Reconstructions of the As-Terminated GaAs(001) Surface Exposed to Atomic Hydrogen

Marsel Karmo,* Isaac Azahel Ruiz Alvarado, Wolf Gero Schmidt, and Erich Runge

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: We explore the atomic structures and electronic properties of the As-terminated GaAs(001) surface in the presence of hydrogen based on ab initio density functional theory. We calculate a phase diagram dependent on the chemical potentials of As and H, showing which surface reconstruction is the most stable for a given set of chemical potentials. The findings are supported by the calculation of energy landscapes of the surfaces, which indicate possible H bonding sites as well as the density of states, which show the effect of hydrogen adsorption on the states near the fundamental band gap.
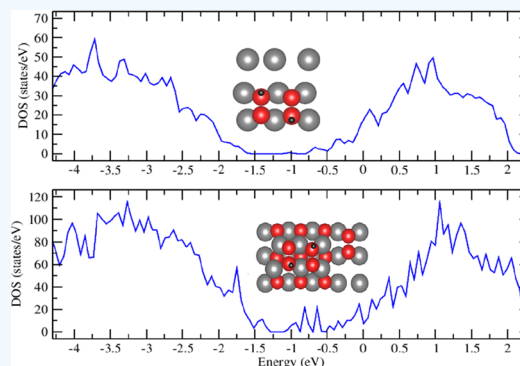
INTRODUCTION

The study of the adsorption of atoms/molecules on surfaces of optoelectronic devices (such as solar cells) has attracted a lot of interest. In this work, we explore atomic hydrogen adsorption on the technologically relevant As-terminated GaAs(001) surfaces,[1] having in mind typical metal−organic chemical vapour deposition/metal−organic vapour-phase epitaxy (MOCVD/MOVPE) growth conditions.[2] In an early density functional theory (DFT) study exploring hydrogen reactions with As-rich GaAs(001) surfaces, Miyamoto and Nonoyama[3] found a strong tendency of atomic hydrogen to attach to the (2 × 2)-2D surface, resulting in As dimer distortion and opening of a surface band gap. Subsequent theoretical studies of the As-terminated GaAs (001) surface without[4] and with hydrogen[5] discussed some reconstructions, which are among others revisited and mostly confirmed in the present work. Much of the experimental work on the interaction of hydrogen with GaAs surfaces examined the temperature influence on atomic-hydrogen adsorption on GaAs surfaces.[6−14] Close to room temperature, the reaction of H atoms with an As-rich surface was reported to lead to a change in the surface stoichiometry mainly through the loss of As atoms.[7] This could lead to rather rough surfaces, which can locally resemble the 2 × 6 reconstruction discussed below. On the other hand, Qi et al.[8,9] proposed that the main mechanism of hydrogen adsorption is the breakup of the As−As or As−Ga dimers, possibly via hydrogen insertion and the formation of As monohydrides and dihydrates.

We investigated those surface reconstructions that are widely considered as the most stable ones for group V-rich growth of GaAs-related III−V compounds. First, we calculate the total energy of those systems, of course, for fixed atom numbers. However, it is the grand canonical surface-formation energy for a given chemical potential, μ_i, that determines whether hydrogen adsorption can actually take place under specific growth conditions.[15] This leads to a phase diagram dependent on the chemical potentials of As and H, showing which surface reconstruction is the most stable for a given set of chemical potentials. Finally, we look at the H-bonding mechanisms by detailed studies of possible adsorption sites and of consequence for the electronic structure and the density of states (DOSs).

RESULTS AND DISCUSSION

The surface reconstructions considered in this work are shown in Figures 1, S1, and S2 as well as listed in Tables 1 and 2 together with the corresponding surface-formation energy, Ω, for As- and H-rich growth conditions ($\Delta\mu_{As} = 0$, $\Delta\mu_H = 0$). As possible hydrogen-adsorption sites, we focus on bonding to top-layer dimers. If two hydrogen atoms bond to adjacent, parallel As dimers, we consider only the "staggered" configuration, which is typically energetically very close to the nonstaggered one but energetically slightly favorable.

Figure 2 shows the phase diagram for the hydrogen-exposed GaAs(001) surfaces obtained as follows: for each point in the
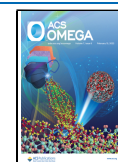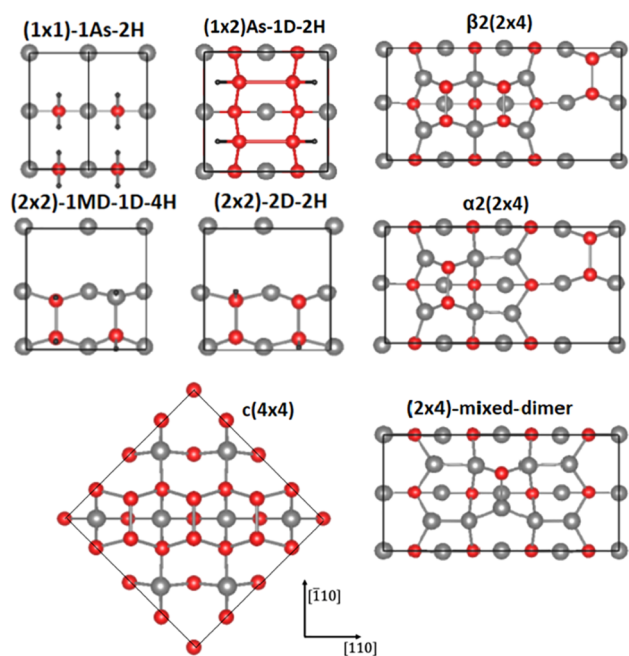
Figure 1. Eight very stable GaAs(001) surface reconstructions with and without H atom adsorbate occurring in the phase diagram in Figure 2. Gray, red, and black circles represent Ga, As, and H atoms, respectively.

Table 1. Surface-Formation Energy Ω of Clean Surfaces and Electronic Configurations[a]

surface reconstruction	Ω (eV/Å^2)	n_{extra}	$2n_{As}^{dangl}$
(1×1)-1As	0.085	2.5	4
(1×1)As-1As	0.014	3.5	4
(1×2)As-1D	−0.027	5	4
(2×1)-1D	0.001	3	4
(2×2)-1D	0.030	6	4
(2×2)-1MD-1D	0.015	4	6
(2×2)-2D	−0.001	6	8
$\xi(4 \times 2)$	0.031	8	8
$\beta2(2 \times 4)$	−0.016	12	12
(2×4)-mixed dimer	0.034	2	2
$\alpha2(2 \times 4)$	0.000	8	8
(2×6)	0.108	8	8
$c(4 \times 4)$	−0.046	20	20

[a]Surface reconstructions fulfilling the electron counting rule (ECR); i.e., those where the number n_{extra} equals twice the number of As-dangling bonds are printed in bold face. Energies are given relative to the configuration $\alpha2(2 \times 4)$ for As- and H-rich growth conditions ($\Delta\mu_{As} = 0$, $\Delta\mu_H = 0$).

($\Delta\mu_{As}$, $\Delta\mu_H$)-plane, the minimum of Ω_j is determined (with j enumerating a surface). As a result, one obtains the regions where surface reconstruction (j) is energetically most favored.

The line at $\Delta\mu_{As} = 0$ marks an As-rich/Ga-poor environment, whereas the line at $\Delta\mu_{As} = -H_f^{GaAs}$ marks an As-poor/Ga-rich environment. The actual values of $\Delta\mu_{As}$ and $\Delta\mu_H$ depend on the preparation conditions; see, e.g., refs 16 and 17. The line $\Delta\mu_H = 0$ corresponds to the situation where the surface is exposed to molecular hydrogen at $T = 0$ K. In order to obtain atomic hydrogen, an energy barrier needs to be overcome to break the molecular hydrogen bond. The structures indicated for $\Delta\mu_H > 0$ in the phase diagram (Figure 2) may form when atomic hydrogen becomes available for the

Table 2. Surface-Formation Energy Ω of Hydrogen-Exposed Surfaces and Electronic Configurations[a]

surface reconstruction	Ω (eV/Å^2)	n_{extra}	$2n_{As}^{dangl}$
(1×1)-1As-2H	0.040	0.5	0.0
(1×1)As-1As-2H	0.390	1.5	0.0
(1×2)As-1D-2H	0.316	3	0.0
(2×1)-1D-2H	0.014	1	0.0
(2×2)-1D-1H	0.042	5	2
(2×2)-1MD-1D-4H	0.002	0	0
(2×2)-2D-2H	−0.041	4	4
$\xi(4 \times 2)$-1H	0.027	7	8
$\beta2(2 \times 4)$-2H	0.007	10	8
(2×4)-mixed dimer-1H	0.074	1	0.0
$\alpha2(2 \times 4)$-1H	0.009	7	6
(2×6)-2H	0.147	10	8
$c(4 \times 4)$-3H	−0.028	17	14

[a]Surface reconstructions fulfilling the electron counting rule (ECR); i.e., those where the number n_{extra} equals twice the number of As-dangling bonds are printed in bold face. Energies are given relative to the configuration $\alpha2(2 \times 4)$ as in Table 1. Here, nH in the names of the reconstructions indicates the number of hydrogen atoms per surface unit cell with $n = 1, 2, 3$, and 4.
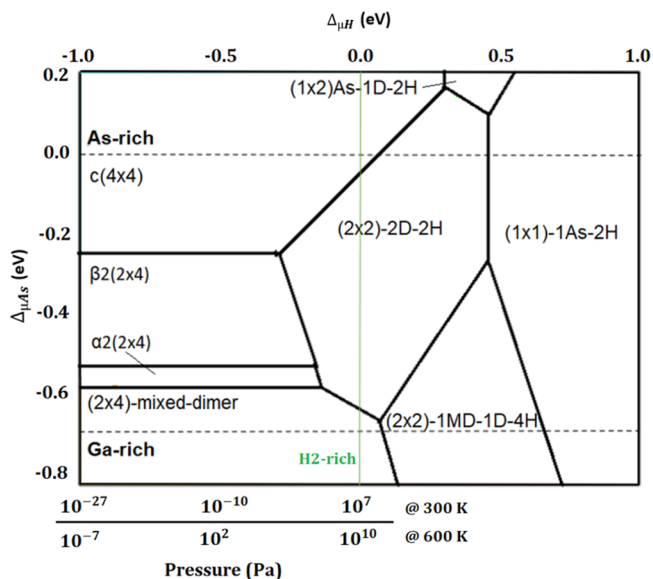

Figure 2. Calculated phase diagram of the hydrogen-exposed GaAs(001) surface. Dashed lines indicate the approximate range of the thermodynamically allowed values of $\Delta\mu_{As}$. The chemical potential of hydrogen, $\Delta\mu_H$, is given with respect to molecular hydrogen at zero temperature (green line: $\Delta\mu_H = 0$). Pressure scales indicate the experimental conditions corresponding to particular $\Delta\mu_H$ values.

surface reaction. When the temperature is increased, the hydrogen chemical potential is continuously lowered, yielding negative values, $\Delta\mu_H < 0$.

In the intermediate section of this diagram, the biggest part from As-rich ($\Delta\mu_{As} = 0$) to Ga-rich ($\Delta\mu_{As} = -0.68$ eV) conditions is occupied by the surface reconstruction (2×2)-2D-2H (see Figure 1). According to the equation for the surface-formation energy Ω, this surface is, thus, the energetically favored one, compared not only to the other mentioned surfaces but also to (2×2)-2D (without hydrogen). Only with the adsorbed hydrogen atom does the (2×2)-2D reconstruction fulfil the following electron counting rule

(ECR):[18] We define the total number of electrons minus twice the number of all bonds including dimer bonds and hydrogen bonds as n_{extra}. The ECR states that those reconstructions are particularly stable when the number of extra electrons (n_{extra}) is allowed to fill all the dangling bonds of the more electronegative elements (As), while all the dangling bonds of the more electropositive elements (Ga) are left empty. No hydrogen is adsorbed on the surfaces on the left side of the diagram (i.e., (2×4) and (4×4)). According to the ECR, these surfaces already have a stable, nonmetallic electronic structure, making the adsorption of hydrogen energetically less favorable; see Tables 1 and 2. This qualitatively agrees with findings from refs 10−13, in particular for the (2×4) and c(4 $\times$ 4) surfaces for the various pressures and temperatures. The converged surface geometries of those reconstructions not present in the phase diagram are given in the Supporting Information. Note in particular that the rather rough 2×6 reconstruction with four incomplete atomic layers is not present in the phase diagram. The reader should be aware that, for very high hydrogen concentrations as consequence of the removal of As atoms,[7] we do not expect hydrogen atoms to bond to Ga dimers but rather hydrogen to bond at Ga−Ga bridging positions as discussed in ref 5.

The phase diagram (Figure 2) predicts that $\beta 2(2 \times 4)$ with two As dimers in the first (i.e., topmost) atomic layer and one in the third one (as given in Figure 1) is found to be energetically favorable over various (2×4) reconstructions for a wide range of the chemical potential, $\triangle \mu_{As}$. Thus, it is worthwhile to look in detail why this structure does not accept hydrogen. Therefore, we calculate potential energy surfaces (PESs) for H adsorption on the stable $\beta 2(2 \times 4)$ phase and compare them with those for adsorption on the (2×2)-2D reconstruction, i.e., the precursor of the stable (2×2)-2D-2H phase:[15] A H atom is placed over the surface; then, the x-and y-coordinates are held fixed while the normal distance (i.e., the z-coordinate) and the coordinates of the surface atoms are allowed to relax. In this way, we created a rough map of the PES on a (5×10) grid for $\beta 2(2 \times 4)$ and on a (5×5) grid for (2×2)-2D. The adsorption energy per adsorbed atom is defined as the difference of the total energy of the adsorbent plus the adsorbate and the sum of the total energies of the adsorbent and one of the adsorbates alone; the latter one is calculated with respect to molecular hydrogen.

$$E_{ad} = E_{tot} - (E_{clean\text{-}surface} + 0.5E[H_2])$$

E_{ad} values below 0 indicate positions that hydrogen atoms like to bond to at $T = 0$ K, whereas E_{ad} values above 0 indicate that the hydrogen atom is pushed away from the surface. In such a map, potential adsorption sites can be identified via negative energy values. Figure 3 shows that there is no bonding site for hydrogen on the $\beta 2(2 \times 4)$ surface and lots of opportunities for the (2×2)-2D surface. This matches well with the phase diagram in Figure 2 and is consistent with the chemical intuition underlying the ECR: Configurations fulfilling the ECR have filled dangling bonds or lone pairs on As, making these sites unattractive for H atoms. In contrast, a half-filled dangling As bond is a perfect site for H adsorption, yielding a rather stable As−H bond.

To further analyze the surface properties, in Figure 4, we compare the DOS of the clean and exposed surfaces. The band gap for the clean (2×2)-2D surface is nearly nonexistent, i.e., 0.1 eV (Figure 4a). It increases up to 0.7 eV when hydrogen is adsorbed, which indicates a change from nearly metallic to
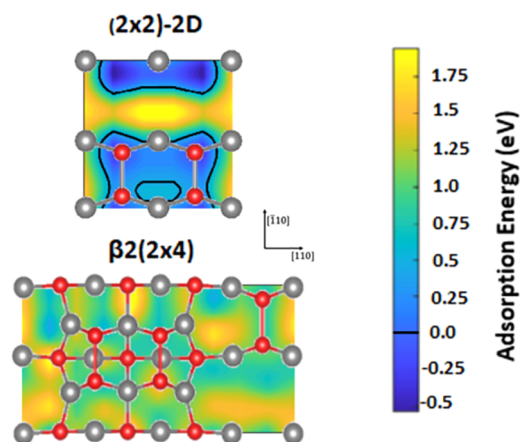

Figure 3. Potential energy surface (PES) for atomic hydrogen adsorption on (2×2)-2D and $\beta 2(2 \times 4)$ GaAs (001) surfaces. Gray and red circles represent Ga and As atoms.
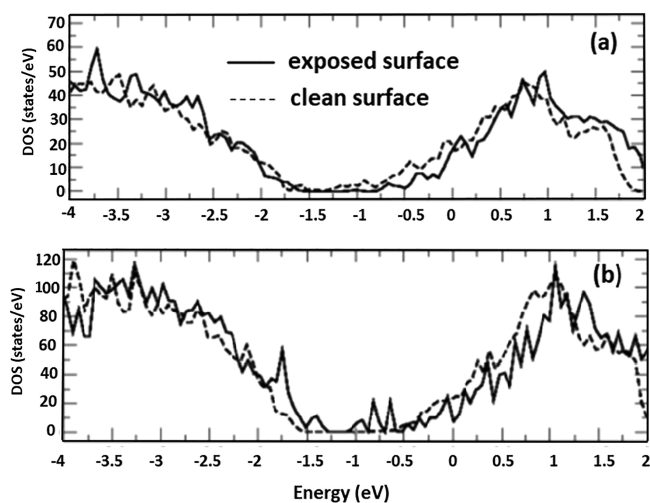

Figure 4. Density of states (DOSs) for clean and hydrogen-exposed (2×2)-2D (a) and $\beta 2(2 \times 4)$ (b) surfaces. In (a), the band gap widens if H is added, whereas in (b), it vanishes.

semiconducting. In contrast to this, the band gap of the clean $\beta 2(2 \times 4)$ surface vanishes when a hydrogen atom is added (Figure 4b). This matches the prediction of the ECR.[4]

■ SUMMARY

DFT calculations were used to determine thermodynamically stable reconstructions for the GaAs(001) surface. From the calculated thermodynamic potentials, we derive the phase diagram for the surface reconstructions as a function of the availability of hydrogen and arsenic. For a wide range of the chemical potentials, the (2×2) surface with one hydrogen adsorbed to each As dimer is energetically favored. This result is similar to those presented for the GaP/InP surfaces in refs 16 and 17. Furthermore, we calculate PES with a single hydrogen atom as an energetic probe for two surfaces and confirm the finding of ref 14 (e.g., no hydrogen adsorption on the $\beta 2(2 \times 4)$ surface). In summary, the present results corroborate the electron counting rule for hydrogen-exposed surfaces. While the semiconducting As-rich (2×4) and c(4 $\times$ 4) surfaces have essentially no affinity for hydrogen, hydrogen adsorption is highly favorable for the metallic (2×2) As-rich GaAs surface. It is essentially passivated by hydrogen.

■ METHODOLOGY

In order to compare the specific surfaces, total energies of slabs with typically 15 atomic bulk fcc layers of alternating As and Ga atoms and approximately 8 layers of vacuum were calculated. The lateral size is given by the particular surface unit cell under investigation. As we are primarily interested in energy differences, we use the same lower slab surface consisting of As and pseudohydrogen with $Z = 0.75$ in all cases. The uppermost four layers were allowed to relax, and the other bulk layers were fixed to the equilibrium geometry of the corresponding bulk calculation, i.e., a lattice constant of 5.765 Å. Calculations were performed with the Vienna Ab initio Simulation Package (VASP)[19] within the generalized gradient approximation (GGA) and with the Perdew−Burke−Ernzerhof (PBE) functional.[20] The cutoff energy for the plane wave basis is chosen to be 400 eV. An automatically generated k-point set with six points for each lateral dimension and one point in vertical direction per (2×2) unit cell is used.

In order to compare the clean surfaces and those exposed to hydrogen, one has to introduce the chemical potential (μ_i, i = Ga, As, H) of the involved atomic species. The specific surface-formation energy, Ω, i.e., the energy per area, can be expressed as[15]

$$\Omega A = E_{tot} - n_{Ga}\mu_{GaAs}^{bulk} - (n_{As} - n_{Ga})\mu_{As}^{bulk} - \frac{1}{2}n_H E_{H_2}$$
$$- (n_{As} - n_{Ga})\Delta\mu_{As} - n_H\Delta\mu_H$$

Here, $\Delta\mu_i = \mu_i - \mu_i^{bulk}$, E_{tot} is the total energy of the slab, A is the surface unit cell area, and n_i is the number of atoms of the species i in the slab. This defines a plane in a $(\Delta\mu_{As}, \Delta\mu_H, \Omega)$ space. In thermodynamic equilibrium, the chemical potential of bulk GaAs (μ_{GaAs}^{bulk}) is given by the sum of the chemical potentials of Ga and As atoms (μ_{Ga}, μ_{As})

$$\mu_{GaAs}^{bulk} = \mu_{Ga} + \mu_{As}$$

The chemical potential of As atoms (μ_{As}) is limited by the chemical potential of an As crystal (μ_{As}^{bulk}) and the heat of formation (H_f^{GaAs})

$$H_f^{GaAs} + \mu_{As}^{bulk} \leq \mu_{As} \leq \mu_{As}^{bulk}$$

where H_f^{GaAs} is given by $H_f^{GaAs} = \mu_{Ga}^{bulk} + \mu_{As}^{bulk} - \mu_{GaAs}^{bulk}$.

For H_f^{GaAs}, μ_{As}^{bulk}, μ_{Ga}^{bulk}, and E_{H_2}, the computed values relative to the vacuum level of the DFT calculation are 0.68 eV, −4.68 eV, −2.9 eV, and −6.77 eV, which are close to those reported in refs 21 and 22. The chemical potential of hydrogen, which is dependent on pressure (P) and temperature (T), is given by

$$\Delta\mu_H(T, P) = \frac{k_B T}{2}\left\{\ln\left(\frac{p\lambda^3}{k_B T}\right) - \ln Z_{rot} - \ln Z_{vib}\right\}$$

where k_B is the Boltzmann constant and Z_{rot} and Z_{vib} are the rotational and vibrational partition functions. These values are calculated according to ref 23 using the vibrational frequency of the hydrogen molecule from ref 24. The wavelength λ is the de Broglie thermal wavelength of the H_2 molecule and is equal to $\lambda = h/\sqrt{2\pi m k_B T}$.

■ ASSOCIATED CONTENT

ⓈI Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c06019.

Relevant geometries of clean and hydrogen-exposed GaAs(001) surfaces (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Marsel Karmo − *Institut für Physik and Institut für Mikro- und Nanotechnologien (IMN), Technische Universität Ilmenau, 98693 Ilmenau, Germany;* ⓞ orcid.org/0000-0003-0088-3336; Email: marsel.karmo@tu-ilmenau.de

Authors

Isaac Azahel Ruiz Alvarado − *Lehrstuhl für Theoretische Materialphysik, Universität Paderborn, 33098 Paderborn, Germany;* ⓞ orcid.org/0000-0002-4710-1170

Wolf Gero Schmidt − *Lehrstuhl für Theoretische Materialphysik, Universität Paderborn, 33098 Paderborn, Germany;* ⓞ orcid.org/0000-0002-2717-5076

Erich Runge − *Institut für Physik and Institut für Mikro- und Nanotechnologien (IMN), Technische Universität Ilmenau, 98693 Ilmenau, Germany;* ⓞ orcid.org/0000-0002-2157-229X

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsomega.1c06019

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Bett, A.; Dimroth, F.; Stollwerck, G.; Sulima, O. III-V compounds for solar cell applications. *Appl. Phys. A: Mater. Sci. Process.* **1999**, *69*, 119−129.

(2) Supplie, O.; Romanyuk, O.; Koppka, C.; Steidl, M.; Nägelein, A.; Paszuk, A.; Winterfeld, L.; Dobrich, A.; Kleinschmidt, P.; Runge, E.; et al. Metalorganic vapor phase epitaxy of III-V-on-silicon: Experiment and theory. *Prog. Cryst. Growth Charact. Mater.* **2018**, *64*, 103−132.

(3) Miyamoto, Y.; Nonoyama, S. First-principles calculations of molecular- and atomic-hydrogen reactions on As-terminated GaAs (100) surfaces. *Phys. Rev. B* **1992**, *46*, 6915.

(4) Schmidt, W.; Bechstedt, F. Geometry and electronic structure of GaAs (001)(2× 4) reconstructions. *Phys. Rev. B* **1996**, *54*, 16742.

(5) Ripalda, J.; Gale, J.; Jones, T. Hydrogen-bridge bonding on semiconductor surfaces: density-functional calculations. *Phys. Rev. B* **2004**, *70*, 245314.

(6) Mokwa, W.; Kohl, D.; Heiland, G. Hydrogen adsorption on GaAs (110) studied by temperature-programmed desorption. *Phys. Rev. B* **1984**, *29*, 6709.

(7) Creighton, J. Hydrogen chemisorption and reaction on GaAs (100). *J. Vac. Sci. Technol., A* **1990**, *8*, 3984−3987.

(8) Qi, H.; Gee, P. E.; Nguyen, T.; Hicks, R. F. Sites for hydrogen adsorption on GaAs (001). *Surf. Sci.* **1995**, *323*, 6−18.

(9) Qi, H.; Gee, P. E.; Hicks, R. F. Infrared study of hydrogen adsorbed on c (2× 8) and (2× 6) GaAs (100). *Phys. Rev. Lett.* **1994**, *72*, 250.

(10) Nannarone, S.; Pedio, M. Hydrogen chemisorption on III-V semiconductor surfaces. *Surf. Sci. Rep.* **2003**, *51*, 1−149.

(11) Toropetsky, K.; Tereshchenko, O.; Petukhov, D.; Terekhov, A. New reconstruction-stoichiometry correlation for GaAs (0 0 1) surface treated by atomic hydrogen. *Appl. Surf. Sci.* **2008**, *254*, 8041−8045.

(12) Khatiri, A.; Ripalda, J.; Krzyzewski, T.; Jones, T. Hydrogen adsorption on GaAs (0 0 1)-c (4× 4). *Surf. Sci.* **2004**, *549*, 143−148.

(13) Kuball, M.; Wang, D.; Esser, N.; Cardona, M.; Zegenhagen, J.; Fimland, B. Hydrogen adsorption on the GaAs (001)-(2× 4) surface: A scanning-tunneling-microscopy study. *Phys. Rev. B* **1995**, *52*, 16337.

(14) Pahlke, D.; Arens, M.; Esser, N.; Wang, D.; Richter, W. Hydrogen induced structure changes of GaAs (100) c(4× 4), (2× 4) and (4× 2) surfaces. *Surf. Sci.* **1996**, *352*, 66−70.

(15) Bechstedt, F. *Principles of Surface Physics*; Springer Science & Business Media, 2012.

(16) Hahn, P.; Schmidt, W.; Bechstedt, F.; Pulci, O.; Del Sole, R. P-rich GaP (001)(2× 1)/(2× 2) surface: A hydrogen-adsorbate structure determined from first-principles calculations. *Phys. Rev. B* **2003**, *68*, 033311.

(17) Schmidt, W.; Hahn, P.; Seino, K.; Preuß, M.; Bechstedt, F. *High Performance Computing in Science and Engineering'03*; Springer, 2003; pp 155−166.

(18) Zhang, L.; Wang, E.; Xue, Q.-K.; Zhang, S.; Zhang, Z. Generalized electron counting in determination of metal-induced reconstruction of compound semiconductor surfaces. *Phys. Rev. Lett.* **2006**, *97*, 126103.

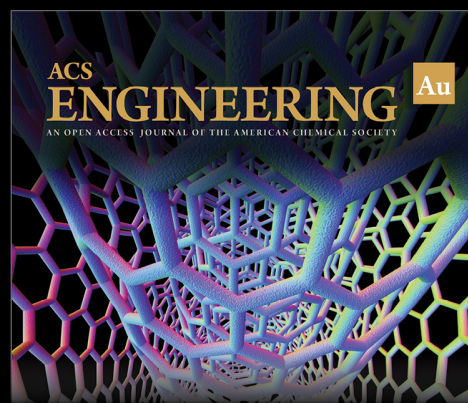(19) *Vienna Ab initio Simulation Package (VASP)*; https://www.vasp.at (accessed October 10, 2021).

(20) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **1996**, *77*, 3865.

(21) Moll, N.; Kley, A.; Pehlke, E.; Scheffler, M. GaAs equilibrium crystal shape from first principles. *Phys. Rev. B* **1996**, *54*, 8844.

(22) Kirklin, S.; Saal, J. E.; Meredig, B.; Thompson, A.; Doak, J. W.; Aykol, M.; Rühl, S.; Wolverton, C. The Open Quantum Materials Database (OQMD): assessing the accuracy of DFT formation energies. *npj Comput. Mater.* **2015**, *1*, 1−15.

(23) Radić-Perić, J.; Perić, M. Evaluation of Partition Functions of Triatomic Molecules Using Data Obtained by ab initio Calculations-Sums of States of Molecules with Spatially Degenerate Lowest Electronic States. *Z. Naturforsch. A* **1987**, *42*, 103−112.

(24) Zhang, R.; Kim, C.-E.; Yu, B.-D.; Stampfl, C.; Soon, A. Mitigation of CO poisoning on functionalized Pt-TiN surfaces. *Phys. Chem. Chem. Phys.* **2013**, *15*, 19450−19456.