrahedral sites just below the surface. Features of the EELS results that support this structure model include: (1) the vibrational frequency of hydrogen modes lie in a range around 132 meV, very close to the value established for β-NbH in which hydrogen atoms occupy tetrahedral sites in the Nb lattice; (2) the EELS spectra exhibit significant inhomogeneous broadening of the hydrogen vibrational levels that we associate with inequivalent tetrahedral sites near the surface; (3) low inelastic scattering cross sections are observed for H/Nb compared with corresponding results for hydrogen on W(100) where it is well established that hydrogen atoms occupy surface bridge sites; and, (4) LEED studies [12,16] have shown that hydrogen atoms chemisorb in lattice locations with the same lattice

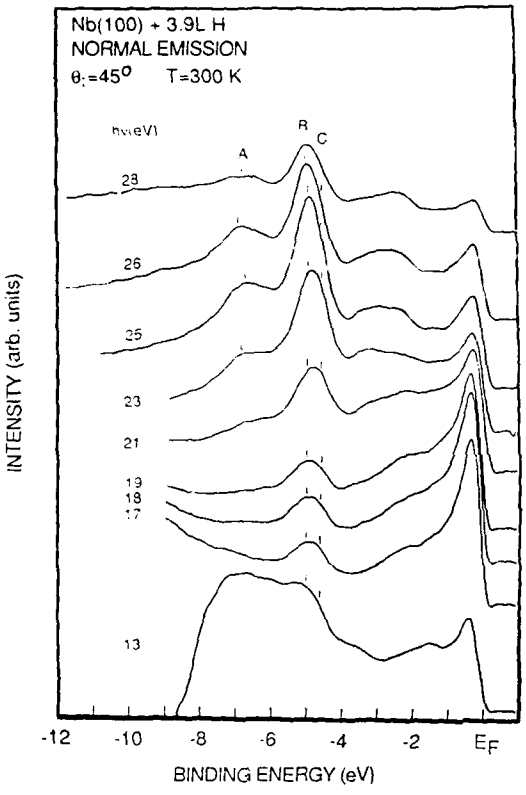


Fig. 3. Photon energy dependence of EDCs for hydrogen treated Nb(100). The enhanced photoelectron cross section of bulk states (ref. [15]) and the hydrogen induced peaks around $h\nu = 25$ eV arise from the enhanced electric field vector strength below the surface that occurs at $h\nu \approx \omega_p$.

structure as Nb. Our EELS results also clearly exhibited the reversible temperature dependent effects described in the present paper, that have also been observed in previous photoemission studies [10,13]. We now present additional evidence based on the photon energy dependent photoemission cross section that supports assigning the peaks labeled B and C to subsurface sites.

Fig. 3 displays normal emission EDCs obtained from hydrogen dosed Nb(100) for selected photon energies ranging from 13 to 28 eV. These spectra show that a significant enhancement of the photoelectron cross section occurs at $h\nu \approx 25$ eV for all the three hydrogen induced peaks, again labeled A, B, and C. Curve fitting of the structures labeled B and C was used to obtain the reduced data displayed in Fig. 4. We have recently studied the bulk and surface electronic properties of Nb(100) using angle resolved photoemission [17]. These experiments yielded accurate values for the location of the Δ_1 bulk

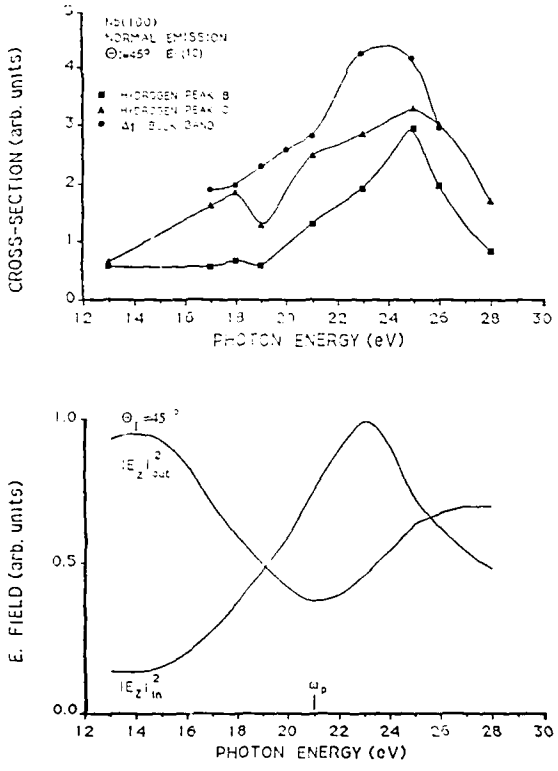


Fig. 4. Upper panel, photoemission cross-section obtained by curve fitting of data displayed in fig. 3, (and from ref. [15]), for the Δ_1 bulk state and the two hydrogen induced states (B and C). Lower panel, calculated z-component of the electric field vector below the surface (refer to text).

bands (Γ–H direction of the three-dimensional Brillouin zone), and two $\bar{\Delta}_1$ symmetry surface resonances. The photon dependent photoelectron cross section for these states was also determined in these experiments. The cross section for the bulk Δ_1 band is displayed in fig. 4. Note that the Δ_1 bulk band cross section, and the cross section of the hydrogen induced peaks exhibit similar enhancement around $h\nu \approx 25$ eV. Since no final bulk band states lie at the correct energy above E_F to explain the cross section enhancement based on a final state resonance [18,19], we attribute this enhancement to an effect based on the behavior of the electric field vector just below the metal surface [17,20]. The lower panel of fig. 4 displays the calculated electric field vector component perpendicular to the surface just outside the surface, and just below the surface based on Fresnel reflection coefficients [21] and using optical constants for Nb obtained by Weaver et al. [22]. The enhanced photoemission cross sections associated with bulk Nb electronic states is

accounted for based on this model. The fact that a similar enhancement is observed for all three hydrogen induced peaks suggests that the hydrogen induced states are subject to the same internal electric fields, as the bulk (Δ_1) states, i.e., that the hydrogen states are located below the surface.

In summary, we have studied the temperature and photon energy dependence of hydrogen induced electronic states on Nb(100) surfaces. Two states having nearly the same binding energy exhibit different temperature dependent occupancy that is consistent with a two-state exchange model in a temperature range below 400 K. Above 400 K, both states are depleted as temperature increases, but the effects are reversible. This behavior is consistent with a surface–bulk exchange model or a model that assumes other near surface sites for hydrogen atoms that are not manifested in photoemission spectra. The photon energy dependence of the photoemission cross section of all prominent hydrogen induced features is similar to that for bulk electronic states of Nb. The only model that appears to account for the cross section dependence of hydrogen induced states and the Δ_1 bulk Nb state is based on an enhancement of the electric field vector below the surface at photon energies near the bulk plasma frequency. This interpretation requires the hydrogen induced states to extend several layers in to the bulk and is consistent with recent vibrational loss studies of the hydrogen Nb system which also conclude that chemisorbed hydrogen atoms occupy tetrahedral sites below the surface. These results also support the notion that the prominent hydrogen induced states in metals that lie typically ~ 6 eV below E_F result from enhancement of direct transitions from bulk metal states [15,23].

We would like to thank the Staff of the Synchrotron Radiation Center, Stoughton, Wisconsin for their assistance. This work was supported by AFOSR-86-0109, the Robert A. Welch Foundation, and the Joint Services Electronic Program, AFOSR-F-49620-86-C-0045.

References

[1] G. Alefeld and J. Volkl, Eds., Hydrogen in Metals I and II, Vols. 28 and 29 of Topics in Applied Physics (Springer, New York, 1978).
[2] M.A. Pick, J.W. Davenport, M. Strongin and G.J. Dienes, Phys. Rev. Letters 43 (1979) 286.
[3] J.W. Davenport, G.J. Dienes and R.A. Johnson, Phys. Rev. B 25 (1982) 2165.
[4] M. Lagos and I.K. Schuller, Surface Sci. 138 (1984) L161.
[5] M. Lagos, G. Martinez and I.K. Schuller, Phys. Rev. B 29 (1984) 5979.
[6] G.J. Dienes, M. Strongin and D.O. Welch, Phys. Rev. B 32 (1985) 5475.
[7] M. Lagos and I.K. Schuller, Phys. Rev. B 32 (1985) 5477.
[8] K.-S. Sohn, T.-S. Park and S.-W. Kim, Phys. Rev. B 37 (1988) 1155.
[9] M.A. Pick, Phys. Rev. B 24 (1981) 4287.
[10] R.J. Smith, Phys. Rev. B 21 (1980) 3131.
[11] M. Strongin, J. Culbert, G.J. Dienes and D.O. Welch, Phys. Rev. B 26 (1982) 2715.

[12] Y. Li, J.L. Erskine and A.C. Diebold, Phys. Rev. B 34 (1986) 5951.
[13] B.-S. Fang, C.A. Ballentine and J.L. Erskine, Phys. Rev. B 36 (1987) 7360.
[14] W. Eberhardt, F. Greuter and E.W. Plummer, Phys. Rev. Letters 46 (1981) 1085.
[15] F. Greuter, I. Strathy and E.W. Plummer, Phys. Rev. B 33 (1986) 736.
[16] T.W. Haas, J. Appl. Phys. 39 (1986) 5854.
[17] B.-S. Fang, C.A. Ballentine and J.L. Erskine, Phys. Rev., submitted.
[18] T.C. Hsieh, P. John, T. Miller and T.-C. Chang, Phys. Rev. B 35 (1987) 3728.
[19] S.G. Louie, P. Thiry, R. Pinchanx, Y. Petroff, D. Chandesiris and J. Lecante, Phys. Rev. Letters 44 (1980) 549.
[20] S.-L. Weng, E.W. Plummer and T. Gustafsson, Phys. Rev. B 18 (1978) 1718.
[21] J.D. Jackson, Classical Electrodynamics, 2nd ed. (Wiley, New York) p. 278.
[22] J.H. Weaver, D.W. Lynch and C.G. Olsen, Phys. Rev. B 7 (1973) 4311.
[23] F.J. Himpsel, J.A. Knapp and D.E. Eastman, Phys. Rev. B 19 (1979) 2872.