

Sticking of atomic hydrogen on the tungsten (001) surface

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Abstract

The sticking of hydrogen atoms with kinetic energies in the range 0.003–10 eV on a clean (001) tungsten surface has been investigated using molecular dynamics simulations. The atoms are found to stick to the surface at 0 and 300 K, with a sticking coefficient smaller than 0.6 for kinetic energies higher than 3 meV. The adsorption sites for H on the W(001) surface are also presented. The dominant site is in perfect agreement with the experimentally found bridge site.

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1. Introduction

The sticking of molecular hydrogen on polycrystalline [1,2] as well as single-crystalline [3] tungsten, and tungsten targets with explicit surface orientations of (001) [4–14], (110) [9,12,15–17], and (111) [9,12] has been experimentally investigated for some time. In contrast, very few studies of atomic hydrogen sticking on tungsten exist.¹ A study by Eckstein and Biersack [18] of the reflection coefficient R for 0.2–1000 eV hydrogen atoms incident on tungsten is the most noteworthy one in this context. In their computational investigation Eckstein and Biersack used a modified version of TRIM, which is conventionally used for the calculation of ranges of ions in solids. For energies below 10 eV an “antireflection” coefficient $1 - R$ of about 0.6 or larger can be calculated from their data. However, it should be pointed out that the sticking coefficient S does not necessarily equal $1 - R$, since a fraction of the ions may become implanted. Also, since TRIM assumes an

amorphous target, it cannot describe well the behavior of ions incident on crystalline targets. In addition, the binary-collision approximation underlying TRIM calculations gives no description of the many-body nature of the W–W and W–H interaction, in contrast to molecular dynamics simulations.

A reactive interatomic potential recently developed at our laboratory [19] was used in the present calculations. The “reactiveness” of the potential means that it should describe *e.g.* breaking of bonds during reactions in smooth way, *i.e.* without discontinuities in the interatomic forces. The choice of atomic instead of molecular hydrogen is motivated by the fact that the potential has been developed with the explicit intent to describe situations where atomic hydrogen dominates over molecular hydrogen. Although the potential reproduces well (i) the bond lengths of the simple cubic (SC), body-centered cubic (BCC), and face-centered-cubic (FCC) phases, the WH_n ($n = 1, 2, 3, 4, 6$) structures, and the W–W and W–H dimers; (ii) the cohesive energy of the BCC phase and the W–W and W–H dimers; as well as (iii) the bulk modulus and elastic constants of BCC W, it naturally falls short if *e.g.* quantum-mechanical tunnelling effects are important.

Due to the small mass of the H atom in relation to the W atom, quantum-mechanical tunnelling effects (QMTE) may be expected to play an important role in the interaction of

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¹ An INSPEC search returned five matches for a search of articles (published since 1969) containing the strings (tungsten), (atomic hydrogen), and (sticking). None of these articles deals with sticking of atomic hydrogen ions on tungsten.

hydrogen ions with the tungsten surface, especially at low temperatures ($T \ll 300$ K). For instance, the migration of hydrogen atoms inside BCC metals is affected by quantum-mechanical tunnelling to a larger extent than for FCC metals, due to the smaller jump distances d between interstitial sites [20]. These effects are noticeable in niobium and tantalum below 300 K. The existence of similar effects for hydrogen in tungsten at or around 300 K is unclear. Even if QMTE do play some role in bulk W, where the jump length for H atoms is $d_{\text{bulk}} = (a/4)\sqrt{2}$ (H atoms occupy the tetrahedral site [21–24]), they need not play as large a role on the W(001) surface, where H atoms bind to the “bridge” site [25] between two W corner atoms, making the jump length $d_{001-s} = (a/2)\sqrt{2} = 2d_{\text{bulk}}$, *i.e.* twice as large as in the bulk.

In this paper we report the results of classical molecular dynamics simulations (MDS) of atomic hydrogen sticking to the clean (001) surface of tungsten for a broad range of energies. The results show that the sticking coefficient decreases monotonically with the kinetic energy of the incident H atom. It is observed that previous findings [18] for the sticking coefficient are off by a factor of 2 or more.

2. Computational methods

2.1. Molecular dynamics simulations

In this study molecular dynamics simulations (MDS) were used to investigate the sticking of atomic hydrogen to the (001) surface of tungsten. Here we do not fully describe the details of the MDS, extensive descriptions can be found in the literature (see for instance Ref. [26] concerning MDS for energetic projectiles).

In the current study of low-energy H atoms incident on W the most important aspect of the MDS is the quality of the interatomic potential. Due to the low energy of the atoms, it is important to model the full many-body nature of the forces between them. In the calculations we used the Tersoff-like potential recently developed in our group [19]. The potential was tailored to describe the angular-dependent interaction between all combinations of the elements H, C and W. The C–C, C–H, and H–H combinations were taken from the literature. The potential has been successfully tested against experimental properties of the W surface and small W–H clusters, as mentioned in Section 1. In detail, the reconstruction of the (211) surface is in excellent agreement with experiments. For the (011) surface the agreement is still fairly good. In comparison, the (001) surface does not develop the experimental reconstruction [27–30]. However, the lateral displacement of the tungsten atoms on the reconstructed (001) surface is ≈ 0.2 Å (Ref. [30]), which amounts to only 6% of the lattice parameter $a = 3.165$ Å of tungsten at zero temperature. The absence of such small displacements is likely to have at most a minor effect on the present results.

A clean tungsten surface was used in the present work. Two irradiation series were carried out—one for the target

at 0 K and one for 300 K. The target consisted of eight conventional BCC unit cells in all Cartesian directions, making a total of 1024 W atoms. Periodic boundary conditions were enforced in the x and y directions, which resulted in two open surfaces. To remove one of them all atoms in the two lowest layers in the cell were kept fixed at all times. In order to model heat conduction from the cascade (the H atom and the W atoms disturbed by the incident atom) into the bulk the temperature was controlled in a region five atom layers thick at the bottom of the target (in the z direction), above the fixed atoms, and in a region two layers thick at all the four side walls. The incident hydrogen atom was never subjected to temperature scaling, even when entering the scaling regions ending on the surface. The simulation cell is shown in Fig. 1.

In all cases the H projectile was placed at approximately $d = 5$ Å outside the target in the z direction. The initial x and y coordinates were randomly chosen within the surface unit cell in every simulation. This unit cell was always centered on the xy -plane, *i.e.* its center was as close as possible to the z axis. Kinetic energies E_i between 0.003 eV and 10.0 eV were used. The simulation time was 15 ps for every individual run. This ensured that the H atom was either stuck on the W surface or well outside it. Approximately 200 runs were carried out for each energy. All runs used the same initial target.

Separate series of cumulative irradiation were also carried out using energies of 0.003 eV, 0.03 eV, and 0.3 eV. The purpose with these series was to determine the hydro-

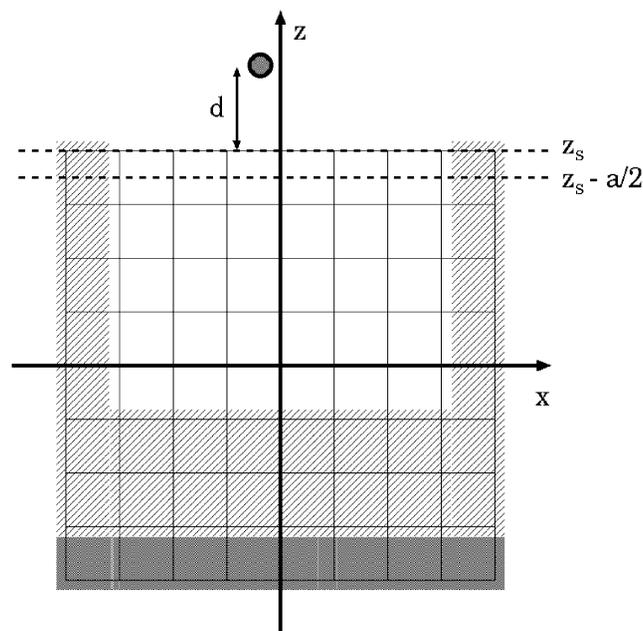


Fig. 1. The simulation cell used in the molecular dynamics calculations. Each square depicts one BCC unit cell. The length of a square border corresponds to the lattice parameter a . The dark area represent the region of fixed atoms. The hatched area illustrates the region where temperature scaling is employed. The coordinates z_s and $z_s - a/2$ and the distance $d = 5$ Å are also shown.

gen saturation coverage (number of adsorbed H atoms divided by the number of W atoms in the topmost surface layer). The target—whose temperature was scaled towards 300 K—was shifted independently in the x and y directions by the random amounts Δx and Δy before each run, which always lasted 20 ps. Here Δx and Δy were chosen in the interval $(0, uL)$, where u is a random number (different for the x and y directions) chosen uniformly between 0 and 1, and L is the side length of the square surface. After each shifting the periodic boundary conditions were enforced in order to move atoms located outside the original boundaries back into the cell. The incident hydrogen atom was always placed at the same position $(0, 0, z_i)$, where $z_i = z_s + d$, z_s is the z coordinate of any W surface atom, and $d = 5 \text{ \AA}$. The flux towards the W target was therefore $f = 7.77 \times 10^{24} \text{ H m}^{-2} \text{ s}^{-1}$. This flux is about one order-of-magnitude larger than the estimated atomic and molecular hydrogen flux in the divertor part of the International Thermonuclear Experimental Reactor (ITER), which is $10^{24} \text{ H m}^{-2} \text{ s}^{-1}$ [31,32].

A total of 500 runs were carried out, giving a total fluence of $F = 7.77 \times 10^{19} \text{ H m}^{-2}$.

2.2. Calculation of sticking coefficient

To calculate the sticking coefficient the final positions of the impinging H atoms were analyzed. The H atom was considered to be stuck on the surface (adsorbed) if the distance between the atom and the closest W atom was smaller than the cut-off distance $r_c = 2.35 \text{ \AA}$ for the W–H interaction, and if the z coordinate of the H atom was $z_H \geq z_s - a/2$. The latter condition means that adsorbed H atoms were required to be above the second surface layer.

The sticking coefficient S is defined as the number of simulations in which the H atom is stuck on the surface in the end of the run, divided by the total number of simulations in the series.

3. Results

3.1. Sticking at the clean W(001) surface

The sticking and “antireflection” coefficients, $S = S(E_i)$ and $1 - R(E_i)$, respectively, for H atoms incident on W(001) at 0 and 300 K, as a function of the kinetic energy E_i , are shown in Fig. 2. In general, it holds that $1 = R + S + I$, where R denotes the probability that atoms have been reflected from the target surface, and I the likelihood that atoms have been implanted or transmitted through the sample. Therefore $1 - R = S + I$. The reason for including the antireflection coefficient $1 - R$ will be explained below. From the figure it can be seen that the sticking coefficient decreases monotonically with the kinetic energy of the incident H atom. Both at 0 K and 300 K the sticking coefficient decreases rapidly after an energy of about 0.3 eV. At an energy of 10 eV the H atom was

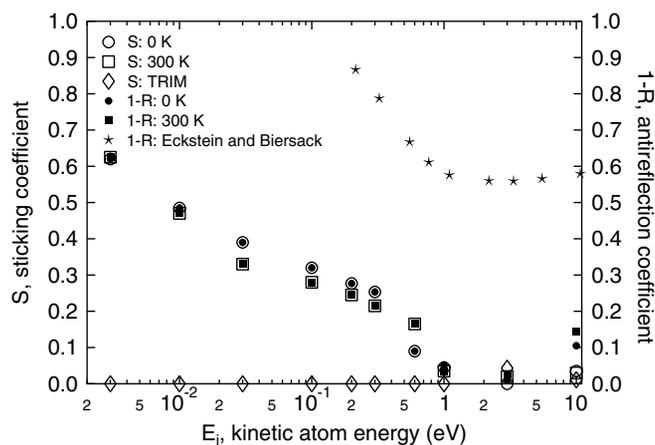


Fig. 2. Sticking and antireflection coefficients of H normally incident on W(001) at 0 and 300 K, as a function of the kinetic energy. Results from TRIM calculations are also displayed. The data labeled ‘Eckstein and Biersack’ is from Ref. [18]. The statistical uncertainties in the present data are small and are covered by the graphical markers.

quite often implanted into the W target. These atoms are clearly not adsorbed, and are therefore not accounted for in the sticking coefficient.

In addition to the molecular dynamics simulations we also performed binary collision approximation (BCA) calculations using the code package TRIM [33]. In these calculations H atoms located in a 1.0 \AA thick layer centered on the W surface were considered stuck (adsorbed). The results are shown in Fig. 2. The sticking coefficient S is non-zero only at energies $\geq 3.0 \text{ eV}$, S increasing with the energy, since the H atoms are penetrating deeper into the sample before coming to rest.

Furthermore, the reflection coefficients $R(E_i)$ as calculated by Eckstein and Biersack [18] using a modified version of TRIM have been included in the figure through $1 - R(E_i)$. The essential change in the TRIM code in this case was the addition of a planar potential above the target surface, in order to accelerate incoming and decelerate outgoing particles, and thereby model the real physical behavior of atoms incident on metallic surfaces. Our MDS values for $1 - R = S + I$, calculated directly from the number of reflected atoms, are lower than those of Eckstein and Biersack by a factor of about 2.

3.2. Adsorption sites

Analysis of the positions of the adsorbed H atoms shows that there are several distinct sites for adsorption. These are denoted A, B, C, D, and E, and shown in Fig. 3. Sites A and E have the same lateral position, but site A is above site E and therefore closer to the vacuum outside the target. We have also included the high-symmetry sites R and S. Sticking at these sites was not observed in our simulations. Some of the sites have special names: Site A (or E) is also known as the “bridge” site [25,27], site R is called the “hollow” site, and site S the “top” site [34].

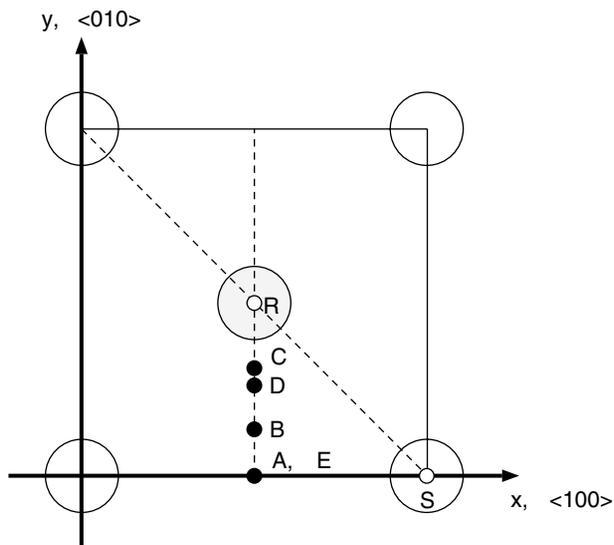


Fig. 3. The sites A–E for adsorbed H atoms on a clean W(001) surface at 0 K. The (001) direction, *i.e.* the z axis, is out of the plane. The high-symmetry sites R and S are also indicated, but sticking was not observed on these sites. The open circles represent W atoms in the topmost surface layer, the shaded circle shows a W atom in the second topmost surface layer, and the dots represent the adsorption sites. Both dashed lines divide the surface unit cell into equal halves.

The occupancies of the adsorption sites for some kinetic energies are shown in Table 1, for sticking at 0 K. The height $h \equiv z_H - z_s$ of adsorbed H atoms above the topmost surface layer, as well as the length of H–W bonds shorter than 3 Å, are shown in Table 2. Here z_s is the z coordinate of the topmost W surface layer far away from the adsorbed

Table 1

The occupancy of the adsorption sites for some kinetic energies, for H atoms incident on W(001) at 0 K

Energy (eV)	Occupancy						Total number of stickings
	A	B	C	D	E	Other	
0.003	72	7	28	15	1	1	124
0.01	70	6	15	5	1	0	97
0.03	48	3	15	10	2	0	78
0.1	41	3	15	5	0	0	64
0.3	44	7	20	5	0	0	76

Table 2

Height $h \equiv z_H - z_s$ of adsorbed H atoms above the topmost surface layer, and the lengths of the H–W bonds, at sites A–E

Site	h (Å)	Bond lengths (Å)	
A	1.04	1.96 (2)	2.92 (2)
B	1.08	1.97 (2)	2.79
C	0.48	1.97 (2)	2.00
D	0.44	1.96 (2)	2.00
E	–0.25	1.90 (2)	1.98 (2)

Bonds longer than 3 Å are not included. The numbers inside the parentheses indicate the number of these bonds.

H atom, and z_H is the z coordinate of the adsorbed H atom. The W target occupies the region $z \leq z_s$.

3.3. Formation and desorption energies

The energetics for H atoms on and inside a lattice is shown schematically in Fig. 4, for a solid which absorbs hydrogen endothermally [35,36]. The total potential energy of the system—half a H_2 molecule interacting with the W target—is denoted E_{tot} . When the H atom is isolated from the clean W target, the energy is

$$E_{\text{ref}} = E_P + \frac{1}{2}E(H_2), \quad (1)$$

where E_P is the energy of the relaxed target and $E(H_2) \approx -4.75$ eV (Refs. [37,38]) is the energy of the H_2 molecule in its ground state. The energy E_{ref} is taken as the reference level for all energies, so that

$$E \equiv E_{\text{tot}} - E_{\text{ref}}, \quad (2)$$

where E and E_{tot} varies with the position of the H atom.

The energy of solution for H in W is denoted E_{sol} , and is defined as the net energy required to insert half a hydrogen molecule into the bulk of the W lattice. The formation energy E_{ads} for H at any of the adsorption sites A–E, also called adsorption or chemisorption energy, is defined in a similar fashion. The desorption activation energy E_{des} is the energy an adsorbed H atom has to spend in order to escape to vacuum. The energy difference $|E_a| = |E_{\text{des}} - E_{\text{ads}}|$ is the activation energy for dissociation of the incident H_2 molecule.

Under experimental conditions it is likely that adsorbed H atoms migrate on the surface, until they find another H atom to recombine and desorb with. Since recombination

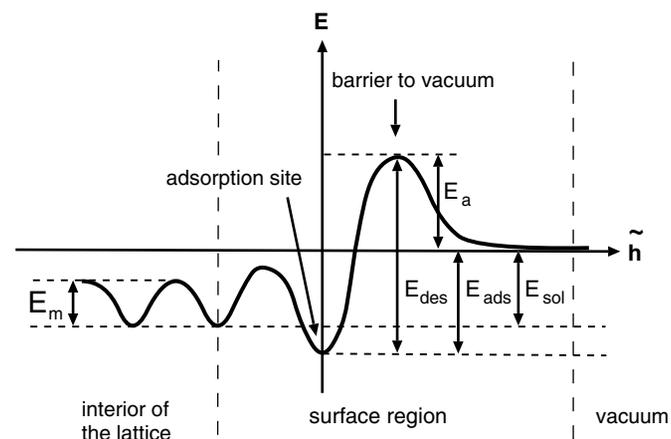


Fig. 4. Schematic energetics of H atoms at the surface of and inside a solid which absorbs hydrogen endothermally. The energy E is defined as in Eq. (2), and $\tilde{h} \equiv z - z_H$ is the height above the adsorption site. E_{sol} is the energy of solution, E_{ads} is the adsorption energy for an H atom stuck on the surface, E_{des} is the desorption activation energy for H atoms, E_a is the activation energy for H_2 dissociation, and E_m is the migration energy of H atoms in the bulk. For the adsorption sites the surface is located at $\tilde{h}_s = z_s - z_H = -h$, with h taking the values indicated in Table 2.

Table 3
Surface formation energies E_{ads} and desorption activation energies E_{des} for H atoms at the adsorption sites A–E

Site	E_{ads} (eV)	E_{des} (eV)
A	0.38	1.18
B	0.38	1.05
C	0.08	0.74
D	0.09	0.95
E	0.002	1.63

most likely lowers the energy needed for the molecule to desorb, due to the covalent nature of the H–H bond and the thereby implied weakened bonding to the W atoms, the experimental desorption energies should be smaller than two times the simulated desorption energies for atomic hydrogen: $E_{\text{des},2,\text{exp}} < 2E_{\text{des},1,\text{sim}}$. We have determined the energies $E_{\text{des},1,\text{sim}}$ (same as E_{des} defined above), so that at least an order-of-magnitude comparison to experiments can be done. The desorption energies for atomic hydrogen were calculated by evaluating the potential energy for a single H atom at succeeding larger distances above the surface. For the atom outside the surface half the potential energy of the hydrogen dimer was added to the potential energy (since the energy of a isolated atom in MDS is zero). The energies for atoms are listed in Table 3 for the different adsorption sites. For sites C and D there exist an additional site about 0.6 Å closer to the vacuum, but the desorption energies have been evaluated for the deeper lying, original sites.

3.4. Cumulative irradiation

The cumulative number of adsorbed (N_{a}) and shallowly implanted (N_{i}) H atoms on W(001) at 300 K, as a function of the number N of impinging hydrogen atoms, is shown in Fig. 5. The average distance $\langle d_{\text{H}} \rangle = \langle z_{\text{H}} \rangle - z_{\text{s}}$ of H atoms to the top surface layer of the W(001) lattice at 300 K, as a

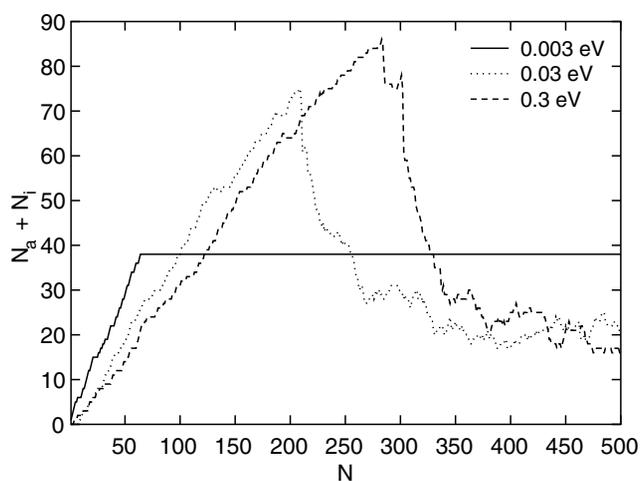


Fig. 5. Cumulative number of adsorbed (N_{a}) and shallowly implanted (N_{i}) H atoms on W(001) at 300 K, as a function of the number N of impinging hydrogen atoms.

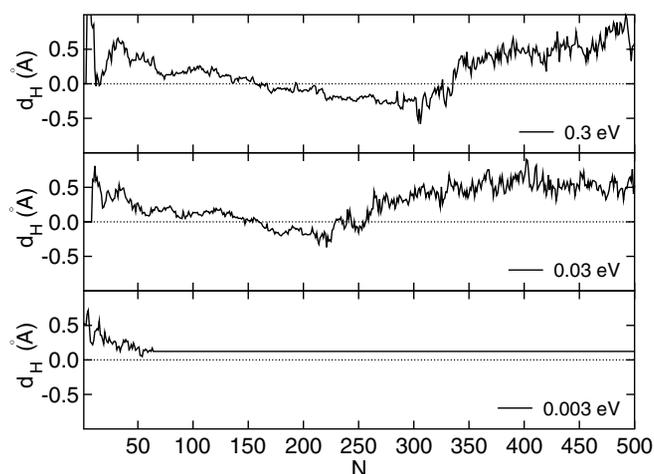


Fig. 6. Average distance $\langle d_{\text{H}} \rangle = \langle z_{\text{H}} \rangle - z_{\text{s}}$ of H atoms to the top surface layer of the W(001) lattice at 300 K, as a function of the number N of impinging hydrogen atoms.

function of the number N of impinging hydrogen atoms, is shown in Fig. 6.

As can be seen from the figures, the higher the kinetic energy the larger the maximum possible coverage and the larger variation in the average distance of the H atoms from the W surface. Visual inspection confirms that not all the H atoms are at or on top of the surface, but some are rather embedded into it. The deepest lying H atoms are 1.7 Å below the top layer, corresponding to a position just below the second surface layer. This “pressing down” of H atoms is caused by their mutual repulsion in combination with their affinity for being bound to tungsten atoms, driven by the energy of incident H atoms. The situation becomes unstable at around $N = 300$ for a kinetic energy of 0.3 eV, as can be seen in Fig. 5. The incident atom triggers

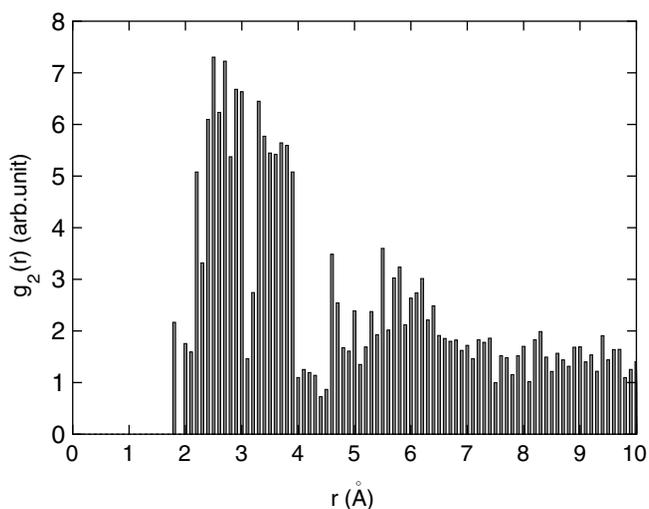


Fig. 7. Pair-correlation function $g_2(r)$ for the H atoms adsorbed on or shallowly implanted into W(001) at 300 K for an incident atom with the kinetic energy 0.3 eV, when the coverage $\theta = 1.3$ has been reached. A spacing of 0.1 Å was used for the calculation.

an avalanche of escaping H atoms, leading to the displacement of implanted H atoms towards the surface, see Fig. 6.

According to the results, the maximum hydrogen coverage achievable by single-ion implantation is about $\Theta = 86/64 \approx 1.3$ for an incident atom with the kinetic energy 0.3 eV. This is a good estimate, provided the $N_a + N_i$ curve in Fig. 5 stays close to the level at $N = 500$. A pair-correlation analysis shows two peaks, one at about 2.5 Å and one at 3.5 Å, as can be seen in Fig. 7. This indicates that there is some ordered structure of the adsorbed H atoms.

4. Discussion

4.1. Sticking at the clean W(001) surface

As mentioned earlier in Section 3.1 we will not compare our results for atomic hydrogen sticking to those for molecular sticking, since there is no *a priori* reason why atoms and molecules should have similar sticking coefficients. For instance, the bond in the H₂ molecule can have different orientations, and the atoms may be vibrating along the bond direction, all of which effect the sticking to some extent. Single atoms do not have these extra degrees of freedom.

Our simulations show that the sticking coefficient of H on the clean W(001) surface never equals unity. The sticking coefficient does not become larger than 0.62–0.63, obtained at the lowest kinetic energy of 0.003 eV. Naturally, we can not rule out that the sticking coefficient might be even larger for lower energies.

Fig. 2 shows that the sticking coefficients obtained by Eckstein and Biersack [18] are at least twice as large as ours. This overestimate is most likely attributable to the inherent limitations of TRIM (which relies on the binary collision approximation), and the addition of the planar potential. The results from regular TRIM calculations, that the sticking probability is zero or very close to it, are also very different from the present findings from the molecular dynamics simulations.

4.2. Adsorption sites; formation and desorption energies

Two binding states were initially reported in experiments on hydrogen adsorbed on single-crystalline tungsten [3,2,5]. Later, it was discovered conclusively by Adnot and Carette [39] that hydrogen is adsorbed only in atomic form on the W(001) surface. Shortly thereafter Barnes and Willis [25] obtained experimental results indicating that only one site, the “bridge site”, is occupied at all coverages. The seemingly different states reported in earlier work can be explained by surface reconstruction driven by hydrogen coverage. Our result, that the H atoms prefer to bind to site A—the bridge site—over a wide range of kinetic energies (see Table 1), is in perfect agreement with this.

According to review articles on the topic of interaction between light molecules and solid surfaces [40,41], the

adsorption energy should be close to the desorption energy for molecular hydrogen on a transition metal surface, such as tungsten. Experimentally reported desorption energies for molecular hydrogen on low-coverage W(001) surfaces are: 1.4 eV (Refs. [5,8]), 1.7 eV (Ref. [11]), and 1.9 eV (Ref. [34]). With the assumption $E_{\text{ads}} \approx E_{\text{des}}$ the atomic adsorption energy becomes 0.7–1.0 eV. In the present study adsorption site A was found to be the dominant one, with an energy $E_{\text{ads}} = 0.4$ eV. This is in reasonable agreement with the experimental findings.

It was mentioned in Section 3.3 that experimental desorption energies $E_{\text{des},2,\text{exp}}$ for hydrogen molecules in general should fulfill $E_{\text{des},2,\text{exp}} < 2E_{\text{des},1,\text{sim}}$, where $E_{\text{des},1,\text{sim}}$ are simulated energies for atomic hydrogen. In the present work the energy $E_{\text{des},1,\text{sim}} = 1.18$ eV was obtained for the preferred site A, yielding the upper limit $2E_{\text{des},1,\text{sim}} = 2.36$ eV ≈ 2.4 eV. The experimental values are 0.5–1.0 eV lower, indicating that the attraction—not accounted for in the estimate 2.4 eV—between desorbing H atoms is of this order.

The present potential does not describe the experimentally observed reconstruction [27–30] of the (001) surface at a temperature of 300 K or below, which entails a lateral shift of each tungsten atom at the surface by a distance of about 0.2 Å. It is possible that these displacements, which amount to only 6% of the lattice parameter, may nevertheless have an effect on the adsorption sites different from site A, which spatially coincides with the experimental one. However, the sticking results should not be dramatically affected by this, since the sticking is actually dominated by site A, as shown in Table 1.

4.3. Cumulative irradiation

Absolute saturation coverages have been measured by Madey [10] to be $\sigma_s = 2.0_{-0.4}^{+0.2} \times 10^{19}$ H atoms m⁻² at $T \lesssim 330$ K. This corresponds to two hydrogen atoms per tungsten surface atom. King and Thomas [8] have found a saturation coverage of $\sigma_s = 1.9 \pm 0.3 \times 10^{19}$ H atoms m⁻² at 300 K. These values can be converted to coverages Θ by dividing by the surface density $\sigma_a = 1/a^2 \approx 10^{19}$ W m⁻² of tungsten atoms, where $a = 3.16$ Å. This gives $\Theta = 2.0$ (Ref. [10]) and $\Theta = 1.9$ (Ref. [8]). The present results indicate that coverage saturates at about $\Theta = 1.3$ for incident atoms with a kinetic energy of 0.3 eV, as can be seen in Fig. 5. Here it is assumed that there are no drastic changes in the number of adsorbed or implanted hydrogen atoms after 500 atoms have been incident in the surface. This coverage amounts to 70% and 74%, respectively, of the experimental values. There may be several reasons for this 26–30% discrepancy. In the experiments the tungsten sample is placed in chamber where it is exposed to a beam of hydrogen molecules, and the pressure changes are monitored. Taking account of the molecular flux and other parameters the saturation coverage can be determined. The vital difference between the experiments and our simulations is the use of hydrogen molecules instead of hydro-

gen atoms. It is possible that the additional degrees of freedom and a more complicated electronic interaction for the molecules allow more H atoms to become trapped on the W(001) surface. For instance, it has been found that molecules having kinetic energies below ≈ 0.15 eV exhibit an increased probability of sticking, compared to molecules with energies around ≈ 0.15 eV and slightly larger [12]. This has been attributed to the existence of a molecular precursor state on the W(001) surface, in which the H₂ is initially trapped, and from which the H atoms adsorb to the surface [12,13]. The trapped molecule can diffuse over the surface until it encounters a favorable location where to dissociate. A hydrogen atom, on the other hand, should be less able to slowly diffuse over the surface, “looking” for an adsorption site, due to its stronger interaction with the tungsten surface atoms. In addition, the presence of impurities, steps, or other defects on the experimental W(001) surfaces may provide additional binding sites for hydrogen, resulting in a higher sticking coefficient than on a pure and flat surface.

In order to investigate the computational possibility of a $\Theta = 2.0$ coverage reported in experiments additional calculations with H atoms at all bridge sites (site A) were performed with the W(001) target at 300 K. When the relaxation was started the initially uniform H layer soon became disordered. At 3.0 ps after the start the H atoms were spread out in a 3.5 Å thick layer, extending down to the second W surface layer. The presence of H atoms close to the second surface layer was also observed in the simulations of cumulative irradiation. The first H atom to be sputtered left the surface at about 3.2 ps. Additional H atoms were ejected after this, but very slowly. At 400 ps after start 24 H had been sputtered, but no additional H atoms had left the surface at 1500 ps when the simulation was ended. The resulting stable coverage is $\Theta = 104/64 \approx 1.6$. These findings together with the earlier results show that stable coverages with $\Theta \gtrsim 1.6$ are not simple—or at all possible—to construct at 300 K using the present potential.

4.4. Experimental validation

We would like to point out that the comparison of the present results to experimental ones is incomplete due to the scarcity of investigations of atomic hydrogen beams incident on a tungsten surfaces. Of all the main results in this study—(i) the sticking coefficient of atomic hydrogen, (ii) the location of the adsorption sites, (iii) the formation energies, and (iv) the desorption energies—only parts (ii) and (iii) could be directly compared to existing experiments. Concerning part (iv) it was necessary to use estimates from molecular results. Finally, the results in part (i) could not be experimentally verified, since there are no findings from experiments or *ab initio* calculations on this at the present.

There is no large conceptual difficulty in how to empirically obtain the sticking coefficient of atomic hydrogen, as

is evident from a study by Dús and Nowicka of atomic hydrogen sticking on silver [42]. In addition to the requirements for a clean target and a high-quality low-pressure vacuum, a successful study of low-energy sticking, with ion energies varying between 0.003 eV and 3 eV, would require a good beam line that lets atoms and not dimers through. When a low-coverage adsorbate has been formed, the desorption energy for hydrogen atoms can be obtained in a manner similar to that for molecules.

5. Conclusions

Hydrogen has a non-zero sticking probability on a clean tungsten (001) surface at 0 K and at room temperature (300 K). The results show that at 300 K the sticking coefficient is a monotonously decreasing function of the kinetic energy of the incident atom, decreasing from 0.6 to 0.2 when the energy increases from 3 meV to 300 meV. The dominant adsorption site—denoted A in the present study—is in perfect agreement with the experimental bridge site.

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