Enhancement of Hydrogen Uptake Rates for Nb and Ta by Thin Surface Overlayers

M. A. Pick, J. W. Davenport, Myron Strongin, and G. J. Dienes

Brookhaven National Laboratory, Upton, New York 11973

It is shown that thin layers of Pd or Pt enhance the uptake rate of hydrogen into bulk Nb with almost every hydrogen atom that hits the surface passing into the bulk. A model for the kinetics is formulated showing that in a composite-system large uptake rates are achieved by combining the surface properties of Pd with the bulk properties of Nb, thereby resulting in a smaller barrier for migration into the bulk.

Both Nb and Ta are known to dissolve large amounts of hydrogen and a number of publications discuss the passage of hydrogen through the surface.[1-6] For Nb and Ta (Refs. 2–6) a high initial sticking coefficient, s, has been observed which then decreases to low values (~ 0.005) after an uptake of approximately fifteen monolayers. It is commonly assumed that the hydrogen-uptake rates for clean Nb and Ta are large.[1,5] While this can be the case when pressures from 0.1 to 0.01 Torr are used[1,5] to charge the sample we emphasize that s is small after the first few layers in agreement with the work quoted above[2-6] and this work, where similar results are found. It is also known[7] that the addition of Pd layers hundreds of angstroms thick provides a system where hydrogen can pass into Nb and it is thought that this is due to the Pd protecting the Nb surface from oxide formation. In our experiments we have found that in both Ta and Nb foils the bulk uptake rate of hydrogen, as measured by the resistivity change caused by the interstitial hydrogen, compares with estimates from the previous data by Ko and Schmidt and others.[2-4] However, we have found that, in contrast to the relatively low uptake rates of hydrogen for clean Nb and Ta, the deposition of a few monolayers of Pd on the surface of these metals dramatically enhances the solution kinetics, as evidenced by an order-of-magnitude increase in the solution rate. For Pd layers ~ 10 Å thick and at 430 K, essentially every H atom incident on the surface enters the bulk and goes into solution. We argue here that the slow rate for clean Nb is due to preferential occupation of surface sites over bulk sites resulting in fewer sites for dissociation. Adding Pd with its lower desorption energy leads to a more nearly equal distribution and keeps the surface relatively free. It should be emphasized that this is an intrinsic effect, as opposed to the case where Pd is merely used to protect the surface from oxidation.[6,7] In our experiments Auger spectroscopy and low-energy electron diffraction (LEED) were used to estimate that there was less than $\frac{1}{10}$ monolayer of impurities on the surface when uptake measurements were made. Furthermore, large uptake rates were observed when Pd was evaporated onto Nb even 10 minutes after cleaning indicating that small amounts of oxygen are not an effective barrier, in agreement with Ref. 6. Although, in this paper, we discuss only Nb, similar results have been obtained for Pd on Ta.

In our experiments 25-μm foils of Ta and Nb (Material Research Corporation MARZ grade, nominal purity 99.996 and 99.994%, respectively) were heated in an ultrahigh vacuum system with a base pressure in the low 10^{-10} Torr range. No titanium sublimation pump was used since it would preferentially pump hydrogen. By using a cold liquid-nitrogen trap, impurities were preferentially pumped and ambient pressures of about 2×10^{-9} Torr were obtained of which 90% was hydrogen. The partial pressures were measured with an Extra-Nuclear quadrupole mass spectrometer. The temperature of the sample was deduced from the resistivity and raised by passing a dc current through it. The foils were cleaned by pulsing to about 2300 K until no impurities could be detected by Auger spectroscopy. LEED studies showed that the samples had recrystallized with (110) planes parallel to the surface. The hydrogen admitted into the chamber was obtained by decomposing a metal hydride. At $P_{H_2} = 10^{-5}$ Torr the impurity level was about two or three parts in 10^4 as observed on the mass spectrometer, leading to a contaminant partial pressure comparable to the ambient pressure in the system. The room-temperature resistance of Nb is 14.8 $\mu\Omega$ cm (Refs. 8 and 9) and increases by 0.64 ± 0.06 $\mu\Omega$ cm/at.% hydrogen.[10] The method was capable of detecting about a few parts of 10^5 in the resistivity. Pd and Pt were deposited on the samples by evaporation from a heated-filament source and the coverage determined by Auger spectroscopy. From the exponential de-

crease of the Auger signal of the underlying metal (Nb or Ta) versus time of evaporation we conclude that the effects of Pd agglomeration are small. We assumed that the Auger line of the underlying metal falls off as $e^{-l/d}$ (l is the layer thickness, d the electron escape depth taken as 5–6 Å). Hence when the Ta or Nb height was reduced to $1/e$, the Pd or Pt thickness was taken to be of the order of 6 Å.

The flux of H_2, Γ, hitting the surface per cm² per sec was calculated from the kinetic-theory expression $\Gamma = 3.5 \times 10^{22} P/(MT)^{1/2}$, where P is in Torr, M is in amu, and T is temperature in K. Our Varian ion gauge pressure was multiplied by 2.2 to attain the pressure of H_2.[11] The uptake rate reached its maximum value after about five layers of Pd and then remained at this level up to 100 layers. For Pt only a small increase in the uptake rate was observed at about one layer and this rate decreased for greater thicknesses.

In Fig. 1 we show the number of hydrogen atoms in bulk Nb versus time for various types of surfaces at $P_{H_2} \sim 2.2 \times 10^{-5}$ Torr. Curve A is Nb with about six layers of Pd and curve E is clean Nb, both at 310 K. Curve D is for clean Nb at 460 K. Curve B is Nb with about six layers of Pd at 455 K and curve C is Nb with about one monolayer of Pt at 460 K. The final n_H value of curve B corresponds to a concentration of about 0.28% H in Nb and this agrees with Sievert's constant determined from other measurements.[12] Furthermore, the saturation value followed the expected $\sqrt{P}$ dependence. Thus both the uptake and outflow rates of H in Nb crucially depend on the surface
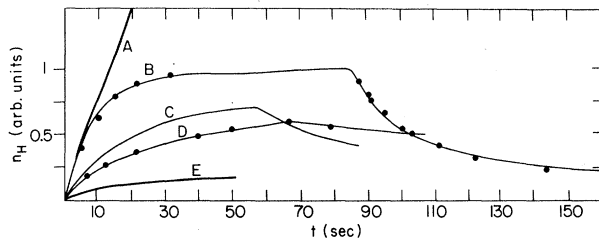
condition. The initial slope of curve B corresponds to almost every hydrogen that hits the surface passing into the bulk. Actually in this particular case the bulk uptake rate (the number going in per unit time divided by the incident flux) is ~0.6 but it has been observed to be nearly unity in other data that we have.

Our physical picture is that the H uptake is determined by the four fluxes shown in Fig. 2. Since the uptake is insensitive to the Pd thickness after, say, five or six layers we assume that diffusion through Pd is not a rate-limiting step for $l < 100$ Å. Calculations also show that in about 1 sec an H atom diffuses about the thickness of the bulk sample and hence this process is also neglected. θ is defined as the atomic fraction of H atoms on the surface and x as the atomic fraction in the bulk.

By balancing fluxes we obtain the differential equations

$$\frac{d\theta}{dt} = \frac{2\Gamma s_0}{N_s}(1-\theta)^2 - K\theta^2 - \nu\theta + \beta(1-\theta)x \qquad (1)$$

FIG. 1. Curve A, Nb with about six layers of Pd at 310 K and at $P_{H_2} \sim 2.2 \times 10^{-5}$ Torr. Curve B, Nb with about six layers of Pd at 455 K and at $P_{H_2} \sim 2.4 \times 10^{-5}$ Torr. Curve C, Nb with about one monolayer of Pt at 460 K and at $P_{H_2} \sim 2.4 \times 10^{-5}$ Torr. Curve D, clean Nb at 460 K and at $P_{H_2} \sim 2.4 \times 10^{-5}$ Torr. Curve E, clean Nb at 310 K and at $P_{H_2} \sim 2.6 \times 10^{-5}$ Torr. n_H is given in arbitrary units. To obtain $x = n_H/n_{Nb}$, multiply n_H scale by 0.0028. Solid circles are values calculated from Eq. (6). $b = 0.46$ for curve B and $b = 2.5$ for curve D.
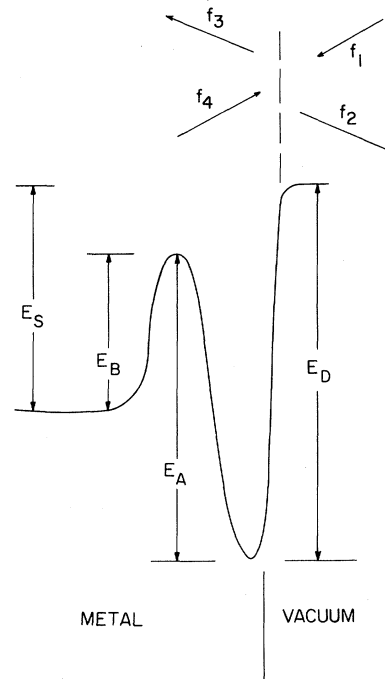

FIG. 2. Idealized surface-barrier model for composite surface defining the barrier energies. The four fluxes shown at the metal-vacuum interface are as follows:

$$f_1 = \frac{2\Gamma s_0}{N_s}(1-\theta)^2, \; f_2 = -K\theta^2, \; f_3 = -\nu\theta, \; \text{and} \; f_4 = \beta(1-\theta)x.$$

and

$$\frac{dx}{dt} = \frac{\nu\theta}{N_l} - \beta(1-\theta)\frac{x}{N_l}, \tag{2}$$

where s_0 is the sticking coefficient for the bare surface; N_s is the number of Nb atoms per cm^2 of surface; N_l is the number of Nb layers in the bulk; K, ν, and β are rate constants given by $K = K_0 \exp(-2E_D/RT)$, $\nu = \nu_0 \exp(-E_A/RT)$, $\beta = \beta_0 \times \exp(-E_B/RT)$, respectively, with preexponential factors of the order of 10^{13}. This model has been written previously by Conrad et al.[13] but no solution was attempted.

At equilibrium $d\theta/dt = dx/dt = 0$; then

$$x_{\max} = \frac{\nu}{\beta}\frac{\theta_{\max}}{1-\theta_{\max}} = \frac{\nu}{\beta}\left(\frac{2\Gamma s_0}{KN_s}\right)^{1/2}. \tag{3}$$

This equation expresses Sievert's law because Γ is proportional to pressure and from Fig. 2:

$$-E_A + E_B + E_D = E_S, \tag{4}$$

where E_S is the heat of solution of hydrogen in niobium and is taken to be 16.48 kcal per mole of H_2.[12]

The two coupled differential equations cannot be solved in general. Computer solutions showed, however, that x and θ are in quasiequilibrium past a very fast initial transient and that $d\theta/dt$ is very small compared to $N_l dx/dt$. With these approximations

$$\left(1+\frac{\beta x}{\nu}\right)^2 \frac{dx}{dt} = \frac{2\Gamma s_0}{N_s N_l} - \frac{K\beta^2 x^2}{N_l \nu^2}. \tag{5}$$

If we now define

$$y = x/x_{\max}, \quad a = 2\Gamma s_0/N_s N_l x_{\max},$$

and $b = (\beta/\nu)x_{\max} = [\theta_{\max}/(1-\theta_{\max})]$

we obtain by integration

$$\tfrac{1}{2}(1-b)^2 \ln(1+y) - \tfrac{1}{2}(1+b)^2 \ln(1-y)$$

$$-b^2 y = at \quad \text{for charging} \tag{6}$$

and

$$1/y - 1/y_0 + 2b\ln(y_0/y) + b^2(y_0 - y) = at$$

$$\text{for degassing.} \tag{7}$$

The initial slopes are $dy/dt = a$ for charging and $dy/dt = -ay_0^2/(1+by_0)^2$ for degassing, where y_0 is the value of y at the start of degassing. In Fig. 3 we show families of curves for Eqs. (6) and (7). The essential physics in this model is that θ and x are in quasiequilibrium and θ is larger than x because the desorption energy is larger than the
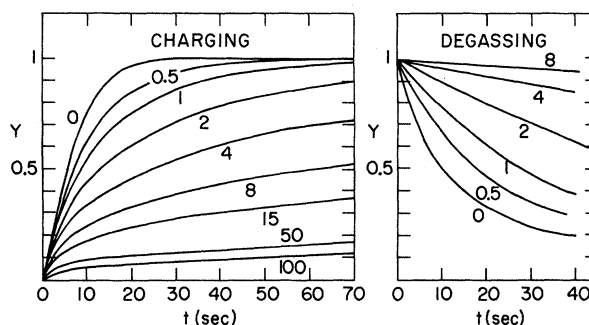

FIG. 3. Curves calculated from Eqs. (6) and (7) for $a = 0.1$, and for different values of b.

solution energy. Therefore a low bulk concentration ($\sim 1\%$) can lead to a surface concentration of ~ 1 and a reduction in the filling rate which goes as $(1-\theta)^2$. In this type of kinetics there is a two-step process but neither step is rate limiting. Rather, the surface acts like a valve which is controlled by the bulk concentration. If the barrier to entry were made very large, then the surface and bulk would go out of equilibrium. This is the usual case in surface physics, where it is assumed that negligible bulk uptake occurs.

The fit of this simple model to the data is shown in Fig. 1 for pure Nb and Nb with the Pd layer. The circles on curves B and D are fits using Eq. (5). The agreement is excellent both for charging and degassing. For curve B the uptake through the pure Nb surface was neglected. Note that a is evaluated directly from the experiment since it is completely determined from the initial slope and $x_{\max}$. We did not attempt to analyze curve A (which represents only part of the data) because it reaches into the concentration region where Sievert's law is not obeyed. The fitting parameters are given in Table I.

From b parameters for D and E and the definition of b we derive 25 kcal/mole H_2 for E_D, the heat of desorption of H_2 from pure Nb. This seems to be a reasonable value and corresponds to the heat of adsorption of 26.5 kcal for state 2 of hydrogen in Nb found by Hagen and Donaldson.[14] The corresponding $E_A - E_B$ value from Eq. (4) is 8.5 kcal/mole H_2. By comparing the b values for B and D we find that E_D for Pd on Nb has been lowered to 21.7 kcal, and the corresponding $E_A - E_B$ to 5.2 kcal/mole H_2. Thus, if E_B is independent of the surface, the barrier to motion into the bulk has been lowered by about 3 kcal.

We believe that this work shows that if a metal adlayer is made thin enough, so that hydrogen

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TABLE I. Fitting parameters for simple model.

Curve in Fig. 1.	Temperature (K)	Surface	x_{max} [a]	a	b
B	455	Pb on Nb	0.0028	0.10	0.46
D	460	Nb	0.0028	0.04	2.5
E	310	Nb	0.0026	0.0005	2000

[a] Atomic fraction of H in Nb.

[b] Extrapolated from run B by Sievert's law using E_{sol} = 16.48 kcal/mole H_2 (Ref. 12).

diffusion through this layer is not a rate-limiting step, then in principle the surface parameters that determine adsorption and dissociation can be varied independently of bulk parameters, such as the heat of solution, to achieve a desired result, such as the high bulk uptake rate. Hence, by using composite systems, both surface and bulk parameters can be optimized by using the proper combination of metals.

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[1] J. A. Pryde and C. G. Titcomb, Trans. Faraday Soc. 65, 2758 (1969).

[2] S. M. Ko and L. D. Schmidt, Surf. Sci. 42, 508 (1974).

[3] L. Johnson, M. F. Dresser, and E. E. Donaldson, J. Vac. Sci. Technol. 9, 857 (1972).

[4] S. M. Ko and L. D. Schmidt, Surf. Sci. 47, 558 (1975).

[5] K. F. Poulter and J. A. Pryde, in Proceedings of the Fourth International Vacuum Congress, Manchester, April 1968 (Institute of Physics and the Physical Society, London, 1969), p. 111.

[6] E. Fromm and H. Uchida, Vak. Tech. 26, 174 (1977).

[7] N. Boes and H. Züchner, Z. Naturforsch. 31a, 754 (1976).

[8] H. Schultz, Mater. Sci. Eng. 3, 189 (1968/69).

[9] G. Perriot, J. Phys. (Paris) 28, 472 (1967).

[10] G. Pfeiffer and H. Wipf, J. Phys. F 6, 167 (1976).

[11] P. A. Redhead, J. P. Halison, and E. V. Koreulsen, The Physical Bases of Ultra High Vacuum (Chapman and Hall, London, 1968).

[12] J. A. Pryde and C. G. Titcomb, J. Phys. C 5, 1293 (1972).

[13] H. Conrad, G. Ertl, and E. E. Latta, Surf. Sci. 41, 435 (1974).

[14] D. I. Hagen and E. E. Donaldson, Surf. Sci. 45, 61 (1974).

Strain Defects in Alkali Halides: A Heuristic Model for Glasses

Baruch Fischer and Michael W. Klein[a]

Department of Physics and Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

We present as idealized solvable model for the low-temperature properties of strain defects dissolved in alkali halides. The predicted specific heat and thermal conductivity are very much like those for glasses. Our calculation suggests a strong analogy between the low-temperature properties of strain defects and those of glasses.

The low-temperature properties of glasses[1] have been of considerable interest during the past few years. A number of anomalous properties of glassy materials have been explained using the idea of two-level tunneling states proposed by Anderson, Halperin, and Varma[2] and by Phillips[3] (AHVP).

Whereas the AHVP model explains the general features of the glass at low temperatures, it considers the tunneling units as essentially isolated and presents no microscopic picture for the origin for the constant density of states at low energies. However, in order to explain the pho-

non-echo[4] and the hole-burning experiments[5] one must consider strain interactions between the two-level tunneling states as was discussed by Black and Halperin.[6] It was recently also pointed out[7] that strain interactions may play an important role in giving the appropriate broad distribution of tunneling states.

The purpose of this paper is to present an idealized model which shows that small concentrations of strain dipoles, like CN^-, dissolved in alkali-halide crystals produce very similar low-temperatures properties to that observed in glasses when strain interactions between the tun-