Surface Energy and the Common Dangling Bond Rule for Semiconductors

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Equilibrium shape and surface energies are among the most basic properties of finite crystals. Yet, an effective approach for accurately calculating individual energy for polar semiconductor surfaces is still lacking, and there is not a general rule regarding surface energies of different orientations. Here, we suggest a wedge-shaped geometry for calculating individual surface energies by direct, first-principles methods. Applications to prototypical semiconductors, Ge, GaAs, and ZnSe, establish a surprisingly simple common dangling bond rule relating surface energies to local chemical similarities.

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Surface energy is a basic physical quantity that has broad applications [1]. For example, semiconductor surface and step reconstruction involves the minimization of surface energy [2]. Low-energy grain boundary formation involves the energy of surfaces at different orientations [3]. The balance between surface energy and epitaxial strain, and between energetics and kinetics, often controls [4–7] surface morphology and facet growth in epitaxial films, as well as nucleation and growth of quantum dots and other epitaxial nanostructures. A century ago, Wulff [8] developed a phenomenological method to determine equilibrium crystal shape, provided that all the surface energies are known. Since then, significant progress has been made, most noticeably by using first-principles calculations with slab geometry to understand surface energy and structure at different growth conditions. In terms of understanding the energetic relationship between semiconductor surfaces of *different* orientations, however, little progress has been made. The reason is simple. For a long time, it was difficult to accurately determine the individual energy for polar surfaces such as zinc blende (111) and $(\bar{1}11)$, owing to the inability to separate them in the "standard" slab geometry.

In the early 1990s, Chetty and Martin [9] developed a local energy density approach for the energy of individual GaAs (111) and $(\bar{1}11)$ surfaces. Although this was the first real attempt to calculate individual polar surface energy, the method suffered from nontrivial and often approximate calculations of the local energy density. It also relied on the existence of symmetry-adapted unit cells. As a result, only a handful of follow-up calculations [10,11] have been carried out since then. The recent calculation by Moll *et al.* [10] disagrees with Chetty and Martin, even though they used exactly the same approach. For example, Moll *et al.* obtained an energy for the ideal (111) surface that is more than 0.5 eV/1 × 1 lower than that of Chetty and Martin, casting doubts on the usefulness of the method.

In this Letter, we present a direct approach to calculating individual energy of polar $(111)/(\bar{1}11)$ surfaces, thereby avoiding the above uncertainties. The method is not necessarily restricted to the $(111)/(\bar{1}11)$ surfaces, is not limited to semiconductors, and is, hence, general. It requires only the separation of a polar surface [e.g., (111)] from its conjugate surface [i.e., $(\bar{1}11)$], forming one-dimensional (1D) periodic nanostructure (see, for example, Fig. 1). We show that, with such an arrangement, surface energy can be unambiguously determined from the total energy difference between two identical structures of different sizes. The method is recursive, allowing one to derive the unknown energy of a given surface from those already known. For the prototype GaAs$(111)/(\bar{1}11)$ surfaces, good agreement with previous results of Moll *et al.,* was obtained. Application to the third-row semiconductors, i.e., Ge, GaAs, and ZnSe, further establishes a novel common dangling bond (CDB) rule: The energies of different surface orientations [e.g., (110) and $(111)/(\bar{1}11)$] could be related to each other via the density of surface dangling bonds in a surprisingly simple way.

To proceed, let us first consider how surface energy is calculated using slab geometry. For a binary AB compound, the sum of the top (t) and bottom (b) surface energies per unit supercell is defined as

$$\sigma^{t+b} = E_{\text{tot}}(\text{slab}) - n_A\mu_A - n_B\mu_B, \qquad (1)$$

where E_{tot} is the total energy of the supercell, n_i ($i = A$ and B) is the number of the ith atom in the cell, and μ_i is the corresponding atomic chemical potential of the ith atom [12]. Let $E_{\text{tot}}(A)$ (and B) be the total energy of elemental solid A (and B) and $\Delta H_f(AB)$ be the formation enthalpy of a bulk AB compound, and one can show that

$$\mu_A = E_{\text{tot}}(A) + E_{\text{tot}}(B) + \Delta H_f(AB) - \mu_B \qquad (2)$$

and

$$E_{\text{tot}}(B) + \Delta H_f(AB) \leq \mu_B \leq E_{\text{tot}}(B). \qquad (3)$$

Equations (2) and (3) imply thermal equilibrium between surface and bulk. If μ_B is outside the allowed range, precipitation of either solid A or solid B will take place. For nonpolar surfaces, one can construct a slab with two equivalent surfaces so

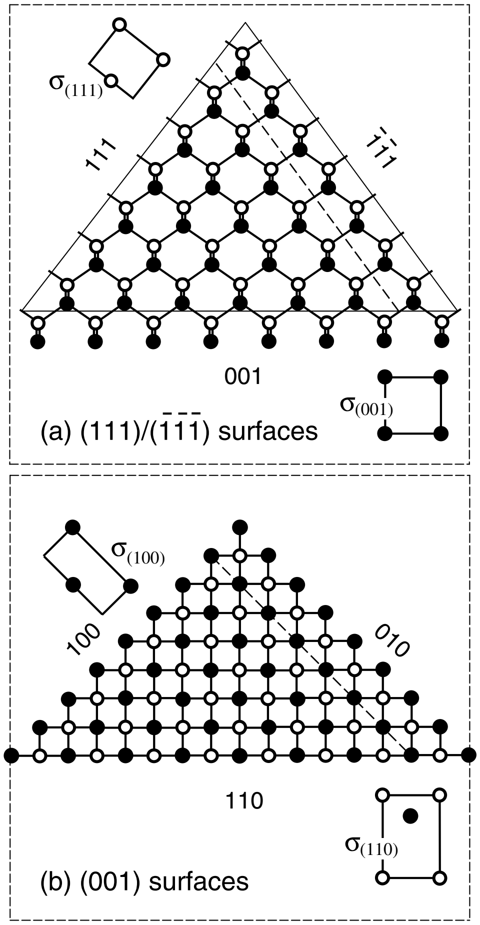

FIG. 1. Cross-sectional view of the wedge-shaped structures for extracting surface energies: (a) for the (111) surfaces from that of the (001) surface, and (b) for the (100) surface from that of the (110) surface. Insets are the corresponding surface unit cells. Open and filled dots represent the two types of binary atoms, whereas pseudohydrogen atoms are not shown.

$$\sigma^t = \sigma^b = \tfrac{1}{2}\sigma^{t+b}. \tag{4}$$

For some of the polar surfaces such as (001), it is also possible to construct a slab such that Eq. (4) holds. For other polar surfaces such as $(111)/(\bar{1}\bar{1}\bar{1})$, however, the top and bottom surfaces are inextricably combined within the slab geometry and are, hence, inseparable.

To separate the (111) and $(\bar{1}\bar{1}\bar{1})$ surfaces, one must abandon the slab geometry and, instead, use a geometry such as the one in Fig. 1(a): Here the two-dimensional triangle is a cross section of a three-dimensional and infinitely long wedge, consisting of two equivalent (111) surfaces and one (001) surface, but not the $(\bar{1}\bar{1}\bar{1})$ surface, with their unit cells shown as insets. The three corners in Fig. 1(a) correspond to the three ridges of the three-dimensional structure. This transforms the problem of separating (111) from $(\bar{1}\bar{1}\bar{1})$ to a problem of eliminating the effect of ridges, which can be done by taking the energy *difference* between similar structures of different sizes. For example, by shrinking the baseline from $n = 8$ to 7 in Fig. 1(a), one has

$$\begin{aligned}\delta E &= E_{\text{tot}}(n = 8; 36AB) - E_{\text{tot}}(n = 7; 28AB) \\ &\quad - 8E_{\text{tot}}(AB) \\ &= 2\sigma_{(111)} + \sigma_{(001)},\end{aligned} \tag{5}$$

where σ is renormalized to the energy per 1×1 surface area. Similarly, a wedge-shaped structure exposing (100) and (110) surfaces can be used for the energy of (001). For example, using Fig. 1(b) one has

$$\begin{aligned}\delta E &= E_{\text{tot}}(n = 8; 36AB + 8B) - E_{\text{tot}}(n = 7; 28AB + 7B) \\ &\quad - 8E_{\text{tot}}(AB) - \mu_B = 2\sigma_{(100)} + \sigma_{(110)}.\end{aligned} \tag{6}$$

In arriving at Eqs. (5) and (6), it is assumed that the ridge energy does not change with wedge size, provided that the size is reasonably large. Because there are always three ridges for any wedged structure, the ridge energy, under the assumption, thus always cancels out in Eqs. (5) and (6). While Fig. 2 below provides a critical test to the assumption, the cancellation effect for slabs has long been known: for example, by taking the energy difference between different sized slabs, one calculates rather accurately the bulk energy.

We calculate surface energy using the density-functional theory [13] within the local-density approximation. First, we consider unreconstructed GaAs surface wedges, passivated by pseudohydrogen atoms, i.e., $q_H = 0.75e$ for each surface As dangling bond and $1.25e$ for each surface Ga dangling bond. Hydrogenation helps not only to maintain local charge neutrality, but also to minimize atomic relaxations, so we can expect fast convergence with respect to supercell size. Figure 2 shows that, over the entire range $n = 6$ to 10, $\sigma_{(111)}$ is converged to within about 0.1 eV/1 × 1. Inequivalent k-point sampling in supercells of different sizes may account for the small fluctuations. The validities of Eqs. (5) and (6) are

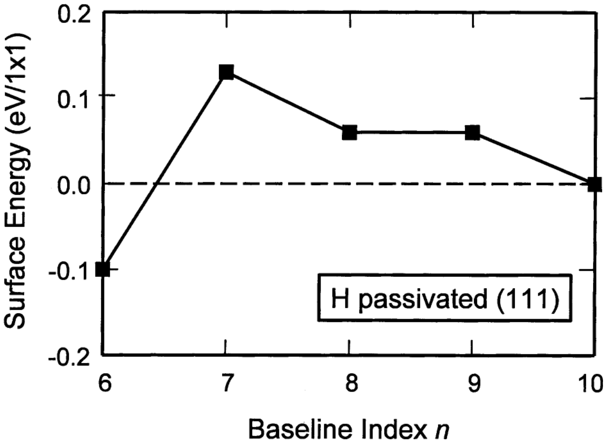

FIG. 2. Calculated (111) surface energy as a function of the baseline index n in Fig. 1(a). The surface is passivated by H ($q = 1.25e$), and the energy zero is set at $n = 10$.

thus established. To further test the method, we also calculated $\sigma_{(\bar{1}11)}$ by swapping As with Ga and the corresponding pseudo-H atoms in Fig. 1(a). The sum, $\sigma_{(111)} + \sigma_{(\bar{1}11)}$, was then compared to the results from standard slab calculation. The difference was 0.12 eV/1 × 1 for $n = 7$ and 0.04 eV/1 × 1 for $n = 8$. For hydrogenated (001) surfaces, differences of the same magnitude were also obtained between slab calculations and those using the geometry in Fig. 1(b). These tests provide evidence that no macroscopic electric field builds up across any of the opposing faces in the present study.

Once the energies for hydrogenated surfaces are determined, it is straightforward to obtain the energy for surfaces without H. This is done, for example, by forming slab geometries with the hydrogenated backsurface of *known* surface energy. For the Ga vacancy-terminated GaAs (111)-2 × 2 surface (Fig. 3), we obtain $\sigma_{(111)} = 1.85\ \text{eV}/a_0^2$, where $a_0 = 5.64$ Å is the lattice constant, or 58 meV/Å^2. This is in good agreement with the result in Ref. [10], 54 meV/Å^2.

The method further allows us to study the general trends in the individual surface energies. Here, we consider the prototypical third-row semiconductors, Ge, GaAs, and ZnSe. We focus on the 2 × 2 reconstructions of the (111)/($\bar{1}$11) surfaces. Figure 3 shows schematically the surface reconstructions—the vacancy, adatom, and trimer models. These low-energy reconstructions, which satisfy the electron-counting (EC) model [14], have been studied before for GaAs [15,16]. For Ge and ZnSe, however, we have also considered the dimer and tetramer models (not shown).

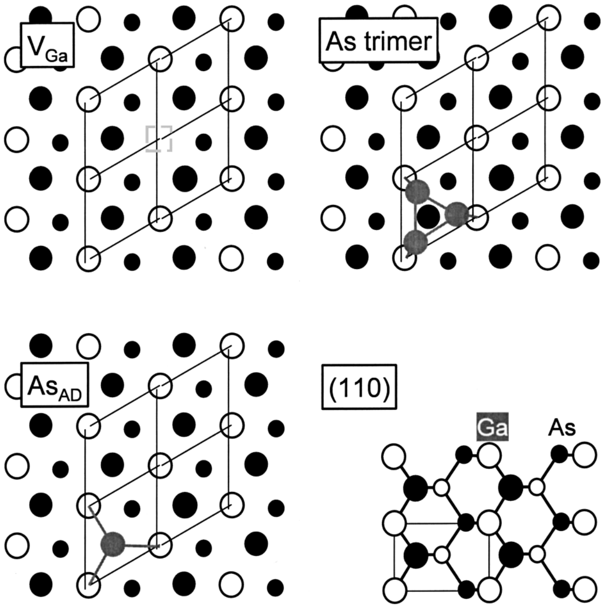

FIG. 3. Top view of the reconstructed GaAs(111)-2 × 2 surfaces. The open and filled dots are the Ga and As atoms, respectively, whereas the square indicates a missing surface atom. Larger dots are closer to the surface than the smaller ones. For comparison, the (110) surface is also shown.

Figure 4 plots the calculated individual surface energy as a function of the atomic chemical potential for the (111)/($\bar{1}$11) and (110) surfaces. It shows that (i) surface energy generally decreases with increasing ionicity of the host, $f_i = 0.0$, 0.31, and 0.63 for Ge, GaAs, and ZnSe, respectively. In other words, a covalent material has larger surface energy than the corresponding ionic materials. The experimental cohesive energies for Ge, GaAs, and ZnSe are 1.94, 1.63, and 1.29 eV/bond, respectively. Thus, the decrease can be qualitatively understood in terms of the weaker bond energies in more ionic materials. (ii) The energies of the vacancy and adatom surfaces are independent of the atomic chemical potentials. The energies of the anion adcluster surfaces are not. Because

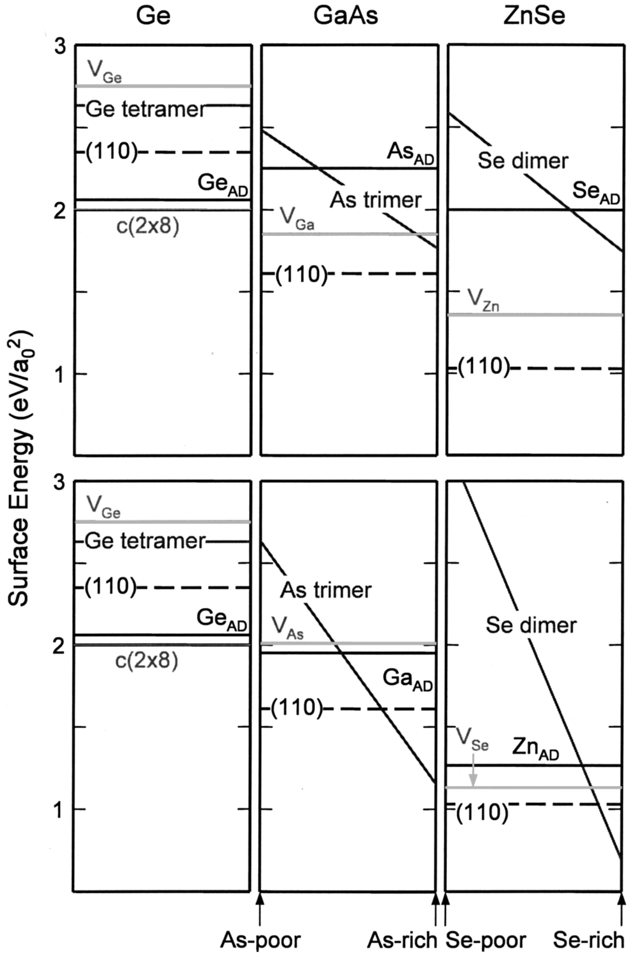

FIG. 4. Calculated energies of (111) surfaces (top panels), ($\bar{1}$11) surfaces (bottom panels), and (110) surfaces (as indicated) for Ge, GaAs, and ZnSe (in units of eV/a_0^2 where a_0 is the bulk lattice constant). The energies of GaAs($\bar{1}$11) and (110) relative to that of GaAs(111) were taken from Ref. [10] and for Ge(111)-$c(2 \times 8)$ from Ref. [17]. Except for Ge, the left-hand side in each panel corresponds to the cation-rich limit and the right-hand side to the anion-rich limit.

TABLE I. Calculated energies for (110) and vacancy-terminated $(111)/(\bar{1}11)$ surfaces. They are normalized to eV per dangling bond pair. Values in parentheses are with respect to those of the (110) surfaces in the first row.

	Ge	GaAs	ZnSe
(110)	1.66 (0.0)	1.14 (0.0)	0.73 (0.0)
(111): V_{cat}	1.59 (−0.07)	1.07 (−0.07)	0.78 (0.05)
$(\bar{1}11)$: V_{an}	–	1.16 (0.02)	0.65 (−0.08)

of these differences, the anion adcluster surfaces are often energetically favored at the anion-rich conditions. (iii) Our calculation also shows that the number of the anion atoms in the stable adcluster configuration is a function of the ionicity, $N_A = 3$ for GaAs and 2 for ZnSe, in accordance with the EC model. Interestingly, although one may argue that the EC model is irrelevant for Ge, we find that the tetramer model ($N_A = 4$) is favored over the trimer model by 0.37 eV/a_0^2. (iv) It is a universal observation that, on the $(111)/(\bar{1}11)$ surfaces, cation adclusters are metastable only with energies outside the range in Fig. 4.

The most important observation from Fig. 4 is that the energies of the $(111)/(\bar{1}11)$ surfaces follow those of the (110) surfaces. This raises an interesting question about whether individual energies have, in fact, common atomistic origin(s) regardless of the surface orientation(s). To investigate such a possibility, we compare, in Table I, the energies of the vacancy-terminated $(111)/(\bar{1}11)$ surfaces and the relaxed (110) surfaces. Despite their orientation differences, threefold-coordinated bulklike atoms are common to all these surfaces. Moreover, each of the surfaces has a number of cation and anion dangling bonds equal to the number of dangling bond pairs (DBP), n_{DBP}. By renormalizing the energies to n_{DBP}, we see that for the (111), $(\bar{1}11)$, and (110) surfaces, the values of Table I are remarkably close in all three cases, Ge, GaAs, and ZnSe, to within ±0.08 eV/DBP.

A common dangling bond rule is, therefore, established: Surfaces of similar local bonding environment, to a good approximation, have the same energy irrespective of their orientations. It is important to note that there are only a handful of such local bonding environments on bulk-truncated low-Miller-index surfaces, i.e., twofold on (001), threefold on $(111)/(\bar{1}11)$ and (110), respectively, and a combination of the two on any other higher-Miller-index surfaces. In most cases, twofold-coordinated atoms spontaneously rebond to lower their energies. Thus, most of the low-energy zinc blende semiconductor surfaces are made of a combination of highly strained (due to rebonding) and bulklike threefold-coordinated atoms. We have not tested the common dangling bond rule for such surfaces with strained and bulklike dangling bonds mixed. However, one of our previous semiempirical studies [2] indicates that a minimum of seven chemical bond-based local structural motifs should be enough to construct surface and step energies for vicinal (001) surfaces, suggesting that the CDB rule could be more general.

The CDB rule may also apply beyond zinc blende semiconductors. It is well known that the energy of certain low-symmetry crystal surfaces is defined only up to a gauge [18]. One such example is the polar surface of the wurtzite crystal. Interestingly, here we observe two isolated subsets of surfaces so the three faces of an arbitrarily wedge-shaped structure are either all nonpolar or all polar, but not a combination, in contrast to zinc blende. Recently, it has been argued that in the absence of a macroscopic field, energies for polar wurtzite surfaces can also be defined [11]. In view of the remarkable similarity between wurtzite and zinc blende with identical bonding environments up to the second nearest neighbors, we suggest that any surfaces with identical local chemical bonds between the two should have very similar energies.

In summary, we have proposed a direct first-principles approach to calculate individual energy for semiconductor polar surfaces. Tests for the $\text{GaAs}(111)/(\bar{1}11)$ surfaces yield fast convergence and accurate results. Application to prototypical third-row semiconductor surfaces establishes a common dangling bond rule and the atomistic origin of the surface energies.

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