

Sticking, Adsorption, and Absorption of Atomic H on Cu(110)

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The sticking coefficient of atomic hydrogen at $T_G = 1815$ K on a Cu(110) surface has been determined to be 18%. In addition to the buildup of a chemisorption layer the absorption of atomic H into subsurface sites is observed. The subsurface sites are thermally less stable than the chemisorption sites. Model calculations for the phononic energy transfer and estimates for the parallel momentum transfer as well as for electron-hole pair excitation indicate that the first two mechanisms dominate the accommodation process.

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The interaction of atomic H with surfaces is an important issue in various research areas ranging from hydrogen storage to nuclear fusion technology. As an example we mention the production of high energy neutral H (D) beams [1]. The yield of the ion sources used to produce some beams depends on the concentration of atomic H in the source, which in turn is determined by the reflection and absorption properties of the wall [2]. Eenshuistra *et al.* [2] reported recently that the measured densities in a multicusp ion source could only be modeled by assuming a H recombination coefficient of $\approx 10\%$ on the walls. This is surprisingly small in view of the strong H metal chemisorption bond [3]. In the present study we report the first measurement of a sticking coefficient for atomic H on a well defined metal surface under UHV conditions and rationalize the result by calculating the energy transfer to substrate phonons.

We used a specially designed source for ultrapure atomic H featuring a tungsten capillary with electron bombardment heating. Details are given elsewhere [4]. From the flux through the capillary and the temperature at the exit ($T_{\text{nozzle}} = 1815$ K) the degree of dissociation can be calculated by means of the tabulated dissociation constant [5]. We obtained an atomic hydrogen flux of $\sim 1.7 \times 10^{14} \text{ s}^{-1}$ and a molecular hydrogen flux of $\sim 2.7 \times 10^{14} \text{ s}^{-1}$ under typical conditions of exposure. The molecular H_2 yields a negligible contribution to the total amount of adsorbed H, because the $v=0$ vibrational state has essentially zero sticking probability. At our nozzle temperature only $\sim 3\%$ of the H_2 molecules are excited into the $v=1$ state, which has a sticking coefficient below 10% in the relevant energy range [6]. About 20% of the H atoms emerge from the hot end of the capillary in a central cone with 30° angular aperture [7] corresponding to the solid angle intercepted by the sample. Saturation of the Cu(110) surface was obtained after nominal exposure of $< 3 \times 10^{-6}$ mbars at 10^{-8} mbar corrected pressure gauge reading in the sample chamber.

After the usual cleaning procedures ultimate sample cleanliness was checked by ultraviolet photoemission spectra (UPS) of the surface state at the Y point of the Brillouin zone [8]. The intensity and the full width at half maximum (FWHM) of UPS surface state peaks are very sensitive measures of sample contamination. A FWHM of 110 meV recorded with a nominal analyzer resolution of 50 meV was considered to be indicative of clean surface conditions [8].

Thermal desorption spectra (TDS) from H/Cu(110) are shown in Fig. 1. The TDS signal from a Cu(110) surface saturated at $T_S = 200$ K with atomic H is very similar to that measured by Anger, Winkler, and Rendulic [9] after saturation with a H_2 supersonic beam [Fig. 1(a) and inset]. An absolute coverage calibration was obtained from TDS spectra of H/Ni(110) (low temperature phase) for which the coverage is known to be 1.5 ML (monolayer) [10]. By comparison, the saturation coverage value for H/Cu(110) was determined to be $\theta_H = 0.45 \pm 0.06$ ML, which is 10% less than the value estimated by Anger, Winkler, and Rendulic. Although this difference might be due to an Eley-Rideal desorption mechanism [11] operating during exposure to atomic H, the experimental uncertainty is too large to arrive at a definitive conclusion.

If the exposure to atomic hydrogen is carried out at a sample temperature $T_S < 110$ K an additional desorption peak appears at $150 < T < 250$ K [Fig. 1(b)]. Such a low temperature TDS peak was not observed after adsorption from a supersonic H_2 beam on Cu(110) at $T_S = 140$ K [12] and therefore seems to be associated with exposure to atomic hydrogen. This parallels the observation of a low temperature TDS peak appearing after exposure of a Ni(111) surface to atomic hydrogen, reported by Ceyer and co-workers [13]. This group demonstrated convincingly that the peak arises from the presence of subsurface hydrogen. By analogy, we, too, assign the low temperature TDS peak to a subsurface H species. This assignment is supported by our inverse photoemis-

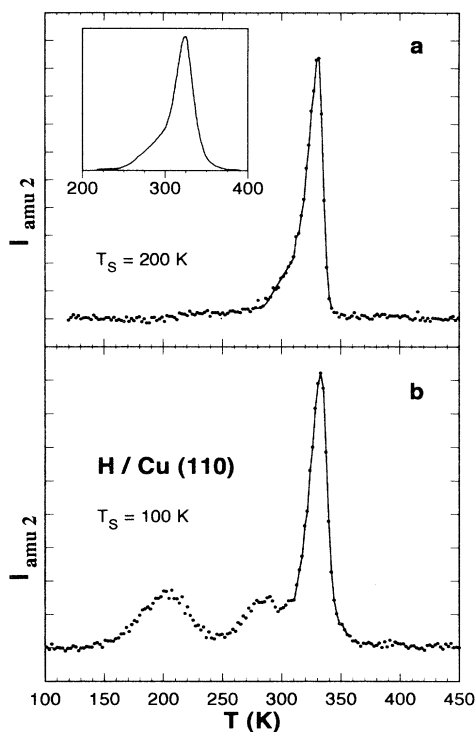


FIG. 1. (a) H_2 TDS from a Cu(110) surface saturated with atomic H at $T_S = 200$ K. The inset shows a H_2 TDS obtained by Anger, Winkler, and Rendulic [9] after saturation of Cu(110) with a supersonic H_2 beam. (b) H_2 TDS from the same surface after exposure to atomic H at $T_S = 100$ K.

sion data [14,15]: On Cu(110) the unoccupied Shockley surface state at the Y point of the surface Brillouin zone [15,16] survives up to $\theta_H = 0.45$, but disappears completely as the population of the low temperature TDS state is increased. In contrast, on Ni(110) the unoccupied Shockley surface state [14] survives the adsorption of H_2 at low temperatures up to H coverages of $\theta_H = 1.5$. Even a pairing row reconstruction occurring at low tempera-

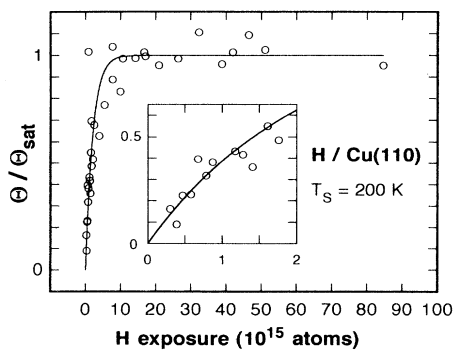


FIG. 2. Relative coverage as a function of exposure for Cu(110) dosed with atomic H at $T_S = 200$ K.

ture and large H coverage causes only a limited attenuation [14]. This behavior indicates that the quenching of the unoccupied surface state on Cu(110) beyond $\theta_H = 0.45$ ML is not due to chemisorbed H, but has to be attributed to the population of subsurface sites. The difference of the TDS spectra in the temperature range between 250 and 300 K is due to an irreversible phase transition, i.e., the missing/added row reconstruction taking place on H/Cu(110). This is discussed in more detail in [15] and references therein.

In Fig. 2 we present a coverage versus exposure curve for atomic H with a gas temperature of 1815 K. All exposures were carried out at a sample temperature of $180 < T_S < 200$ K. From the slope at $\theta_H = 0$ one obtains a sticking coefficient $s_0 = (18 \pm 6)\%$ for near normal incidence on Cu(110).

The sticking is determined by the loss of normal energy. There are three channels for the energy transfer in a H/Cu collision: phonon excitation, parallel momentum transfer, and electron-hole pair excitation.

We have calculated the phonon excitation probability using a soft cube model. Details of the forced oscillator calculation are given in Ref. [17]. The parameters of the model were optimized to obtain a large energy transfer. The H/Cu interaction was modeled by a Morse potential joined to an inverted parabola in the repulsive region to mimic the qualitative behavior of the potential sketched in Fig. 3 (to be discussed later). The well depth was 2.2 eV, the range parameter 0.5 \AA^{-1} . The corresponding vibrational energy is 0.07 eV in accord with the lowest values given in calculations [18] and experiments [19,20]. The matching point for the parabola was taken to be -1.5 eV, and the barrier height (top of the parabola) was at 0.3 eV (energies with respect to the asymptotic H level). The Debye energy was taken to be 260 K (compare [21]). The result of the calculation for the sticking coefficient due to phonon excitation is presented in Fig. 4 for a quasithermal beam. The value at $T_G = 1815$ K is 0.13, while the experimental result is 0.18 ± 0.06 . The average energy transfer to phonons is about 800 K.

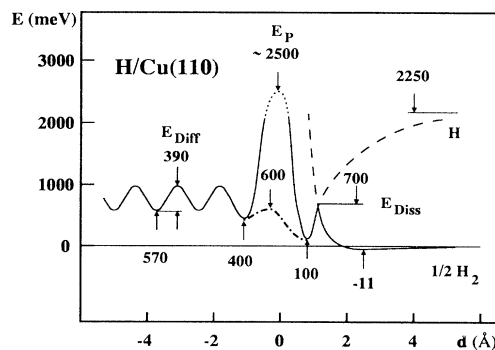


FIG. 3. One-dimensional potential energy diagram for H_2 and H on Cu(110). Explanations are given in the text.

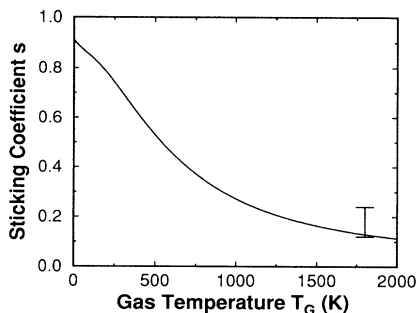


FIG. 4. Sticking coefficient s as a function of gas temperature T_G calculated for the phonon mechanism (surface temperature $T_S = 200$ K; for further parameters see text) in comparison with the experimental result at $T_G = 1800$ K.

In general, this energy transfer is rather inefficient in H-metal interactions for the following reason: Because of the low H mass and the deep interaction potential the collision time is short compared to the inverse Debye frequency, which results in a weak coupling to the phonons. However, soft portions of the potential with low frequencies and low barrier heights occurring on a corrugated surface lead to larger collision times. Accordingly, the weight in the Fourier transform of the interaction force is shifted towards lower frequencies and the coupling is improved. We have taken into account this effect by choosing a rather soft potential (small range parameter). The calculated sticking coefficient therefore may be considered as an upper limit for the phonon mechanism. Less favorable parameters would require substantial contributions from either parallel momentum transfer or electron-hole excitation or both.

Actually, we believe that parallel momentum transfer yields a sizable contribution to sticking. Because of the large well depth of about 2 eV the H trajectories sample a strongly corrugated two-dimensional energy surface [18], which gives rise to an efficient normal to parallel energy transfer. A detailed calculation would require an accurate knowledge of the two-dimensional energy surface going beyond our present simplified analysis. A rough estimate, however, indicates immediately that one can easily obtain energy transfers from normal to parallel energy comparable to phonons: For a corrugation $\delta a/a$ one obtains parallel momentum transfers of the order of $\delta p/p \approx 2\delta a/a$ and energy transfers of $\delta E/(E+D) \approx 4(\delta a/a)^2$. Hence for $\delta a = 0.1a$ one can expect energy transfers of the order of about 900 K, depending on the corrugation profile. The corresponding trajectories will undergo multiple (inelastic) collisions and finally lead to sticking. The quantum analog of this (selective adsorption) is known to lead to an increased sticking coefficient for low energy He [22].

Concerning the electron-hole pair mechanism there are unfortunately no relevant data for H/Cu. An upper limit, however, can be obtained from experimental results for

the width of H vibrations on W [23]. The energy transfer scales with the *velocity* of the H atom, at least for the dominant part, due to a crossing of the affinity level with the Fermi level [24]. For a low energy incident H this velocity in the region of the well is about 4 times larger than for the first excited vibrational level. With a width of 26 cm^{-1} for the latter [23] we would predict an average energy transfer of about 150 K for a scattered particle. For H/Cu with a fully occupied d band we expect values well below this. Therefore the electron-hole pair mechanism is probably the least important one for H/Cu sticking.

We conclude with a brief discussion of the barrier for surface permeation (E_p in Fig. 3). A H atom permeating through the copper surface from inside the crystal, as in the experiments of Comsa and David [25], experiences a barrier which is lower than the bulk diffusion barrier E_{diff} (dash-dotted line in Fig. 3). This was already noted by Comsa and David [25] and was explained in terms of a larger relaxation of the Cu atoms in the surface layer by Jacobsen and Nørskov [18]. In contrast, from the gas phase a H atom arrives with large kinetic energy and therefore can be considered as moving towards a rigid Cu lattice. The resulting unrelaxed surface permeation barrier is of the order of some eV as pointed out by Jacobsen and Nørskov [18]. A tentative potential energy diagram for H on Cu(110) is shown in Fig. 3. The heat of solution is taken from McLellan and Harkins [26], the activation energy for diffusion from Katz, Guinan, and Borg [27], the dissociation barrier from Küchenhoff and Brenig [28]. The binding energy in the physisorbed state is taken from Ref. [29], the binding energy in the chemisorbed state is obtained from the low coverage limit of the desorption energy determined by Anger, Winkler, and Rendulic [9]. For the surface penetration barrier in the relaxed case we followed Jacobsen and Nørskov [18] and the nonrelaxed barrier is the one used in the present calculation. However, our results allow only a rough estimate of the barrier height. Hence the upper part of the barrier is shown as a dotted line only. The one-dimensional energy diagram is not meant to represent a simple cut, but rather a path of lowest energy across the potential energy surface. Note that the desorption energy [9] as well as the barrier for surface permeation [30] changes with H coverage.

In summary, the sticking coefficient of atomic H on Cu(110) is determined as $(18 \pm 6)\%$. Because of the large reflection probability atomic H can survive several wall collisions. The phononic energy transfer depends strongly on the shape of the two-dimensional potential energy surface. The measured sticking coefficient can be accounted for by a phononic accommodation mechanism in cooperation with normal to parallel energy transfer. The basic reason for a H sticking coefficient falling far off unity lies in the large mass mismatch. Therefore the present result is likely to be characteristic for most metals.

The H atoms which are trapped on Cu(110) form a chemisorption layer, but a small fraction is also absorbed into subsurface sites. The present result and data from the literature allow the construction of a potential energy diagram which provides insight into the complicated kinetics of H adsorption, absorption, and desorption from Cu.

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