

## H-enhanced mobility and defect formation at surfaces: H on Be(0001)

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(Received 16 November 1995)

First-principles calculations of the interaction of H with the close-packed Be(0001) surface reveal that adsorbed H reduces barriers and formation energies for Be surface defects. A H atom adsorbed on top of a Be adatom reduces the Be atom's surface-diffusion barrier by a factor of 3. Preferential binding of H to surface defects reduces the formation energy of steps, adatoms, and vacancies on Be(0001). Because H adatoms repel each other on the flat surface, but not if adsorbed at the defects studied here, the formation of these defects is especially facile at high H coverage. These results explain the experimental findings that the H-induced vacancy reconstructions, which dominate the high H coverage regime, form at as low as 100 K.

The H-Be(0001) adsorption system involves the simplest of adatoms interacting with an *sp*-bonded, or "simple" metal. Nevertheless, attempts to apply modern surface experimental probes to the structure of this technologically significant adsorption system have initially produced "more confusion than enlightenment."<sup>1-3</sup> Recently Stumpf and Feibelman proposed a H-induced vacancy reconstruction of the (close packed) Be(0001) surface at high H coverages.<sup>4</sup> In these H-induced vacancy reconstructions, H adatoms sit on bridge sites tilted toward surface vacancies. The lowest-energy reconstruction requires 1-ML H coverage and consists of a honeycomb array of Be vacancies, each decorated by three bridge-bonded H's. This structure has been confirmed quantitatively by Pohl, Hannon, and Plummer (PHP) in a low-energy electron diffraction *I-V* analysis.<sup>2</sup> The vacancy structures are only favorable at high H coverages (from 2/3 to 1 ML). At low coverage the adsorption geometry is more conventional—threefold hcp sites are occupied with little change in the underlying lattice. Because of the low diffusion barrier between the hcp sites and the strong H-H repulsion in this phase, the H adlayer must be disordered at room temperature.

Although the static interaction of H and Be(0001) is now understood quite well, there remain questions concerning the kinetics of the interaction, which is the focus of this paper. The H-induced honeycomb structure forms spontaneously at about 100 K, if enough H is allowed on the surface.<sup>2</sup> This means that at 100 K, atomic processes necessary for the formation of the honeycomb structure, like vacancy formation and Be surface self-diffusion, occur at rates faster than about one event per second. Assuming the standard prefactor for diffusion processes,  $10^{12} \text{ s}^{-1}$ , and given that the transformation occurs in less than a minute experimentally,<sup>2</sup> I estimate that the barrier for surface self-diffusion and the barrier for vacancy formation have to be below 1/4 eV. This barrier is about four times less than expected for vacancy formation on a close packed surface.<sup>5</sup>

Even though a complete model of the kinetics of the formation of the H-induced vacancy structures remains to be developed, some important ingredients of such a model are reported here.

(i) A H adatom adsorbed on top of a diffusing Be adatom reduces the Be diffusion barrier by a factor of 3.

(ii) H reduces the formation energy of surface defects like steps or adatoms.

(iii) Because of the H-H repulsion on the flat Be(0001) this reduction of defect formation energies and barriers depends strongly on the H coverage. The higher the H coverage the higher is the H chemical potential and the H's ability to reduce formation energies and barriers.

Similar mechanisms should be important in understanding surface problems where kinetics and energetics are changed by adsorbates that bind stronger to substrate atoms than among themselves. Examples include adsorbate enhanced surface diffusion,<sup>6</sup> epitaxial growth influenced by surfactants, etching or sputtering of surfaces, and chemical surface reactions mediated by coadsorbed catalysts.

### I. ELECTRONIC STRUCTURE CALCULATIONS

The results reported here are based on density-functional calculations with the local-density approximation (LDA) for exchange and correlation (XC). Details of the plane-wave pseudopotential technique and the H-Be(0001) calculations are described in Refs. 4 and 7. To approximate the Be(0001) surface I use repeated slabs at least nine layers thick, with 12 to 36 atoms per layer, separated by five layers of vacuum. Stepped surfaces are constructed in two different ways. I compute step energy differences via 12-atomic, hexagonal islands on Be(0001) which have two possible aspect ratios.<sup>5</sup> For adsorption at steps, I construct a pair of steps by removing half of the atoms of a  $6 \times 3$  or  $6 \times 4$  surface layer. This produces steps in the surface cell three or four atoms wide. The outer three Be layers and the H adlayers are relaxed.

### II. H ADLAYERS ON Be(0001)

At coverages below and at 1 ML all the H atoms are on the surface, because subsurface sites are too high in energy.<sup>4</sup> At low H coverage most of the H atoms sit on flat parts of the surface. The low calculated energy barrier for H surface diffusion ( $E_D \approx 0.15 \text{ eV}$ ) suggests disorder down to low temperatures in this phase. The H-H interaction is repulsive, i. e., the adsorption energy decreases with coverage (see Fig. 1).

At higher coverages and at temperatures above about 100 K, PHP find that H-induced reconstructions form.<sup>2</sup> Thus,

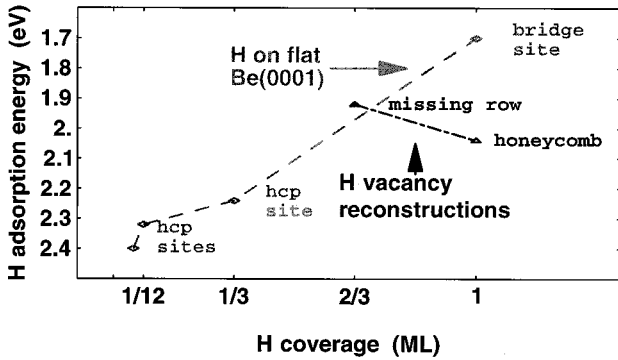


FIG. 1. Calculated H adsorption energy as a function of coverage on flat and reconstructed Be(0001).

at high H coverage, the reconstructed phases are more stable (see Fig. 1) and the barriers to form them are low. The H-H interaction is attractive in the vacancy reconstructions.

The key to understanding the stability of the H-induced vacancy structures is that Be has a quasigap in the bulk but a high Fermi density of states at the flat Be(0001) surface. This indicates that Be, a first row element, has a tendency to form covalent bonds and that the flat Be(0001) surface is in a state quite unusual for Be. H is ideally suited to saturate dangling bonds, as on semiconductor surfaces, and thus to reopen a gap at the surface. Indeed, H binds to Be surfaces by having strong and short covalent bonds to Be surface atoms, if those atoms are low coordinated. This ability to form strong H-Be bonds is the major driving force for the vacancy reconstruction. Vacancies in the top Be(0001) layer reduce the coordination of the Be surface atoms. This makes the surface atoms at the vacancies more reactive. Compared to 1 ML of H on the flat Be(0001), the binding energy per H-Be bond in the H-induced honeycomb structure is approximately doubled and the H-Be bond length is reduced by nearly 10%. At the same time a 5-eV-wide quasigap forms in the H-honeycomb surface layer.

### III. H ON TOP OF Be ADATOMS

H also interacts strongly with a Be adatom on the close packed Be(0001) surface. Be adatoms have only three neighbors, six fewer than an atom in flat parts of the Be(0001) surface. Adding one H atom to a Be adatom results in a very

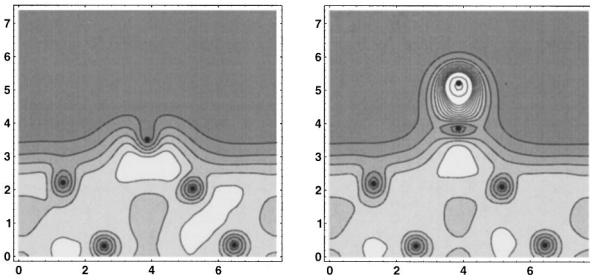


FIG. 2. Valence charge density plot of Be (left) and Be+H (right) adsorbed on Be(0001). Dots indicate the position of the atoms. The contour spacing is normally 59 millielectron/Å<sup>2</sup> and 295 millielectron/Å<sup>2</sup> close to the H. The maximum charge density is 1360 millielectron/Å<sup>2</sup> (left) and 340 millielectron/Å<sup>2</sup> (right).

strong and short H-Be bond. The H adsorbs preferentially on top of the Be adatom (see Fig. 2). The H-Be bond length is computed to be 5.5% shorter and the binding energy per bond is 0.99 eV or 73% greater than each of the two bonds a H adatom has in the H-induced honeycomb structure.

	Be	H
flat Be(0001)	2.04	2.40
at A step	2.49	2.07
at B step	2.74	2.35
on Be adatom		2.33
at Be at A step		2.55
at Be at B step		2.35

This strong bond has two consequences. It makes the Be-H ad-dimer more stable than a single Be adatom, reducing the formation energy of a Be (+H) adatom. Furthermore, the strong Be-H bond weakens the Be-substrate bonds reducing the diffusion barriers.<sup>8</sup>

#### A. Formation energy of the hydrogenated Be adatom

The site on top of a Be adatom is a relevant adsorption site. Its energy is at least 0.5 eV lower than for all other sites at the Be adatom. In fact, H prefers this site to sites on flat Be(0001) for H coverages above about 1/15 ML (see Tables I and II). Thus H reduces the Be adatom formation energy.

The formation energy of nonhydrogenated Be adatoms is defined as the energy difference between the cohesive energy of Be and the adsorption energy of Be on Be(0001) at low coverage. This energy is 1.27 eV (see Table II). For a hydrogenated Be adatom the formation energy changes by the difference between the H adsorption energy on the Be adatom (2.33 eV) and on the flat surface at the given coverage. For example, at a H coverage of 1/3 ML ( $E_{\text{ad}}^{\text{H}} = 2.24$  eV), it costs only 1.18 eV to form a hydrogenated Be adatom.

TABLE II. Formation energy of steps and Be adatoms on Be(0001). If H adsorbs at a given H coverage preferentially at the step or the adatom, the reduced formation energy is given. All energies are relative to the energy of clean Be(0001), the Be cohesive energy, and the energy of H at the given coverage on flat Be(0001).

H coverage	0 ML	1/18 ML	1/3 ML
A step (+H) per step atom	0.27		
B step (+H) per step atom	0.34		0.23
Be adatom (+H) on flat Be(0001)	1.27		1.18
Be (+2 H) adatom at A step	0.83	0.54	0.22
Be (+2 H) adatom at B step	0.58	0.54	0.36

TABLE III. Increase in energy (eV) of a Be adatom and of a hydrogenated Be adatom relative to adsorption at the equilibrium fcc site at 1/12 ML coverage.

	bridge	hcp	top
Be adatom	0.06	0.04	0.39
Be+H on top	0.02	0.02	0.09

The formation energy reduction is more significant at higher H coverage. However, at higher H coverage, the interaction between adsorbed H atoms and the H-Be dimer should also be stronger, and this as yet unknown interaction might affect the formation energy of the Be-H dimer. To get an idea of the high H coverage limit I calculate different structures with 1-ML H coverage and with Be adatoms. In all of these structures the formation energy of the hydrogenated Be adatom is between 0.9 eV and 0.7 eV.

### B. Be plus H diffusion

Figure 2 shows that the strong H-Be bond weakens the bonds of the Be adatom to its Be(0001) surface neighbors. An isolated Be adatom on a fcc site is 2.00 Å from its three nearest neighbors, 8.1% less than the bulk nearest-neighbor distance. With a H atom sitting on top this bond length increases to the bulk bond length of 2.18 Å. The height above the surface also increases from 1.36 Å to 1.69 Å, when a H atom is added to the Be adsorbate. The top adsorbed H acts to pull the adatom away from the surface.

The weakening of the backbonds of the hydrated Be adatom reduces the diffusion barrier for hopping across the twofold bridge site from the equilibrium threefold fcc site to a neighboring threefold hcp site from 0.06 eV to 0.02 eV (see Table III). The energy differences between fcc, hcp, and top sites are also reduced.<sup>9</sup>

The H-induced reduction of the self-diffusion barrier on the flat Be(0001) is not very important for the mechanism of the vacancy-phase formation, because the formation barrier is very small even without a H on top. This mechanism, however, might contribute to the H enhanced mobility observed on a large number of metal surfaces.<sup>6</sup> It is also likely that H has similar effects on the surface self-diffusion on semiconductors, given that H-semiconductor bonds are relatively strong. Recent calculations on the low index surfaces of Al show that the same mechanism works for the pair H and Al.<sup>10</sup>

## IV. NUCLEATION OF THE HONEYCOMB RECONSTRUCTION AT STEPS

It is reasonable to assume that the growth of vacancy structures should start at preexisting steps. For Al(111) it was found that the barrier for vacancy formation at steps is lower than in the flat surface.<sup>5</sup> Therefore the Na-induced  $\sqrt{3}$  reconstruction starts to grow at steps.<sup>11</sup> Furthermore, atoms removed from the step do not have to diffuse far to find a low-energy adsorption site. The step itself provides them. I start the study of the vacancy formation at steps with the properties of ideal steps, then with H and Be adsorbed, and

finally I discuss the energetics of vacancy formation at the steps.

### A. Adsorption at close packed steps

On close packed surfaces [i.e., fcc(111) or hcp(0001)] two geometrically different types of densely packed steps exist.<sup>5</sup> The *A* step has rectangular [or (100)-like] microfacets, the *B* step has triangular [or (111)-type] microfacets. In general these steps have slightly different formation energies. This difference has been studied for a few fcc(111) surfaces (Al, Pt, Ir).<sup>5,12,13</sup> In these studies the *A* step tends to have a higher formation energy (0–15 % of the *B* step formation energy). On Be(0001) the *B* step has a 26% lower formation than the *A* step (0.34 eV per *B* step atom and 0.27 eV per *A* step atom; see Table II).

The source of the energy difference between the *A* and *B* steps is still unclear. The number of bonds broken in forming either step is identical. Nevertheless, it is interesting, because the different stability of the two steps leads to a different reactivity.

Both H and Be preferentially adsorb at the less stable *B* steps (see Table I). H sits at the tilted bridge sites between step edge atoms, as in the missing row  $3 \times 1$  reconstruction (see Ref. 4), with the *B* step preferred by 0.28 eV over the *A* step. Above a H coverage of 1/12 ML, H adatoms prefer these *B* step sites to sites on the flat Be(0001) surface, stabilizing the *B* steps. At  $\Theta_{\text{H}} = 1/3$  ML, H covered *B* steps are even more stable than *A* steps, which will not hold H atoms on bridge sites at this coverage at all (see Table II).

At steps Be adatoms prefer fivefold sites. At *B* steps their energy is 0.25 eV lower than at *A* steps. Therefore, *B* steps are rougher in thermal equilibrium. This reverses with H coadsorption. H adatoms bind strongly to the two twofold sites bridging the adatom and the neighboring step edge atoms.<sup>14</sup> Two H atoms bind with 2.35 eV each at the Be adatom at *B* steps and with 2.55 eV at *A* steps. Thus, H again stabilizes the initially less stable defect, the Be adatom at the *A* step, reducing the Be adatom formation energy. For example, the energy needed to take a Be atom out of the bulk and two H atoms from a 1/3-ML H overlayer and to adsorb these three atoms at the *A* step is only 0.22 eV. This is lower than the adatom formation energy at the *A* step with no H coadsorbed, which is 0.84 eV. At the *B* step the formation energy changes less with H coadsorbed: from 0.58 eV to 0.36 eV at  $\Theta_{\text{H}} = 1/3$ .

### B. Vacancy formation at steps

To grow the H-induced honeycomb structure, vacancies have to be created. There are many ways to do this, especially in the presence of H. Ideally, all of them should be studied. Nevertheless, by studying three vacancy formation processes at the *B* step one can already draw some important conclusions.

In all three cases I approximately calculate the barrier for vacancy formation in a *B* step by moving one step atom half way out of the step to the nearest twofold site in front of the step. Without H the energy in this configuration is 1.5 eV higher than in the initial state, the ideal step. Therefore, without H, the vacancy formation barrier might be as high as 1.5 eV.

When a H atom sits on the detaching Be atom, the Be atom is partially saturated. Thus, as discussed above for H on top of a Be adsorbate, the detachment barrier should be lowered. However, calculations imply that the H does not want to stay on the detaching Be step atom; it remains at the step.

In another attempt I put H atoms on the step so that all of the Be atoms neighboring the detaching Be atom in the upper terrace are bound to H. This weakens the bonds of these neighbors to the detaching Be atom, and indeed gives a 0.2-eV reduction of the approximate detachment barrier.

This reduction is, however, far too small to account for the formation of the honeycomb structure at a temperature as low as 100 K. The largest part of the vacancy formation barrier is the formation energy of a vacancy plus a Be atom adsorbed nearby at the step. The additional barrier, which is the energy difference between the saddle point and this final configuration, is very small. Thus, only if the formation energy of the vacancy-atom pair is reduced can the barrier for its formation get smaller. Because the vacancy structure is the stable structure when the H coverage approaches 1 ML this formation energy must drop to zero. I therefore conclude that increasing H coverage reduces both the vacancy formation barrier and energy at the same time.

## V. CONCLUSIONS

I have presented the results of first-principles calculations of the interaction of H with Be(0001), where several phases are identified: the H on flat Be(0001) phase, the  $H\sqrt{3}\times\sqrt{3}R30^\circ$  honeycomb vacancy phase, and the  $H\text{-}3\times 1$  missing row phase. All of these phases are now observed in experiment.<sup>2</sup>

The H-induced reconstructions form at 100 K. This implies reduced barriers ( $< 1/4$  eV) for the motion of Be in the presence of H. The barriers for Be self-diffusion are reduced by a factor of 3 when a H atom adsorbs on the diffusing Be adatom. The adsorbed H weakens the bonds of the Be adatom to the surface and lifts it away from the surface. On Al surfaces a very similar mechanism works, which indicates that it is quite common.<sup>10</sup>

Calculations of vacancy formation at steps on Be(0001) indicate that the very high barriers without H coadsorbed (about 1.5 eV) are only reduced significantly at H coverages close to 1 ML. At high coverage, H reduces the formation energy of adatoms, steps and vacancies, and thus also the barriers.

All of the H effects on the energetics on Be surfaces stem from the fact that H generally binds more strongly at higher-energy surface structures. At low H coverage this reduces the energy differences between low- and high-energy surface structures, at high H coverage it even reverses their energetic ordering. For example, *B* steps become more stable than *A* steps, and vacancy structures are more stable than the flat surface.

## ACKNOWLEDGMENTS

I thank Karsten Pohl, Jim Hannon, E. Ward Plummer, and Peter J. Feibelman for their close collaboration. This work was supported by NEDO, The New Energy and Industrial Technology Development Organization of Japan, and by the U.S. Department of Energy under Contract No. DE-AC04-94AL85000.

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<sup>8</sup>The idea that coadsorption lowers diffusion barriers is not completely new. For example, Feibelman found that an Al dimer has a lower diffusion barrier than a monomer on Al(100); P. J. Feibelman, *Phys. Rev. Lett.* **58**, 2766 (1987).

<sup>9</sup>The reduction of the corrugation is even more pronounced if two H atoms are adsorbed on a Be adatom. However, the Be<sub>2</sub>H<sub>2</sub> dihydride is unstable. The adsorption energy of the second H atom is only 1.85 eV, 0.5 eV less than for the first H atom.

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<sup>14</sup>These sites at the *A* step are similar to the adsorption sites of H in the honeycomb structure (Ref. 4). The tilt is in the same direction relative to the second layer.