ELSEVIER

Materials Science and Engineering B67 (1999) 1–6

MATERIALS SCIENCE & ENGINEERING B

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Theory of the (3 × 2) reconstruction of the GaAs(001) surface

N.A. Modine [a,b,*], Efthimios Kaxiras [b]

[a] *Sandia National Laboratories, Albuquerque, NM 87185, USA*
[b] *Department of Physics, Harvard University, Cambridge, MA 02138, USA*

Received 25 January 1999

Abstract

We discuss an ab initio density functional theory investigation of a (3 × 2) reconstruction of the Ga-rich GaAs(001) surface. Recent experiments identified this new reconstruction as a stable surface of epitaxially grown GaAs doped with indium or carbon (L. Li, et al., Appl. Phys. A 66 (1998) S501; L. Li, et al., Ultramicroscopy 73 (1998) 229). Using our recently developed real-space pseudopotential density functional code, we investigate this (3 × 2) reconstruction and evaluate stabilization mechanisms for the model proposed by the experimentalists, which does not satisfy the electron counting rule. In order to study the effect of In substitution, we consider the dependence of the surface energies of competing reconstructions on surface strain and relative chemical potentials. The effects of carbon substitution are modeled using a charged (3 × 2) reconstruction. These studies support and clarify the proposed structure and stabilization mechanisms. We provide a simple physical explanation for the behavior of the surface energy of the (3 × 2) reconstruction.

Keywords: Density functional theory; (3 × 2) Reconstruction; GaAs(001) surface

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1. Introduction

Epitaxial growth of zincblende III–V semiconductors is the cornerstone of such important technologies as wireless and optical communications and solid state lasers, light emitting diodes and optical sensors. The surface reconstructions observed under growth conditions play a central role in determining virtually all processes that take place during epitaxial growth. These processes include sticking coefficients, diffusion rates, incorporation barriers, and island shapes. GaAs is the best studied and most thoroughly understood III–V semiconductor. However, very close to the well charted territory of the GaAs(001) surface, reconstructions are observed which would not be expected from the conventional phase diagram as a function of the relative chemical potential between Ga and As.

Epitaxial growth is not an equilibrium process since it involves a flux of constituents onto (adsorption) and away from the surface (desorption and incorporation). Experiments designed to study the reconstruction of III–V systems typically can not be done at equilibrium as the relatively rapid desorption of Group V dimers prevents a steady-state from being achieved unless an inward flux of the Group V element is provided. Despite these facts, it is customary to treat different regions of the surface (and hence different reconstructions) as though they were in thermodynamic equilibrium with each other. This is a specific example of a frequently useful approach in which parts of nonequilibrium systems are treated as though they were in internal equilibrium. We refer to this as the 'surface equilibrium approximation', and it allows the application of thermodynamic concepts, such as surface energies and chemical potentials, to the problem of determining the prevalent surface reconstruction.

The relative stability of different reconstructions is determined by a comparison of their surface energies, which are functions of several parameters: (1) the chemical potentials of the constituent atoms; (2) the charge on the surface, which is determined by the Fermi energy; (3) the in-plane strain at the surface (the system is free to relax perpendicular to the surface); and (4) the temperature. Historically, the chemical potentials are the only parameters that have been explicitly considered in the determination of reconstruction stability. In

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[*] Corresponding author.

0921-5107/99/$ - see front matter
PII: S0921-5107(99)00202-0

this paper, we show that the effects of surface charge and in-plane strain can also be calculated. In principle, it is possible to extend the treatment to finite temperature in a straightforward manner for temperatures where a harmonic approximation to the vibrational entropy is valid. However, such calculations would require the computation of the full phonon spectrum of the system, which at present is too computationally demanding for the complex reconstructions of III–V (001) surfaces. Here the finite-temperature free energy is approximated by its zero temperature value. In any case, the main effect of temperature on the surface reconstruction comes from changes in the chemical potentials due to changes in the Group V dimer desorption rate. This effect is implicitly treated correctly via the chemical potential dependence of the surface energy. Accordingly, neglecting entropy effects is a reasonable approximation. While these approximations are not rigorously founded, they have a long and successful history in determining qualitative trends in surface reconstruction of compound semiconductors.

A case in point, where the relative chemical potential of Group III and Group V species, the surface strain, and the surface charge all play a role, is the (3×2) reconstruction of the GaAs(001) surface. The recent experiments of Li et al. [1,2] observed this reconstruction under Ga rich conditions using low energy electron diffraction (LEED) and scanning tunneling microscopy (STM) for two sets of conditions: (A) after thermal surface decomposition of CCl_4, and (B) after growth of $In_xGa_{1-x}As$ $(0.01 < x < 0.10)$ films. Li et al. hypothesized that in (A) the carbon acts as an n-type dopant [1], while in (B), the strain induced by indium is responsible for stabilizing the (3×2) reconstruction [2]. In addition, Li et al. proposed an atomic model (discussed in detail below) for the observed (3×2) reconstruction [1,2]. This structure is particularly unusual and exciting for two reasons: (i) it is not typically observed on normal GaAs(001) surfaces for any temperature or flux conditions (although it may have been occasionally reported on nominally clean surfaces, e.g. the $c(6\times4)$ of Drathen et al. [3]); (ii) it does not satisfy the electron counting model.

The electron counting model (ECM) is a very simple proposal that has been remarkably successful in predicting the reconstructions of low-index III–V surfaces [4–10]. In essence, the model states that the surface should reconstruct in such a way that all dangling bonds on Group III atoms are unoccupied and all dangling bonds on Group V atoms are completely full (i.e. Group V dangling bonds form lone pairs). The structure proposed by Li et al. needs one additional electron per (3×2) surface unit cell in order to satisfy the ECM. This observation motivated their proposal that C near the surface of GaAs stabilizes this reconstruction by acting as an n-type dopant. This is an unorthodox and interesting proposal because typically C acts as an acceptor in bulk GaAs, and therefore this explanation suggests that proximity to the surface changes the nature of C incorporation.

In the following, we investigate the mechanisms proposed by Li et al. for stabilizing the (3×2) reconstruction. We discuss the computational method used to compute fully relaxed atomic configurations and their energies, we introduce an analysis that determines surface energies from these calculations, and we interpret the stability of the (3×2) reconstruction in light of our results.

2. Computational method

In order to determine the structure and energy of the (3×2) and competing reconstructions, we perform first-principles electronic structure calculations based on density functional theory (DFT). Such calculations, while more computationally demanding than empirical methods, have a demonstrated ability to provide quantitatively accurate results for systems complicated by the interplay of several features present in III–V surface reconstructions. These features include the presence of several atomic species, interatomic charge transfer, over- or under-coordinated atoms, and an asymmetric distribution of bonds. For our calculations, we use the recently developed adaptive coordinate real-space electronic structure (ACRES) code [11–13] with the local density approximation (LDA) exchange-correlation functional of Perdew and Zunger [14] and the pseudopotentials of Hamann, Schlüter, and Chiang (HSC) [15]. Since charge distribution is relatively uniform in this system, we do not use adaptation in our calculations. In order to represent a surface, we use a slab model with the desired reconstruction on one surface and fictitious hydrogen-like atoms with the appropriate charge (3/4 when saturating As dangling bonds) to terminate the other surface [16]. For the hydrogen-like atoms, we used pseudopotentials constructed by Kim and Chelikowsky [17] specifically for terminating GaAs surfaces. This method avoids unphysical charge transfer between the front (reconstructed surface) and back (terminated) sides of the slab. The hydrogen-like atoms and the neighboring two atomic layers on the back side are held fixed, and the rest of the atoms are relaxed using ab initio forces.

3. Computational results

Fig. 1 shows a relaxed structure derived from the atomic model suggested by Li et al. To make the reconstruction clear, we have included both a top view and a perspective view. The structure involves alternating ridges and trenches with a height difference of two atomic layers. Both the ridges and the trenches contain a centered row of Ga dimers oriented parallel to the ridges.

In order to evaluate the stability of the (3 × 2) reconstruction, it is necessary to compare its surface energy with that of other low energy reconstructions. Li reports [18] that the (2 × 6) reconstruction of Biegelsen et al. [19] is observed on the clean GaAs(001) surface under the same flux and temperature conditions for which the (3 × 2) reconstruction is induced by the special treatments described earlier. Fig. 2 shows a relaxed structure derived from the atomic model for the (2 × 6) reconstruction proposed by Biegelsen et al. [19].

Like the (3 × 2) structure, the (2 × 6) structure consists of ridges alternating with trenches, but these features are roughly twice as wide in the (2 × 6) structure. A major difference between the two structures is that in the (3 × 2) structure, the outermost layer of both the trenches and ridges consists of Ga dimers, while in the (2 × 6) structure, the outermost layer consists of Ga dimers in the trenches and As dimers on the ridges. Both the Ga and the As dimers of the (2 × 6) structure are arranged in zig–zig patterns, which are not present in the (3 × 2) reconstructed surface. Since the two structures have different stoichiometries, we must include chemical potential effects in our analysis if we wish to compare surface energies. We discuss next how the surface energies can be defined so that their comparison addresses the question of which structure is dominant under the relevant experimental conditions.

4. Theory of the analysis

The traditional method of computing surface energies for a system composed of a single species is to take advantage of the fact that for thick slabs

$$E^n_{\text{slab}} \to 2\sigma + nE_{\text{bulk}} \qquad (1)$$

where E^n_{slab} is the total energy of a relaxed slab containing n atoms that has the desired reconstruction on both sides, σ is the surface energy, and E_{bulk} is the bulk total energy per atom. The problem with this method is that, as the slab thickness is increased in order to get better converged values of σ, two large quantities that grow with the slab thickness (E^n_{slab} and nE_{bulk}) must be subtracted to find a small, constant σ. Therefore, this method is unstable with respect to increasing slab thickness if there are any technical differences in the way that E^n_{slab} and E_{bulk} are computed. This problem has led to the development of more stable methods. Boettger observed that the bulk energy can be consistently approximated by the difference in energies between two slabs of different thicknesses [20]. Fiorentini and Methfessel refined this idea by noting that Eq. (1) is a linear equation with a slope given by the bulk energy [21]. Therefore, linear extrapolation of the energies of a series of slabs of sufficient thickness to zero thickness gives an accurate expression for the surface energy:

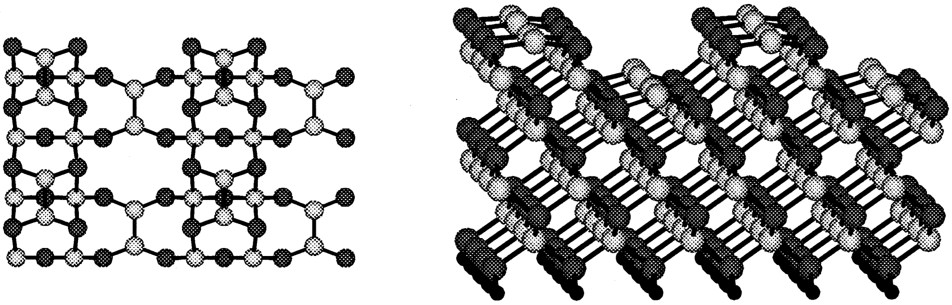

Fig. 1. Top (left panel) and perspective (right panel) views of the DFT relaxed GaAs(001) (3 × 2) structure. The light grey spheres indicate Ga atoms, the dark grey spheres indicate As atoms, and the small black spheres indicate terminating pseudohydrogen atoms. The four atomic layers closest to the surface are shown in the top view, while an entire slab is shown in the perspective view.

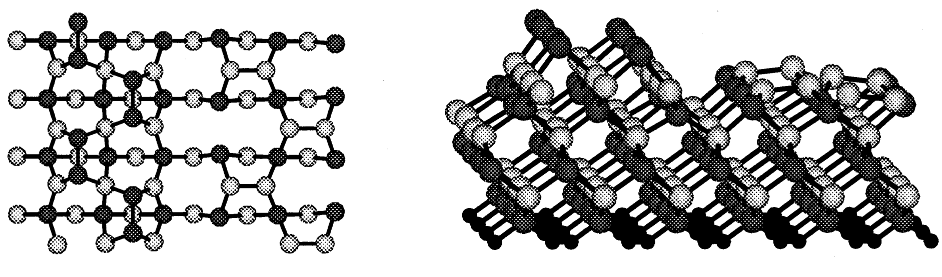

Fig. 2. Top (left) and perspective (right) views of the DFT relaxed GaAs(001) (2 × 6) structure. Notation is the same as in Fig. 1.

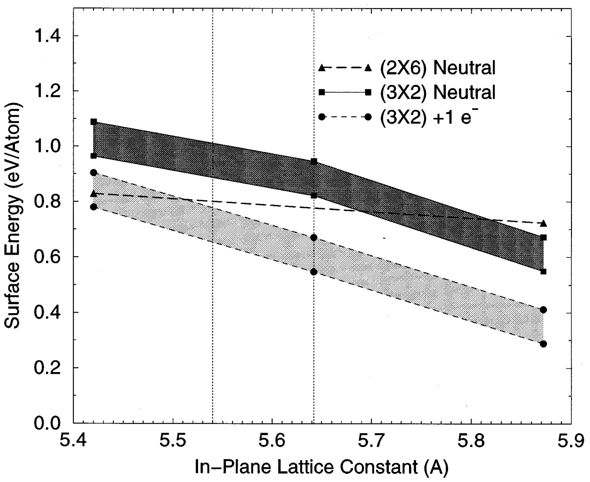

Fig. 3. Calculated surface energies for the (2 × 6) and charged and neutral (3 × 2) reconstructions of the GaAs(001) surface as a function of in-plane lattice constant. For the (3 × 2) reconstructions, the shaded regions indicate the range of surface energies resulting from the allowed range of Ga and As chemical potentials. The (2 × 6) reconstruction is stoichiometric, so its surface energy is independent of the chemical potentials. The left and right dotted vertical lines indicate the LDA equilibrium and experimental lattice constants, respectively.

$$\sigma = \frac{1}{2} \lim_{n\to 0} E^{n}_{\mathrm{slab}} \qquad (2)$$

where lin indicates linear extrapolation. The method of Fiorentini and Methfessel has the advantage that it averages out some finite size effects, which can lead to errors in the approach of Boettger [21].

In order to apply the method of Fiorentini and Methfessel [21] to the III–V systems of interest in this paper, we have generalized it to the case of a non-stoichiometric binary system modeled with an asymmetric slab. In thermodynamic equilibrium, the stability of structures with different stoichiometries can be evaluated by comparing their grand-canonical potentials. As discussed above, the surface equilibrium approximation allows us to use this thermodynamic concept, and we approximate the actual grand-canonical potential by its zero temperature value, denoted by Ω. In analogy to Eq. (1), we can write the expression

$$\Omega^{N_{\mathrm{As}},N_{\mathrm{Ga}}}_{3\times 2} = \sigma_{3\times 2} + \sigma_{\mathrm{H}} + \frac{1}{2}(N_{\mathrm{As}} + N_{\mathrm{Ga}})\Omega_{\mathrm{bulk}} \qquad (3)$$

where $\Omega(N_{\mathrm{As}}, N_{\mathrm{Ga}})/(3\times 2)$ is the grand-canonical potential of a relaxed slab containing N_{As} As atoms and N_{Ga} Ga atoms that has the (3 × 2) reconstruction on one surface and the hydrogen-like termination on the other surface. Correspondingly, $\sigma_{3\times 2}$ is the surface grand-canonical potential (referred to in the following as the 'surface energy' for the sake of simplicity) of the (3 × 2) reconstructed surface, σ_{H} is the surface energy of the hydrogen-like terminated surface, and Ω_{bulk} is the grand-canonical potential per formula unit of the bulk material.

Applying the approach of Fiorentini and Methfessel, substituting the usual definition of the zero temperature grand-canonical potential in terms of the energy, substituting the actual numbers of atoms in the model slabs, and solving for $\sigma_{3\times 2}$ converts Eq. (3) into

$$\sigma_{3\times 2} = \lim_{N\to 0} E^{N}_{3\times 2} - \Delta_{\mu} - \sigma_{\mathrm{H}} - N_{\mathrm{H}\mu_{\mathrm{H}}} \qquad (4)$$

where we have defined $N = N_{\mathrm{As}} + N_{\mathrm{Ga}}$ and $\Delta_{\mu} = \mu_{\mathrm{As}} - \mu_{\mathrm{Ga}}$. $E_{3\times 2}$ is the total energy of the slab described in the definition of $\Omega(N_{\mathrm{As}}, N_{\mathrm{Ga}})/(3\times 2)$ and N_{H} and μ_{H} are the number and chemical potential of the hydrogen-like atoms, respectively. The surface energy of the terminated surface can be obtained by applying an analogous procedure to slabs with both sides terminated with hydrogen-like atoms. Combining results, the factors involving the chemical potential of the hydrogen-like atoms cancel out, and we obtain

$$\sigma_{3\times 2} = \lim_{N\to 0} E^{N}_{3\times 2} - \frac{1}{2}\lim_{N\to 0} E^{N}_{\mathrm{H}} + \frac{1}{2}\Delta_{\mu} \qquad (5)$$

where E^{N}_{H} is the total energy of the double terminated slab. A similar procedure applied to the (2 × 6) reconstructed slab gives

$$\sigma_{2\times 6} = \lim_{N\to 0} E^{N}_{2\times 6} - \frac{1}{2}\lim_{N\to 0} E^{N}_{\mathrm{H}} \qquad (6)$$

with terms defined analogously to those in the (3 × 2) case. In this case, the difference in chemical potentials cancels out indicating that this reconstruction is stoichiometric. Note that Eqs. (5) and (6) give surface energies per reconstruction unit cell. In order to compare these values, they must be normalized by dividing by the area of a reconstruction unit cell.

5. Results of the analysis

Fig. 3 shows the calculated surface energies for a range of lattice constants. The dotted vertical line on the left indicates the LDA equilibrium lattice constant, while the dotted vertical line on the right indicates the experimental lattice constant. The darker shaded region outlined by solid lines indicates the surface energy of the neutral (3 × 2) reconstruction. The height of the region represents the range of chemical potentials possible in a system in equilibrium with the bulk. The lower limit corresponds to a system in equilibrium with bulk Ga, while the upper limit corresponds to a system in equilibrium with bulk As. This estimated range of allowed chemical potentials was identified using standard procedures [22–26]. Experimentally, the (3 × 2) and (2 × 6) reconstructions are found under Ga rich conditions, and Ga droplet formation is frequently observed in experiments. Thus, we would expect the experimental systems to correspond to values near the lower limit of the region. As expected from the physical principles behind the ECM, the calculated band structure and state occupations for the uncharged (3 × 2) structure show that there is a partially occupied surface state in the GaAs gap. The lighter shaded region outlined by dashed lines shows the effects of adding an electron, which fills the state and moves it out of the gap. A factor dependent on the chemical potential of an electron appears in the calculation of this value, and we have approximated the real Fermi energy (which depends on details of the donor states) by the Kohn–Sham Fermi energy from our LDA calculations. This should at least remove zero order effects due to the arbitrariness of the overall potential. For comparison, we have also included the surface energy of the (2 × 6) reconstruction, which is indicated by the long-dashed line. As noted above, the surface energy of this reconstruction is independent of the difference in chemical potentials, and therefore its surface energy at each lattice constant is given by a definite value rather than the range of values associated with the (3 × 2) systems.

6. Discussion

Our results are in excellent agreement with the experimental results of Li et al. [1,2], and they provide support for the proposed stabilization mechanisms for the (3 × 2) reconstruction. Fig. 3 shows that the (2 × 6) reconstruction is stable under normal conditions, but in-plane expansion would make the (3 × 2) reconstruction preferred. This clarifies the proposal of Li et al. that the strain induced by the indium is responsible for the (3 × 2) reconstruction [2], and it shows that a simple expansion of the in-plane lattice constant is sufficient to explain the observed change in reconstruction. Even though the InGaAs layer is nominally pseudomorphic, the relatively high density of steps on the experimental surface [18] should allow the in-plane lattice constant to expand toward that favored by the InGaAs alloy. Our calculations show that it is not necessary to invoke more complicated explanations such as a strain gradient in the InGaAs layer or a bowing of the surface due to the lattice mismatch.

In addition, we have investigated the effect of charge on the surface energy, and Fig. 3 shows that the addition of one electron per unit cell to the system stabilizes the (3 × 2) reconstruction. Therefore, our results support the suggestion of Li et al. [1] that C atoms incorporated into the surface act as donors. X-ray photoelectron spectroscopy (XPS) experiments that show less than one C atom per (3 × 2) unit cell [18] have challenged the validity of this explanation, but if a linear dependence of the surface energy on electronic charge is assumed, then the present calculations indicate that as little as one C atom per six (3 × 2) unit cells would stabilize the (3 × 2) structure at the experimental lattice constant. One might expect that if strain due to In atoms (which have a larger covalent radius than Ga atoms) stabilizes the (3 × 2) structure, then strain due to C atoms (which have a smaller covalent radius than Ga atoms) should have the opposite effect. However, the two cases are not analogous — the In atoms are incorporated throughout an epitaxially grown layer of substantial thickness, effectively increasing the substrate lattice constant, while the C atoms are added after growth is complete and presumably incorporate only in the top few layers of the surface. Carbon incorporated in this fashion should help compensate for the larger lattice constant favored by the (3 × 2) reconstruction, reducing its surface energy. Although we have not actually included any C in our calculations, and therefore we can not estimate the size of this effect, this line of reasoning shows that strain effects can be expected to further lower the amount of C required to stabilize the (3 × 2) reconstruction.

Finally, our calculations allow us to gain physical insight into the mechanisms responsible for the stabilization of the (3 × 2) reconstruction. Based simply on the ECM, we can expect the (3 × 2) structure to be stabilized by the addition of one electron per (3 × 2) unit. However, our DFT calculations go further in that they actually show a partially filled surface state in the gap that fills and moves out of the gap as an electron is added to the structure. Thus, the DFT calculations demonstrate the fundamental physics behind the ECM. Furthermore, we get a simple picture for the strain dependence of the surface energy. Fig. 1 shows that the Ga dimers in the outermost layer of the (3 × 2) structure move inward until they are almost in the same plane as the second layer As atoms. This can be understood based on simple chemical bonding arguments combined with the dangling bond occupations given by the ECM: A dangling bond on a Ga atom is unoccupied. Therefore, it is favorable for the orbitals to hybridize in such a way that the energies of the bonding orbitals are minimized without regard for the energy of the dangling bond orbital. Since the s orbital is lower in energy than the p orbitals, this is achieved by forming sp^2 bonding orbitals and a p_z dangling bond orbital. As a result, triply coordinated Ga atoms on a surface want their neighbors to be arranged in a planar structure so that the bonding orbitals can achieve the 120° angles required by a sp^2 character. In contrast, the ECM requires a dangling bond on an As atom to be fully occupied, which is achieved by using the low energy s orbital as the lone-pair orbital. As a result, the bonding orbitals of a triply coordinated As atom at a surface are principally p^3 in character, and the bonds of such an atom want to be arranged at right angles. The above considerations provide a physical explanation for the flat-topped, sharp-edged ridges apparent in the relaxed (3 × 2) structure in Fig. 1. Since the bond lengths stay nearly constant as the Ga dimers move inward, this structure tends to expand the surface, resulting in the substantial decrease in surface energy with increasing in-plane lattice constant shown in Fig. 3. In contrast, Fig. 2 clearly shows that the above principles also hold for the As dimer terminated regions of the (2 × 6) structure resulting in a very peaked structure that tends to contract the surface. Therefore, the surface expansion from the Ga dimer terminated regions of the (2 × 6) structure nearly cancels with a surface contraction from the As dimer terminated regions, and the net result is the rather moderate dependence of the surface energy of the (2 × 6) structure on in-plane lattice constant seen in Fig. 3.

7. Conclusions

We have shown that DFT calculations can be used to understand the effects of strain and doping on surface reconstructions. In particular, we have investigate the mechanisms responsible for the stabilization of a (3 × 2) reconstruction of the GaAs(001) surface. Our results support and clarify previously suggested mechanisms and suggest a simple physical picture for the observed behavior. Additional support for a donor mechanism in the C doping experiments would be provided by calculations identifying the preferred incorporation site and electronic behavior of a near surface C atom. The same computations would also allow an investigation of the effects of strain due to the incorporation of C atoms into the surface layers.

Acknowledgements

This work was supported by ONR, and by NSF and DARPA under the Virtual Integrated Prototyping Initiative for Thin Films. The computations were performed using the NRL Thinking Machines CM-5 and with a grant of HPC time from the DoD HPC ARL Major Shared Resource Center. The ACRES software was developed by the DoD HPCMP CHSSI program.

References

[1] L. Li, H. Qi, S. Gan, B.-K. Han, R.F. Hicks, Appl. Phys. A 66 (1998) S501.
[2] L. Li, B.-K. Han, R.F. Hicks, H. Yoon, M.S. Goorsky, Ultramicroscopy 73 (1998) 229.
[3] P. Drathen, W. Ranke, K. Jacobi, Surf. Sci. 77 (1978) L162.
[4] W.A. Harrison, J. Vac. Sci. Technol. 16 (1979) 1492.
[5] D.J. Chadi, J. Vac. Sci. Technol. A5 (1987) 834.
[6] M.D. Pashley, Phys. Rev. B 40 (1989) 10481.
[7] C.B. Duke, Surf. Sci. 65 (1993) 543.
[8] J.E. Northrup, Phys. Rev. B 50 (1994) 2015.
[9] S.B. Zhang, A. Zunger, Phys. Rev. B 53 (1996) 1343.
[10] C.D. MacPherson, R.A. Wolkow, C.E.J. Mitchell, et al., Phys. Rev. Lett. 77 (1996) 691.
[11] N.A. Modine, G. Zumbach, E. Kaxiras, in: E. Kaxiras, J. Joannopoulos, P. Vashishta, R. Kalia (Eds.), Materials Research Society Proceedings, vol. 408, Material Research Society, Pittsburgh, PA, 1996, p. 139.
[12] G. Zumbach, N.A. Modine, E. Kaxiras, Solid State Commun. 99 (1996) 57.
[13] N.A. Modine, G. Zumbach, E. Kaxiras, Phys. Rev. B 55 (1997) 10289.
[14] J.P. Perdew, A. Zunger, Phys. Rev. B 23 (1981) 5048.
[15] D.R. Hamann, M. Schlüter, C. Chiang, Phys. Rev. Lett. 43 (1979) 1494.
[16] K. Shiraishi, J. Phys. Soc. Jpn. 59 (1990) 3455.
[17] H. Kim, J.R. Chelikowsky, Phys. Rev. Lett. 77 (1996) 1063.
[18] L. Li, Personal communication, 1998.
[19] D.K. Biegelsen, R.D. Bringans, J.E. Northrup, L.-E. Swartz, Phys. Rev. B 41 (1990) 5701.
[20] J.C. Boettger, Phys. Rev. B 49 (1994) 16798.
[21] V. Fiorentini, M. Methfessel, J. Phys. C 8 (1996) 6525.
[22] E. Kaxiras, K.C. Pandey, Y. Bar-Yam, J.D. Joannopoulos, Phys. Rev. Lett. 56 (1986) 2819.
[23] E. Kaxiras, Y. Bar-Yam, J.D. Joannopoulos, K.C. Pandey, Phys. Rev. Lett. 57 (1986) 106.
[24] E. Kaxiras, Y. Bar-Yam, J.D. Joannopoulos, K.C. Pandey, Phys. Rev. B 85 (1987) 9625.
[25] E. Kaxiras, Y. Bar-Yam, J.D. Joannopoulos, K.C. Pandey, Phys. Rev. B 35 (1987) 9636.
[26] G.-X. Qian, R.M. Martin, D.J. Chadi, Phys. Rev. B 38 (1988) 7649.