

Hydrogen-bridge bonding on semiconductor surfaces: Density-functional calculationsJ. M. Ripalda,¹ J. D. Gale,² and T. S. Jones³¹*Instituto de Microelectrónica de Madrid, CSIC, PTM Tres Cantos, Madrid 28760, Spain*²*Nanochemistry Research Institute, Department of Applied Chemistry, Curtin University of Technology, P.O. Box U1987, Perth 6845, Western Australia*³*Centre for Electronic Materials and Devices and Department of Chemistry, Imperial College London, SW7 2AZ London, United Kingdom*

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The relative stabilities of hydrogen bridge bonds on diamond C(001), Si(001), Ge(001), and GaAs(001) surfaces have been studied within the framework of density functional theory. Hydrogen-bridge bonds are found to be stable on cation terminated GaAs(001) and almost stable on *p*-type doped Si(001) surfaces with an excess energy of 0.08 eV per bridge. Bridge bonds are unstable on *n*-type doped Si(001) and anion terminated GaAs(001). H-bridges are metastable on intrinsic group IV surfaces, and the excess energy cost diminishes monotonically across the C-Si-Ge series. In stark contrast with group IV semiconductors, the (2×1) monohydride dimer structure is not stable on GaAs(001).

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Bonds where hydrogen bridges two atoms hold together the two complementary strands in DNA. Hydrogen bridge bonds are also the cause for water being a liquid rather than a gas at room temperature, and have a crucial role in protein folding. Interstitial hydrogen in bulk semiconductors is often found to adopt this bonding geometry.¹ Examples of its importance abound in the fields of chemistry, biology, and materials science, however until recent years, this type of bonding has received little attention in studies of the interaction of hydrogen with semiconductor surfaces.

The widespread interest in the chemistry of hydrogen on semiconductor surfaces does not only stem from a fundamental scientific perspective. The most commonly used methods for commercial semiconductor deposition make use of hydrogenated precursors in a hydrogen rich environment. It is therefore of crucial technological importance to fully understand the chemistry of hydrogen on semiconductor surfaces.

Hydrogen adsorption on Si(001) and diamond C(001) are two of the most extensively studied systems in surface science.^{2–5} Hydrogen typically adopts a terminal geometry on top of the (2×1) dimers of the Si(001) and diamond C(001) surface, with one hydrogen atom per surface site (monohydride). At saturation coverage (two H atoms per surface atom), the (2×1) reconstruction dimers are split and a (1×1) dihydride surface results. Tok *et al.*⁶ have recently found that bridging H is metastable on Si(001) and plays a key role as an intermediate step in H adsorption.

Not as much is known about the interaction of hydrogen with compound semiconductors. Qi *et al.*⁷ and Hicks *et al.*⁸ have detected Ga-H-Ga bridge bonds on GaAs(001) using vibrational spectroscopy, and H bridge bonds have also been experimentally detected on InP(001).⁹ Scanning tunneling microscopy (STM) observations of H:GaAs(001) surfaces reveal small domains with unit cell dimensions of (1×2) , $c(2 \times 2)$, and $c(4 \times 2)$; apparently being different arrangements of the same dimer building block.^{10,11}

In the present work we have studied the relative stabilities

of H bridge bonds on diamond C(001), Si(001), Ge(001), and GaAs(001) surfaces. In the framework of density functional theory we find H bridges to be either stable or metastable in all studied cases except in the case of *n*-type doped Si(001) and anion terminated GaAs(001). We find H bridge bonds to be stable on cation terminated GaAs(001) and almost stable on *p*-type Si(001), with an excess energy of 0.08 eV.

We have used the generalized gradient approximation (GGA, Perdew–Burke–Ernzerhof functional),¹² including spin polarization. A basis set of localized atomic orbitals and norm-conserving pseudopotentials were used. All calculations were performed using the SIESTA methodology, as described elsewhere.¹³ The basis set was double zeta for all the main group elements and triple zeta for H. Polarization functions were included in the basis sets of all elements, and confinement radii were set such that the energy shift of the atomic orbitals (relative to the unconfined orbitals) was 0.005 Ry. The method of Monkhorst and Pack was used to sample reciprocal space with a grid dimension of 6 along each surface vector.¹⁴ As a model we have used symmetric slabs containing 10 atomic layers with adsorbed H on the top and bottom layers. A thicker slab was used as a test in the case of monohydride Si(001), and a 0.02 eV change in surface formation energy was found. Since most of our results involve energy differences between the various calculated structures, partial error cancellation is expected. For GaAs(001) it is not possible to use a symmetric slab due to the polar nature of this surface. Consequently, the opposing surface was terminated with hydrogen atoms whose positions were subsequently held fixed. Unit cell sizes of (2×1) , (3×1) , (4×2) , (4×3) , and (6×3) with up to 192 atoms have been used. To study the effect of doping on the stability of H bridge bonds we have included a single P or B atom in the fourth Si atomic layer of (4×2) , (4×3) , and (6×3) Si(001) supercells including a single, isolated bridge bond.

Using the conjugate gradients, we have optimized the ge-

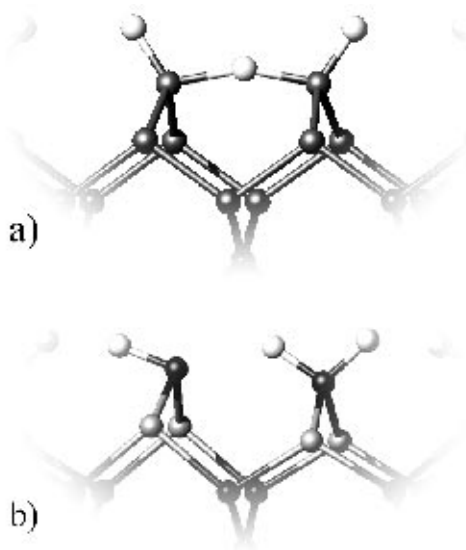


FIG. 1. (a) Bridging hydrogen structure on Si(001)-(2 \times 1). White atoms are hydrogen and dark atoms are silicon. (b) Structure found for H-As terminated GaAs(001) at 1.5 H/As coverage.

ometry of (2 \times 1) unit cells with three hydrogen atoms (1.5 hydrogen atoms per surface site) on C(001), Si(001), Ge(001), H-Ga terminated GaAs(001), and H-As terminated GaAs(001). For all the intrinsic group IV surfaces and the H-Ga terminated GaAs(001) surface, the final geometry included two terminal H atoms and one bridging H atom in the configuration shown in Fig. 1(a). The bond length at the twofold coordinated H site is 1.30 Å on C(001), 1.79 Å on Si(001), 1.84 Å on Ge(001), and 1.77 Å on H-Ga terminated Ga(001). The bridging H is not in the same horizontal plane as its first neighbors, the angle between the bridge bonds and the surface normal ranging from 75° to 79°. Geometry optimization of H-As terminated GaAs(001) at 1.5H/As coverage resulted in the configuration shown in Fig. 1(b).

To compare the relative stability of the bridge structure with competing configurations with a different surface unit cell size, or a different hydrogen coverage, we present in Figs. 2 and 3 the surface formation energy as a function of the hydrogen chemical potential. The equivalence of the given chemical potentials in terms of molecular H₂ pressure and system temperature is given in Table I on the basis of the thermodynamical analysis method by Reuter and Scheffler.^{15,16} Positive chemical potentials are attainable with atomic H sources, but this implies nonequilibrium conditions. It can be seen that the bridging geometry is metastable on C(001), Si(001), and Ge(001), and is stable on both cation and anion terminated GaAs(001). The excess energy cost of the bridging geometry diminishes monotonically across the C-Si-Ge series.

For all group IV semiconductors the competing structures included in Fig. 3 are the well-known monohydride and dihydride structures, as well as the mixed (3 \times 1) structure that includes one monohydride dimer and one dihydride unit.^{2,5} In the case of H-Ga and H-As terminated GaAs we have studied (2 \times 1) and (1 \times 1) unit cells with hydrogen cover-

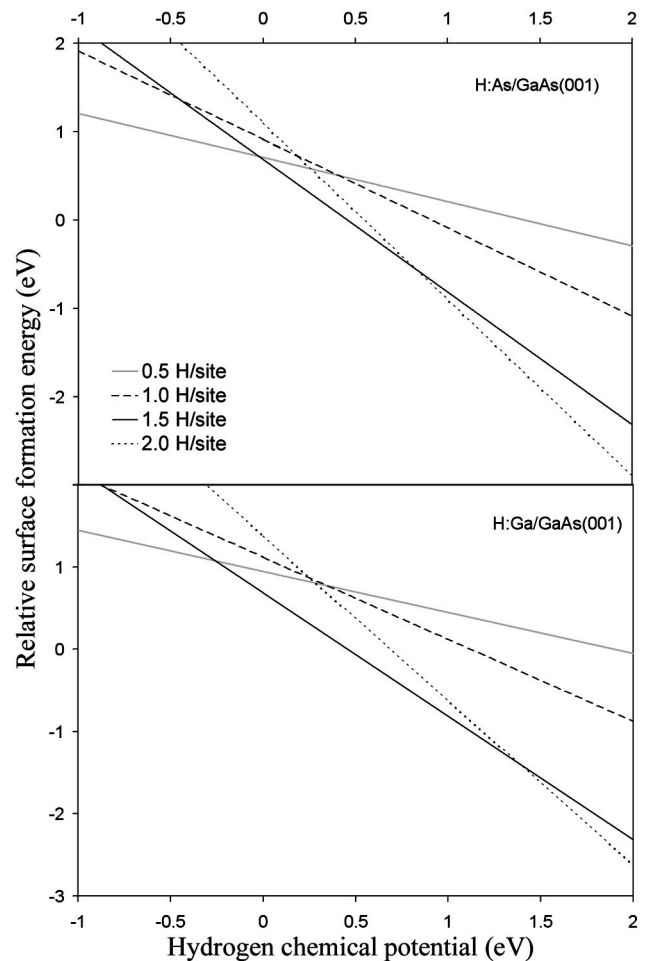


FIG. 2. Relative surface formation energy per (1 \times 1) substrate unit cell as a function of hydrogen chemical potential for various structures with hydrogen coverages of 0.5, 1, 1.5, and 2 hydrogen atoms per surface site. The cases of H-As and H-Ga terminated GaAs(001) surfaces are compared. In this plot the origin of the surface formation energy scale is arbitrary.

ages of 0.5, 1, 1.5, and 2 hydrogen atoms per surface atom. In stark contrast with the group IV surfaces, the GaAs(001) monohydrides are not stable in either the cation or anion terminated cases, as can be appreciated from the surface formation energy plots shown in Fig. 2. On the H:Ga/GaAs(001) monohydride surface, the most stable structure is quite similar to the bridge structure shown in Fig. 1(a), but with one missing terminal hydrogen at one end of the bridge. The monohydride dimer structure typical of the group IV surfaces is also a local minimum in the H:Ga/GaAs(001) case, but the total energy is 0.1 eV higher than in the bridging case. A previous LDA (local density approximation) study on the H:Ga/GaAs(001) surface suggested that the arrangement of the surface dimers in $c(2\times 2)$ and $c(2\times 4)$ brickwork arrangements may further reduce the surface formation energy by 0.02–0.07 eV.¹¹

The most stable H-As terminated monohydride structure has a (1 \times 1) unit cell with no dimerization and H atoms in a tilted, terminal configuration. The monohydride dimer structure typical of the group IV surfaces is only a local minimum

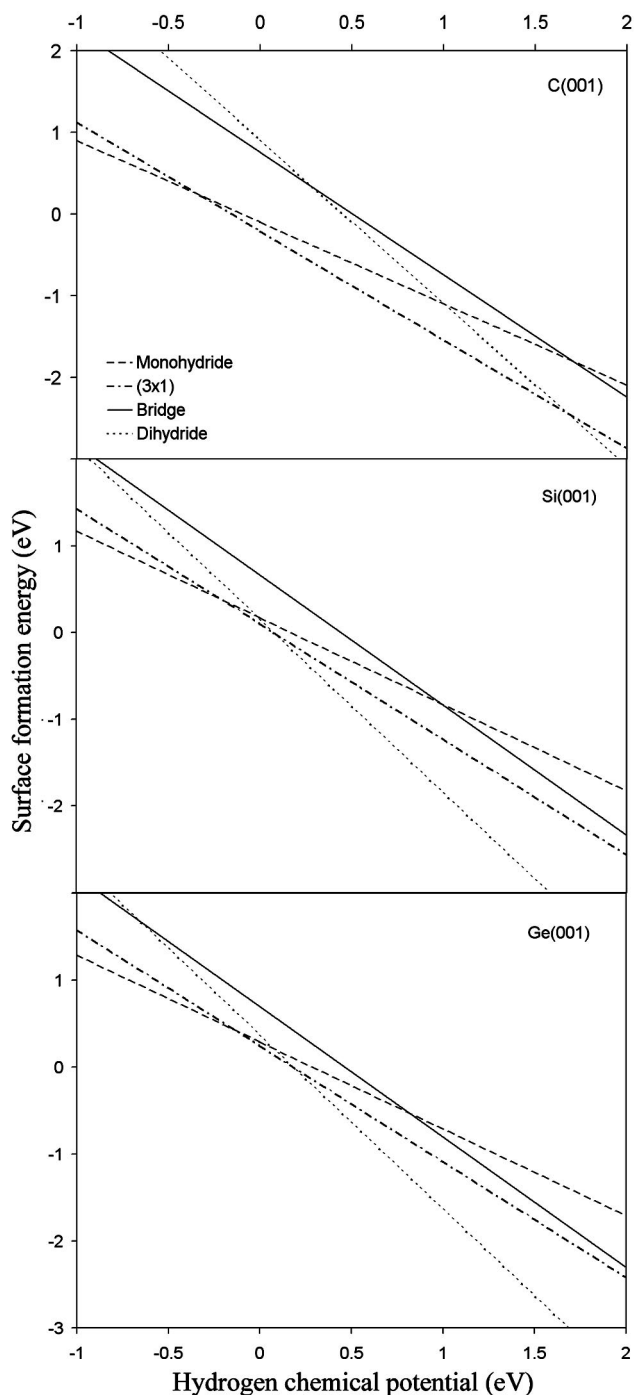


FIG. 3. Surface formation energy per (1×1) substrate unit cell as a function of hydrogen chemical potential for the most important C(001), Si(001), and Ge(001) reconstructions, as well as for the bridge structure in Fig. 1(a).

in the H: As/GaAs(001) case, and has a total energy 0.17 eV higher than the H-As monohydride (1×1) structure.

On Si(001), bridges are most stable on the (3×1) reconstruction, with an excess energy of 1.11 eV per bridge. On a *p*-type doped (3×1) Si(001) surface the excess energy is just 0.08 eV per bridge, while on the (2×1) monohydride intrinsic Si(001) surface it is 1.20 eV. Bridges are unstable on *n*-type doped Si(001), and a geometry similar to that in Fig.

TABLE I. Hydrogen chemical potential (eV) as a function of molecular H_2 pressure and system temperature (Refs. 15 and 16).

| T (K) | μ_H at 1 atm H_2 | μ_H at 0.1 atm H_2 | μ_H at 10^{-2} atm H_2 | μ_H at 10^{-3} atm H_2 |
|---------|------------------------|--------------------------|--------------------------------|--------------------------------|
| 300 | -0.08 | -0.11 | -0.17 | -0.26 |
| 600 | -0.19 | -0.25 | -0.37 | -0.55 |
| 1100 | -0.40 | -0.51 | -0.73 | -1.05 |

1(b) results. The presence of a vacancy in the fourth Si atomic layer of a (2×1) monohydride substrate is found to increase the binding energy of an isolated H bridge by 0.59 eV. Many other types of defect might alter the stability of H bridges, but their study is beyond the scope of this paper.

We have found that the most favorable surface adsorption site for a single excess H atom on a perfect (3×1) or (2×1) Si(001) surface is the bridge site. Processes compet-

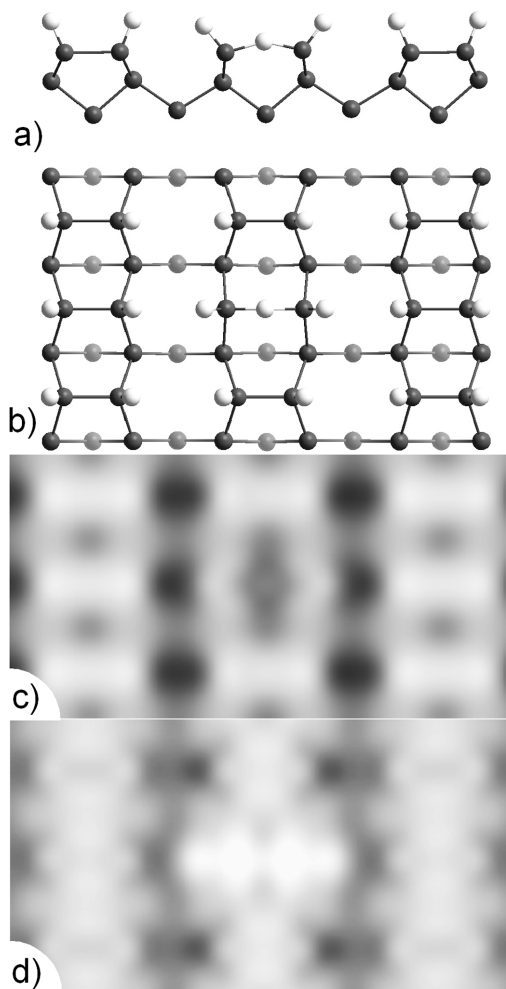


FIG. 4. Monohydride Si(001)- (2×1) surface with one bridging hydrogen as a defect: (a) side view, (b) top view, (c) top view of a surface of constant local density of filled states. (d) Top view of a surface of constant local density of empty states. Only states 2 eV above/below the Fermi level have been included. The full range of the greyscale represents a height difference of 2.5 Å.

ing with adsorption at the bridge site are Eley-Rideal abstraction¹⁷ and subsurface H adsorption.¹⁸ Possible decay processes for H bridges are H₂ desorption leaving a dangling bond behind (with a barrier of 0.8–1.3 eV),⁶ diffusion and recombination with dangling bonds, and associative recombination with another H bridge into a H₂ molecule or 2 dihydride H-Si-H units.

From STM observations of monohydride Si(001) surfaces, Buehler and Boland have inferred the existence of a nearly stable type of hydrogen bonding on H:Si(001) that is clearly different from the terminal monohydride and dihydride species, but they could not determine the exact bonding geometry.¹⁹ A clear and distinctive signature was observed for this type of hydrogen site; in filled states STM imaging it appears as a dark center with brighter sides, symmetric about the dimer row, while in empty states imaging it appears as a bright and diffuse spot with a diameter of about 7 Å. We have calculated the local density of empty and filled states for an isolated bridging hydrogen on a H:Si(001)-(2×1) surface and the corresponding surfaces of constant electron state density are shown in Fig 4. The similarity with the experimental STM images presented by Buehler and Boland is clear, but we cannot explain how H bridge bonds would be stable in this particular case, as the substrate in these experiments was *n*-type doped.

We have also calculated the vibrational spectrum of the (2×1) bridge structure on Si(001) and Ge(001). The bridging atom on Si(001) is involved in three vibrational modes at frequencies of 719, 818, and 962 cm⁻¹, corresponding to an in-plane vibration perpendicular to the Si-H-Si bond, a vi-

bration parallel to the Si-H-Si bond, and a vibration perpendicular to the surface, respectively. On H:Ge(001) these bridging hydrogen vibrational modes have reduced frequencies of 687, 770 and 909 cm⁻¹, respectively. Bridging hydrogen is expected to represent a small fraction of the hydrogen atoms on a Si(001) surface (even if *p*-type doped), and using conventional vibrational spectroscopies these signals would be difficult to separate from vibrational modes due to monohydride (620–660 cm⁻¹), and dihydride (907 cm⁻¹) species, as well as typical contaminants (Si-OH, 790 cm⁻¹). However, it might be possible to resolve the signal from bridging hydrogen using a local probe such as inelastic tunnelling spectroscopy with an STM instrument.^{19,20}

In conclusion, we find bridging H to be stable on cation terminated GaAs(001) and almost stable on *p*-type Si(001) with a 0.08 eV excess energy per H bridge. The bridge site is the most stable H adsorption site on perfect (2×1) and (3×1) Si(001) surfaces. Bridges are unstable on anion terminated GaAs(001) and *n*-type Si(001); in all the other studied cases it is either stable or metastable. Bulk vacancies in Si reduce the excess energy of the H bridges and other types of defect might have a similar effect. In stark contrast with group IV semiconductors, monohydrides are not stable on GaAs(001).

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