H-Induced Reconstruction and Faceting of Al Surfaces

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First principles calculations show that chemisorbed H causes vacancy reconstructions and faceting of all Al low index surfaces. On Al(111) H-decorated vacancies are stable; on H-covered Al(100) vacancies are easily activated thermally. H-covered Al(110) forms a missing row reconstruction with H-decorated vacancies on the {111} microfacets. At high H coverages, low index Al surfaces are unstable against faceting. Al(111) and Al(110) form {211} facets, on Al(100) islands and pits with {311} and {211} facets are stable. The H-induced structural changes are caused by the preferential binding of H at low coordinated Al surface atoms and at {100} microfacets or, more generally, at "surface tetrahedral" sites. [S0031-9007(97)03350-4]

Al is the most widely used interconnect material in semiconductor devices [1]. Shrinking dimensions in chip design mean that the quality of interconnects and thus the control of the Al deposition is more important. Al is often deposited with H coadsorbed on the growing film. An example is chemical vapor deposition (CVD), where H is a necessary by-product [2]. However, H reduces the Al film quality. For example, Al(111) grows layer-by-layer at 150 K in the absence of H [3], and calculations of Al surface diffusion on flat and stepped Al(111) predict smooth growth at even lower temperatures [4]. With coadsorbed H, Hinch *et al.* report step bunching on Al(111) films grown by CVD at 400–500 K. H affects film growth in other cases too, e.g., H is detrimental to Si [5,6] and Ni [7] epitaxy, while H improves growth on GaAs(100) [8] and C(100) [9].

A growing Al film roughens if the lateral Al mass transport is hindered or if the total surface energy can be reduced by forming facets off the growth direction [6]. To determine the Al surface mobility or stability with H adsorbed the structure of the H-covered surface must be known first, especially since H can reconstruct surfaces [10]. Indeed, H adlayers lead to low energy reconstructions of Al surfaces. Figure 1 summarizes the results reported here. For example, H induces a honeycomb vacancy reconstruction on Al(111) [see Fig. 1(g)]. On Al(110) a missing row (MR) reconstruction is formed with H-decorating vacancies on the three rows wide {111} microterraces [see Fig. 1(f)].

Al mobility is reduced upon H adsorption, especially on the reconstructed Al surfaces [11]. This might be one reason why H suppresses Al layer-by-layer growth. A second reason for rough growth is that Al surfaces are unstable against faceting at high H coverages. The facet orientation is 211 for Al(111) and Al(110) and {311} and {211} for Al(100). Al(211) and Al(311) are surfaces with narrow {111} terraces and {100}-faceted steps [see Figs. 1(e) and 1(h)]. H induces vacancies on Al(211) and vacancies and double steps on Al(311). The driving force for all these reconstructions is that they allow the H to adsorb at tilted bridge sites at {100} microfacets.

The study of H adlayers on Al surfaces reported here is based on the generalized gradient approximation (GGA) [12]. The electronic wave functions are expanded in plane waves up to a cutoff energy of 20 Ry. Al atoms are represented by pseudopotentials [12,13], protons by their Coulomb potential. The calculated Al lattice constant is 4.03 Å. I model the Al surfaces by repeated slabs of 10-25 Å thickness in orthorhombic or monoclinic supercells. H is adsorbed on one side only. The adsorbed H atoms plus the top 4–8 Å of the Al slab are relaxed. H-adsorption energies are quoted relative to free H [14]. To evaluate k-space integrals I use special k points at a density equivalent to 500–20 000 points in the full Brillouin zone of a one atom cell. Details of the computational technique are published [4,15]. Earlier studies show that at this level of approximation metal surfaces and the H-surface interaction are described accurately [4,10,16]. A case in point is a recently predicted novel H-induced reconstruction, the honeycomb vacancy reconstruction of Be(0001) [10]. The H-Be(0001) reconstruction is now confirmed quantitatively in experiment [17].

The calculated properties of H adlayers on Al surfaces, like adsorption energy and coordination, depend on surface orientation. On the flat Al(111) surface H prefers threefold fcc sites with an adsorption energy (E_{ad}^{H}) of 1.89 to 1.99 eV depending on coverage [see Fig. 1(b)]. The hcp and bridge sites are 0.07 and 0.03 eV higher in energy. On Al(110), the H-adsorption sites are coverage dependent. Up to 1 ML H adsorbs on top sites ($E_{ad}^{H} = 2.05 - 2.09$ eV) and between 1 and 2 ML the H adsorbates change to bridge sites [see Fig. 1(a)]. On Al(100), H adsorbs at bridge sites [see Fig. 1(d)]. The adsorption energy of H on Al(100) is higher than on unreconstructed Al(111) or Al(110), with a maximum of 2.13 eV at 1 ML.

It may seem that adsorption of H on Al(111), Al(100), and Al(110) is unrelated. However, a very close relation can be established by considering the adsorption of H at close packed steps on Al(111). There are two types of steps. One is a {100} microfacet (called an *A* step), where H binds at tilted bridge (TB/*A*) sites
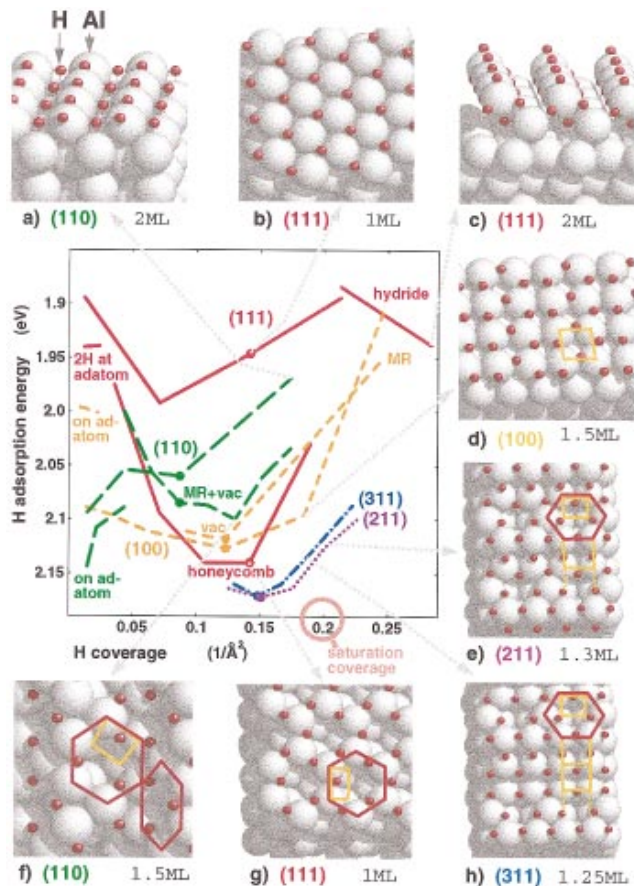
FIG. 1(color). H-adsorption energy on five different Al surfaces as a function of coverage for different phases and select diagrams of their atomic structure. Adsorption energies include Al vacancy and adatom formation energies where applicable. Dots indicate 1 ML coverage. The experimental saturation coverage on Al surfaces is marked. Red hexagons indicate vacancies on {111} facets, orange squares indicate {100} microfacets.

($E_{\text{ad}}^{\text{H}} = 2.19$ eV for 1 H per step atom) as on Al(100). The other step is a {111} microfacet (called a B step), where the step atoms have the same nearest-neighbor environment as surface atoms on Al(110). At B steps H adsorbates prefer top sites ($E_{\text{ad}}^{\text{H}} = 2.12$ eV) as on Al(110) up to 1 ML coverage. The tilted bridge site (TB/B) is 0.16 eV less favorable. The TB/B site is unstable because it would be the high energy hcp site if there were no step [18]. On the other hand, the TB/A site corresponds to a fcc site and is therefore stable. The same kind of fcc-hcp site and TB/A-TB/B asymmetry has been found for H on Be(0001) [10] and O on Pt(111) [18] before. If an adatom binds stronger at fcc than at hcp sites, it prefers the TB/A site over the TB/B site and vice versa.

The fcc-hcp anisotropy reflects a more general rule. Twofold to fourfold coordinated H adatoms prefer surface sites which correspond to tetrahedral interstitial sites of the continued Al lattice over sites that correspond to octahedral voids. For example, the fcc site corresponds to a tetrahedral site and is 0.07 eV more stable than the hcp site which is a octahedral site of the infinite lattice. For twofold sites the "tetra-octa" binding energy difference is even higher. It is 0.16 eV if bridge sites at A and B steps are compared and 0.15 eV for 1 ML of H on bridge sites on Al(100) compared to Al(110). The high energy at the "surface octahedral" site also explains the preference of H for top over bridge sites on Al(110) and at B steps and for twofold over fourfold sites on Al(100). The origin of the energy difference is the higher concentration of high energy (i.e., close to the Fermi energy) Al electronic states at surface tetrahedral compared to surface octahedral sites. This higher concentration allows for a stronger H-Al covalent bond. The situation is exactly reversed for H adsorption on the hcp-metal Be [10,11,16].

The strong H-step interaction lowers the formation energy of steps on H-covered Al(111), especially of A steps. Compared to flat Al(111), H adsorbates gain 0.20 eV or more at A steps and at least 0.13 eV at B steps. Calculations within the LDA predict step formation energies of 0.25 eV per A-step atom and 0.23 eV per B-step atom [4]. Within the GGA these formation energies are about 25% lower. Thus H adsorption increases the equilibrium step concentration at low coverage and at higher coverages A steps actually become stable. H also changes the equilibrium island shape [4].

H bonds to steps are stronger than to the flat surface because step atoms have fewer neighbors than surface atoms on Al(111). H-adatom bonds are still stronger because adatoms have even fewer neighbors. The binding energy of H on top of single Al adsorbates is 2.52 eV on Al(111), 2.34 eV on Al(110), and 2.63 eV on Al(100). On Al(111) even a second H attaches strongly to an adatom ($E_{\text{ad}}^{\text{H}} = 2.31$ eV). Thus H adsorption reduces the adatom formation energy dramatically [16]. On Al(110) H-Al ad-dimers are actually stable (see Fig. 1). A significant concentration of H-decorated adatoms could account for the high energy H vibrational modes on Al surfaces which were assigned to terminal H [19]. Other high energy modes, assigned to bridging H, stem from H adsorbates strongly bound at bridge sites at steps and vacancies.

Around a surface vacancy on a {111} facet are three TB/A-like sites [see Figs. 1(e)–1(h)]. A vacancy with all of these TB/A sites occupied by H atoms has a low energy. Maximizing the concentration of these H decorated vacancies on Al(111) leads to a stable high H-coverage structure, the $\sqrt{3} \times \sqrt{3}$R30° honeycomb vacancy reconstruction [see Fig. 1(g)]. The H-adsorption energy in the honeycomb phase ($E_{\text{ad}}^{\text{H}\sqrt{3}}$) is 2.14 eV, which is 0.19 eV higher than on unreconstructed Al(111) at the same 1 ML H coverage. $E_{\text{ad}}^{\text{H}\sqrt{5}}$ includes the vacancy formation energy

$$E_{\text{ad}}^{\text{H}\sqrt{3}} = -1/3(E^{\sqrt{3}} - 3E^{\text{H}} - E_{6\text{lay}}^{1\times1} - 2E_{7\text{lay}}^{1\times1}). \quad (1)$$

Here $E^{\sqrt{3}}$ is the total energy per unit cell of a $6 + \frac{2}{3}$ layer Al(111) slab that has a honeycomb array of H-decorated vacancies on one side, E^{H} is the energy of a free H atom [14], $E_{6\text{lay}}^{1\times1}$ is the energy per unit cell of a six layer Al(111)

slab, and $E_{7\text{lay}}^{1 \times 1}$ the energy of a seven layer slab. The definition of $E_{\text{ad}}^{\text{H}\sqrt{3}}$ minimizes the errors introduced by the finite slab thickness. It also exemplifies how H-adsorption energies are calculated in similar cases.

H adsorption in the honeycomb structure is an example of how far the H adsorption energy is determined by the local binding geometry. The actual value of $E_{\text{ad}}^{\text{H}\sqrt{3}}$ is very close to that estimated from the surface vacancy formation energy (0.18 eV) and the adsorption energy of H at a TB site at an extended A step (2.19 eV). The estimate is 2.19 eV − 0.18/3 eV = 2.13 eV instead of 2.14 eV in the full calculation.

Besides the honeycomb array of vacancies there are a few other arrangements of H-decorated vacancies on Al(111) which have H-adsorption energies within 0.02 eV of that in the honeycomb array. (Atomic arrangements where vacancies are arranged as clusters or rows are unfavorable.) Thus the H-induced vacancy phase on Al(111) is likely disordered in experiment and thus difficult to detect in a scattering experiment [19]. The formation of the vacancy phase might also be kinetically hindered since it requires long-range transport of Al surface atoms [16,17].

On Al(110) it is more complicated to construct TB/A-like sites for the H adlayer. It requires a 2×1 missing row reconstruction with (111) terraces three atomic rows wide. Then four surface atoms per four 2×1 cells are removed from the center of the (111) terraces, which gives a MR/vacancy phase with a 2×2 or 4×2 unit cell and a total of 1 ML Al removed. Without the H adsorbed it costs 0.46 eV per 2×1 cell to form the MR/vacancy array. H adsorbates bind at the TB/A sites around the vacancies [see Fig. 1(f)] with a maximum adsorption energy at 1.5 ML coverage of 2.10 eV. The 2×2 and the 4×2 phase are degenerate, which likely causes disorder in the [1$\bar{1}$0] direction resulting in 2×1 periodicity. In fact, 2×1 periodicity has been observed on H-covered Al(110) [19]. The reconstruction already forms at $T \geq 85$ K and is clearly visible with low energy electron diffraction (LEED). This is consistent with the properties of the MR/vacancy phase. The clear LEED image indicates a significant reconstruction of the Al surface and the low formation temperature excludes long range Al mass transport.

H-decorated vacancies are less stable on Al(100) than they are on Al(111) or Al(110). The reason is that H binds strongly already on flat 100 facets. The most stable vacancy reconstruction of H-covered Al(100) is a 2×2 vacancy array where all bridge sites are covered by 1 ML of H. The H-adsorption energy is 2.12 eV in this vacancy phase compared to 2.13 eV for 1 ML H on flat Al(100). Thus it costs energy to form vacancies. However, this energy is so small that a high concentration of thermally activated vacancies can be expected on H-covered Al(100).

To find stable reconstructions of H-covered low index Al surfaces let us now consider vicinal surfaces. It is possible for surfaces to lower their energy by forming facets, even though this increases the surface area. I limit the search for energetically favorable facets to two orientations, Al(211) and Al(311). Both have A steps and {111} terraces, on which vacancy reconstructions can form [see Figs. 1(e) and 1(h)] [20]. Thus H should attach strongly at these surfaces. Indeed, H prefers Al(211) and Al(311) to all other surfaces studied at high coverage (see Fig. 1).

In order to facet a low index surface, the extra H-adsorption energy on Al(211) and Al(311) has to compensate for the surface area increase ΔA. ΔA is small for faceting into vicinal orientations. (211) is vicinal to (111) with an angle of 19.5° with $\Delta A = 6\%$ and to (110) with an angle of 30° with $\Delta A = 15\%$. (311) is vicinal to (100) with an angle of 25.2° with $\Delta A = 11\%$. To find out if a surface S is unstable against faceting at a given H coverage Θ a constrained minimization problem has to be solved. In general, several phases i will coexist, each occupying a fraction f_i of the surface. In equilibrium the vector $\{f_i\}$ minimizes the total surface energy

$$\gamma_S(\Theta) = \sum_i f_i(\gamma_i^S - \Theta_i^S E_{i\,\text{ad}}^{\text{H}}) \qquad (2)$$

under the constraints $\sum_i f_i \Theta_i^S = \Theta$ and $\sum_i f_i = 1$. Θ_i^S is the H coverage and γ_i^S is the clean surface energy of phase i projected on S. $E_{i\,\text{ad}}^{\text{H}}$ is the H-adsorption energy in phase i. For $E_{i\,\text{ad}}^{\text{H}}$ and Θ_i, see Fig. 1. The calculated surface energies (in meV/Å^2) are $\gamma_{111} = 47.2$, $\gamma_{110} = 57.9$, $\gamma_{100} = 53.3$, $\gamma_{211} = 52.5$, and $\gamma_{311} = 55.4$ [21].

It turns out that Al(111) and Al(110) form {211} facets and Al(100) forms {311} and {211} facets above certain coverages, if not kinetically hindered. On Al(111) the threshold H coverage is 1 ML, with complete faceting into {211} orientations at 1.3 ML. On Al(110) formation of {211} facets starts at zero coverage and completes at 1.9 ML. H-covered Al(100) first forms {311} facets above 1 ML and 211 facets above 1.4 ML. The measured H saturation coverages on Al(111), Al(110), and Al(100) are 1.3, 2.4, and 1.6 ML [22]. At those coverages all three surfaces should be heavily faceted in thermal equilibrium.

It is likely that H phases with orientations and reconstructions similar to the (211) and (311) phases discussed, i.e., with a high concentration of TB/A-like sites, are equally stable. The result would be that faceted Al surfaces are disordered in experiment, especially at higher temperatures. However, this does not alter the important conclusion: Low index Al surfaces are unstable against vacancy reconstructions and faceting at H coverages that are readily achievable in experiment.

With this result a number of experimental observations at H-covered Al surfaces become less mysterious. As discussed before, the observed 2×1 reconstruction of H-covered Al(110) [19] is very likely a disordered MR/vacancy phase. The measured high frequency, Al-hydride-like, H vibrations [19] are caused by Al-hydride-like structures, i.e., H adsorbed on Al adatoms and other low coordinated Al surface atoms at steps and vacancies.

It is not understood today why up to 50% of the surface H desorbs as Al hydride and not as H_2 [22]. The highest hydride fraction is found for Al(111), the surface where, if unreconstructed, more Al-Al bonds have to be broken to form the hydride than on any other surface. However, there is an energetical advantage for Al-hydride desorption from a vacancy covered Al(111) surface. H_2 desorption would leave a high energy array of surface vacancies behind, desorption of Al hydride creates a nearly vacancy free low energy surface. An alternative mechanism for Al-hydride desorption off Al(111) involves the formation of a surface hydride as a precursor [see Fig. 1(c)]. The surface hydride forms at 2 ML H coverage on flat Al(111) without barrier and is metastable. Thus it should be observable at low T in experiment.

The most important effect of H adsorbed on Al surfaces is its influence on epitaxial growth. The dramatic change from layer-by-layer to rough growth with H adsorption [2,3] is likely caused by the H-induced restructuring of Al surfaces. One factor is the increase of the Al surface diffusion barriers on the reconstructed surfaces [11], another is the faceting instability at high coverage. The observed step bunching on Al(111) during CVD [2] might be direct evidence of the faceting instability in the presence of transient surface H. However, for a detailed understanding of H-modified Al epitaxy, more experimental and theoretical work is necessary. The interplay of H-induced faceting and H-modified surface diffusion as an explanation of rough growth has been invoked for a quite different system, Si(111), before [6]. This indicates that H effects similar to those discussed here are of more general importance in epitaxy and should be taken into account in developing film deposition techniques.

Knowledge about the H-Al surface interaction can help to understand H embrittlement, an important materials science issue. Whether a material breaks under load is partially determined by the energy of the surface or interface created during fracture [23]. For example, Ga leads to (100) fracture planes in part because Ga prefers to bind to Al(100). In H embrittlement the fracture faces are H covered. H prefers surface adsorption to absorption in bulk Al, thus H lowers the Al surface energy and promotes fracture. The surface energy is lowest for surfaces with a high concentration of {100} microfacets with H adsorbed at TB/A sites. Surfaces like this might be the fracture faces in H embrittlement of Al.

In this Letter I propose that H leads to vacancy reconstructions and faceting of the three low index Al surfaces. The driving force is the preference of H for TB/A sites. This model helps explain several puzzling observations like the Al-hydride desorption or the H-induced rough growth morphology on H-covered Al surfaces. More generally, the "tetra-octa" model of site preference for H on Al (and Be) surfaces developed here will help to understand other chemisorption systems.

[1] D. Pramanik, Mater. Res. Soc. Bull. **20**, 57 (1995); J. R. Creighton and J. E. Parmeter, Crit. Rev. Solid State Mater. Sci. **18**, 175 (1993).

[2] B. J. Hinch, R. B. Doak, and L. H. Dubois, Surf. Sci. **286**, 261 (1993).

[3] G. Polanski and J. P. Toennies, Surf. Sci. **260**, 250 (1990).

[4] R. Stumpf and M. Scheffler, Phys. Rev. Lett. **72**, 254 (1994); Phys. Rev. B **53**, 4958 (1996).

[5] J. E. Vasek et al., Phys. Rev. B **51**, 17 207 (1995).

[6] M. Horn-von Hoegen and A. Golla, Surf. Sci. **337**, L777 (1995); Phys. Rev. Lett. **76**, 2953 (1996).

[7] C. F. Walters, Z. Y. Zhang, D. M. Zehner, and E. W. Plummer (unpublished).

[8] Y. Morishita et al. Appl. Phys. Lett. **67**, 2500 (1995); A. M. Dabiran et al., Surf. Sci. **298**, 384 (1993).

[9] M. Frenklach et al., Nature (London) **372**, 535 (1994).

[10] R. Stumpf and P. J. Feibelman, Phys. Rev. B **51**, 13 748 (1995).

[11] R. Stumpf (unpublished).

[12] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996). The calculations presented here are fully selfconsistent within the GGA. Using the local density approximation (LDA) instead gives qualitatively similar results. The main differences are that in LDA clean Al surface energies are 25% and vacancy formation energies on Al(111) are 160% higher. Thus in LDA the energy gain from faceting and vacancy reconstructions is smaller.

[13] D. R. Hamann, Phys. Rev. B **40**, 2980 (1989).

[14] The energy of H within the GGA is 0.9182 Ry, with the 20 Ry plane-wave cutoff it is 0.8958 Ry. To correct for the GGA and the cutoff error I choose 1 Ry − (0.9182 Ry − 0.8958 Ry) as H reference energy.

[15] R. Stumpf and M. Scheffler, Comp. Phys. Commun. **79**, 447 (1994).

[16] R. Stumpf, Phys. Rev. B **53**, 4253R (1996).

[17] K. Pohl, J. B. Hannon, and E. W. Plummer (unpublished).

[18] P. J. Feibelman et al., Phys. Rev. Lett. **77**, 2257 (1996).

[19] H. Kondoh, M. Hara, K. Domen, and H. Nozoye, Surf. Sci. **287**/**288**, 74 (1993); J. Paul, Phys. Rev. B **37**, 6164 (1988).

[20] On Al(311) the {111} terraces are only two rows wide. However, upon H adsorption, it is favorable, to increase the terrace width by forming double steps [see Fig. 1(h)].

[21] The ratio $\gamma_{110}/\gamma_{111} = 1.23$ indicates that Al(110) is marginally unstable against faceting into (111) facets ($\Delta A = 22\%$) at $T = 0$. This is, however, never observed at $T \neq 0$. The reason might be that the surface energy anisotropy and thus $\gamma_{110}/\gamma_{111}$ decreases with T. In fact, at the melting temperature $\gamma_{110}/\gamma_{111} = 1$.

[22] A. Winkler, G. Pozgainer, and K. D. Rendulic, Surf. Sci. **251**/**252**, 886 (1991); H. Kondoh, M. Hara, K. Domen, and H. Nozoye, Surf. Sci. **268**, L287 (1992).

[23] R. Stumpf and P. J. Feibelman, Phys. Rev. B **54**, 5145 (1996).