Semiconductor Surface Sublimation Energies and Atom-Atom Interactions

Srinivasan Krishnamurthy, M. A. Berding, and A. Sher
SRI International, Menlo Park, California 94025

A.-B. Chen
Department of Physics, Auburn University, Auburn, Alabama 36849

(Received 7 December 1989)

The energy required to remove an atom from semiconductor surfaces is calculated using a Green's-function approach. Contrary to intuition, we find that, in some cases, less energy is needed to remove an atom from the nearly full surface than from a nearly empty surface. The results are explained in terms of the relative energies of anion and cation dangling bonds, and the charge transfers between them. The deducted effective pair-interaction energies and their effects on surface morphology and growth perfection are discussed.

PACS numbers: 68.55.Nq, 68.35.Md

In recent years, considerable advances have been made in the field of epitaxial growth of semiconductors, with molecular-beam epitaxy (MBE) being one of the most important techniques. Modeling of the MBE-growth process entails a description of the incoming and outgoing fluxes of atoms from the surfaces, as well as the in-surface migration and reactions of the constituents. An important contribution to the outflux arises from the sublimation of the constituents from the growth surface. Attempts to determine the activation energy for surface sublimation processes have been made in a variety of experiments on GaAs (Refs. 1-3) and CdTe.[4,5] Because the values obtained depend on the experimental environmental conditions,[6] the reported values differ substantially. Moreover, the experiments, which permit evaporation of many layers, measure quantities related to bulk cohesive energies rather than to the activation energies that are more relevant to growth and that depend on surface orientation. Yet in the modeling of MBE growth, it is essential to have accurate values of the activation energies needed by the constituent atoms to escape from sites on a given surface to the vapor.[7]

In this Letter, we present the energies calculated with a Green's-function (GF) approach for atoms removed from isolated positions on the surface or from a nearly full surface. The difference in sublimation energies in these two limits is explained in terms of the energy difference between the cation and anion dangling bonds, and the charge transfers between those states. The energies affect surface order-disorder transitions and growth perfection, as discussed.

We use a second-neighbor, tight-binding Hamiltonian with four orbitals per atom to obtain the bulk electronic structures.[8-10] A tight-binding GF method is used to calculate the surface sublimation energies (SSE). The GF is calculated using a novel and computationally efficient difference-equation approach developed recently.[11] The bond length and the interatomic and intra-atomic Hamiltonian matrix elements for the atoms on the surface are assigned their bulk values, and only nonreconstructed surfaces are considered.

The calculation of these SSE proceeds in two steps. First, the GF for the ideal flat surface is calculated in terms of the bulk GF using Dyson's expansion. Bulklike and surfacelike states are treated on an equal footing, and the density of states is calculated as a continuous function of energy. The highest occupied state E_m, which can differ from the valence-band maximum, is identified by applying the condition that no net field exists in the ideal stoichiometric crystal. Second, the modified GF for the surface with an atom either removed from or added to the ideal surface is calculated in terms of the ideal surface GF. The electronic contribution to the total energy can be obtained from the change in the density of states, which is calculated directly from the unperturbed GF and the perturbed Hamiltonian. This procedure avoids problems associated with calculating small energies by taking the difference between two large energies.

The surface sublimation energy is defined as the difference between the total energy of a surface plus a free atom and that of the surface with the atom bonded to it. In this convention, the atoms with positive SSE require energy to go from the surface to vapor, and those whose SSE is less than or equal to zero will give up energy in going from the surface to vapor. In the tight-binding model, the total energy is written as the sum of the electronic energy of the occupied state and the repulsive energy between the nearest-neighbor pairs. We demand that our energy parameters produce correct bond length, cohesive energy per bond (0.82, 1.03, 1.63, and 2.32 eV, respectively, for Te, CdTe, GaAs, and Si), and band gap for the bulk. We calculate SSE for two classes of cations and anions for each surface.

When the perturbation to the surface involves the removal of an atom from the ideal surface, leaving a surface vacancy behind, we refer to the process as the surface sublimation from a *concentrated* surface. The energy needed to remove the atom in this limit is denoted as E_c. This removal entails breaking a number of bonds —those with the layer below and the in-plane, second-neighbor, surface bonds. When the perturbation to the surface involves the addition of an atom to the ideal surface, thus beginning a new layer of atoms, we refer to the removal of that atom as surface sublimation from a *dilute* surface. Here, the removal of an atom necessitates breaking bonds only with the layer below. The energy needed to remove the atom in this limit is denoted E_d. Table I lists the calculated E_c and E_d of anions and cations in Si, GaAs, CdTe, and HgTe for (111), $(1\bar{1}\bar{1})$, and (100) orientations. Also given are the values of E_m, with respect to the top of the valence band and the number of bonds that the surface atom makes with the layer below. Note that, for a compound AB, the (111) surface will be terminated with either triply bonded A atoms or singly bonded B atoms. Opposite bonding arrangement is found in $1\bar{1}1$ surface.

Several interesting deductions can be made from the calculated values of E_c and E_d. First, the calculated energies for different surfaces do not always increase linearly with the number of nearest-neighbor bonds and the values are significantly different from their respective bulk cohesive energies, which are commonly used in the simulation of crystal growth. Second, we find these energies to be sensitively dependent on the crystal orientation. However, for a given crystal orientation, the energy bond (averaged over the dilute and concentrated limits) for the removal of an anion plus a cation layer equals the bulk cohesive energy, as it should. Also, the cohesive energy division between anion and cation layers depends on the surface orientation. The cleavage energies obtained from our calculations, which also reflect this orientation dependence, are in good agreement with experiments.[12]

Surface kinetics studied with these energies will predict morphology and growth rates that differ substantially from those obtained using bulk cohesive energies. For example, our calculations suggest that Hg would not be bound to the $(1\bar{1}1)$ surface in the dilute limit, but it would be loosely bound in the concentrated limit. Therefore, we predict that a very large overpressure will be needed to grow HgTe in the $(1\bar{1}1)$ orientation. However, if the SSE were deduced from the bulk cohesive energy, which is 0.82 for HgTe, mercury atoms would be calculated to be more stably bound to the surface and the predicted growth properties would be quite different.

Third, E_c is expected to be larger than E_d, because conceptually the removal of an atom from the concentrated surface requires breaking additional attractive bonds. Our results obtained for (110) surfaces, not shown in Table I, are consistent with this interpretation. Even in the absence of first-neighbor bonds on the surface, all dangling bonds in the concentrated case interact to form a partially filled band with resulting lower energy. The removal of an electron from this surface will, in general, require more energy than if the dangling states were isolated, as in the dilute case. As seen from Table I, this conventional interpretation in terms of net attractive interactions between atoms is consistent with the trends observed in Si, in HgTe, and (in most cases) in GaAs. However, for other cases, we find that E_c is smaller than E_d.

In order to understand the mechanisms that drive semiconductors to have $E_c < E_d$, i.e., effective repulsive surface-pair interactions, we examine the nature of the anion and cation surface states. Notice that $E_c < E_d$ occurs only for polar surfaces in wide-gap materials. For an unreconstructed surface, the surface states normally occur in the fundamental gap. Compounds have both cation- and anion-derived hybrid surface states, but the cation-derived states most often lie higher in energy.

As an illustration, the surface density of states arising from two ideal surfaces, the Cd singly bonded and Te triply bonded $(1\bar{1}1)$, are shown in Fig. 1. Because the energy separation between the peaks in these states is proportional to the energy difference between hybrid states, it is larger in the II-VI than in the III-V compounds. Now let us consider the removal of a Cd atom from an ideal Cd-terminated $(1\bar{1}1)$ surface. The highest occupied surface level is at the cation surface-state energy, 1.25 eV above the valence-band maximum. When a cation is removed, a surface state from the anion previously

TABLE I. Orientation-dependent SSE and the highest occupied level (measured with respect to the top of the valence band). All energies are in electronvolts. η is the number of broken bonds with the layer below.

Orientation	Removed atoms	η		Si			GaAs			CdTe			HgTe	
			E_m	E_d	E_c	E_m	E_d	E_c	E_m	E_d	E_c	E_m	E_d	E_c
(111)	*a*	1	0.0	2.5	4.6	0.4	2.3	3.8	0.7	3.9	4.2	0.0	1.8	3.8
	c	3	0.0	4.2	6.4	0.55	3.2	3.3	1.6	2.7	0.6	0.0	−0.3	1.1
$(1\bar{1}1)$	*a*	3	0.0	4.2	6.4	0.0	4.6	5.0	0.0	5.2	2.1	0.0	2.8	2.8
	c	1	0.0	2.5	4.6	1.3	3.3	2.7	1.3	2.2	1.3	0.0	−0.2	0.3
(100)	*a*	2	0.0	3.7	5.6	0.3	3.4	4.7	0.7	5.0	2.6	0.0	2.4	3.1
	c	2	0.0	3.7	5.6	0.1	2.6	3.6	1.6	2.1	0.1	0.0	−0.2	1.0

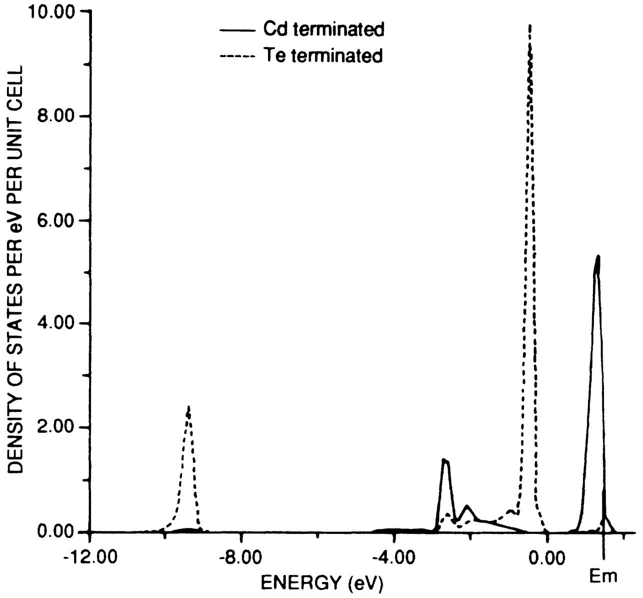

FIG. 1. Density of dangling surface hybrid states of anions (dashed line) and cations (solid line) for $(1\bar{1}1)$-oriented CdTe. E_m is the energy of the highest occupied level for a Cd-terminated $(111)B$ surface.

bonded to the removed cation is created. The surface density of states for the isolated anion surface state created is similar to that shown in Fig. 1 for the pure anion-terminated surface, with only minor differences in the widths and heights in the peaks. Because this anion surface state lies near the top of the valence band, the electrons from the cation surface states will transfer into this level.

As this process reduces the energy of the final configuration, the SSE for removal of a cation in this concentrated limit is also reduced. However, for an isolated cation removed from the underlying $(1\bar{1}1)$ anion surface, E_m is at the top of the valence band, which is very close to the newly exposed anion surface states. The reduction in the SSE from charge transfer is smaller than that in the concentrated case just considered. Apparently, the difference in the charge-transfer energies between E_d and E_c outweighs the band-broadening energy gained in E_c and results in $E_d > E_c$. The charge-transfer processes are reversed for surface sublimation of anion from the $(1\bar{1}1)$ surface. Since three bonds are broken, more electrons are involved in the reversed charge transfer, and the difference between E_d and E_c is also larger.

We conclude that the charge transfer between the cation and anion dangling states will always increase E_d and decrease E_c. The magnitude of this effect depends on the amount of charge transferred and the separation between the relevant energy levels. Whenever the effect is substantial, E_c becomes smaller than E_d and an effective repulsive surface-pair interaction results.

Because silicon contains two identical atoms in the unit cell, no charge transfer is expected and E_c is always larger than E_d. The surface-pair interactions are always attractive. Although charge transfer occurs in GaAs, the energy difference between the maximum occupied level and the newly exposed dangling-bond state is very small. The value of $E_c - E_d$ is reduced to make the surface-pair interactions weak and still attractive in most cases, but the interaction is repulsive for the Ga-terminated $(1\bar{1}1)$ surface. Because of an increased energy difference in the hybrid states in II-VI compounds, the energy separation between the dangling-bond states is large. In CdTe, for example, the effect of the charge transfer is substantial and causes E_c to be less than E_d for every case in Table I except for anions on the $(111)A$ surface. Although HgTe is a II-VI compound, charge transfer does not occur because HgTe is a semimetal with no forbidden gap. In HgTe, the dangling states are resonant in the band and the conduction-band edge is always the maximum occupied level. The cation dangling states are never occupied and, consequently, charge transfer does not occur and E_c is always larger than E_d. The reduction in the difference of E_c and E_d due to the charge transfer is expected to be large for all wide-gap II-VI compounds.

The relative magnitudes of the surface energies have profound consequences on the growth habits of these crystals. When E_c is larger than E_d, the effective interaction between the surface atoms is attractive and going from below the critical temperature to above it, the surface will undergo a phase transition from smooth to rough. The smooth surface will have islands while in the rough limit, the atoms will occupy the sites randomly. Well below the critical temperature, the islands contain few vacancies.

When E_c is smaller than E_d, however, the effective surface-pair interaction is repulsive. At growth temperatures below the order-disorder transition temperature, the atoms on the surface will arrange themselves to maximize the number of atom-vacancy bonds, resulting in superlattice arrangements. The preferred order superlattice arrangements depend on surface composition. At temperatures above the transition temperature, the arrangement of atoms will be nearly random. We conclude from Table I that Si, HgTe, and most GaAs surfaces grow in the smooth-to-rough transition region, while most CdTe and singly bonded Ga-terminated $(1\bar{1}1)$ surfaces grow in the superlattice-ordered-to-random transition region. The surface phase is determined by the growth temperature. Hence, the surface morphology is critically dependent on the nature and the magnitude of the interactions between the surface atoms.

In this Letter, we considered only ideal surfaces and illustrated that the charge-transfer mechanism will always reduce the effective atom-atom interaction on the surface. However, it is known from detailed calculations that reconstruction,[13-15] dimerization,[14] and relaxation of adatom and the surface layer lower the surface energy substantially.[15,16] Although the effective interaction depends on the difference of E_cE_d, effect due to these mechanisms will have to be included for quantitatively more accurate results. While the removal of the approximations will refine our reported values, the underlying mechanism of charge transfer will always be present. For one special case, Chaid,[16] in agreement with an experiment,[17] has demonstrated that a superlattice will form at the relaxed $\frac{3}{4}$ Ga-filled (111) surface of GaAs. His predicted long-range order is mainly driven by the same kind of charge shifts as those we find in our GF method. The magnitude of effective surface energies causes the estimated order-disorder transition temperatures to be in excess of typical MBE-growth temperatures and, consequently, must impact on the nature of the surface and its growth considerably.

The financial support provided for this work through ONR Contract No. N00014-88-C0096, NASA Contract No. NAS1-18226, and AFOSR Contract No. F49620-88-K-0009 is gratefully acknowledged.

---

[1] T. Kojima, N. J. Kawai, T. Nakagawa, K. Ohta, T. Sakamoto, and M. Kawashima, Appl. Phys. Lett. **47**, 266 (1985).

[2] J. M. Van Hove and P. I. Cohen, Appl. Phys. Lett. **47**, 726 (1985).

[3] A. J. Springthorpe and P. Mandeville, J. Vac. Sci. Technol. B **6**, 754 (1988).

[4] J. D. Benson, B. K. Wagner, A. Torabi, and C. J. Summers, Appl. Phys. Lett. **49**, 1034 (1986).

[5] J. J. Dubowski, J. M. Wrobel, and D. F. Williams, Appl. Phys. Lett. **53**, 660 (1988).

[6] R. Heckingbottom, J. Vac. Sci. Technol. B **3**, 572 (1985).

[7] For a review, see A. Madhukar and S. V. Ghaisas, CRC Crit. Rev. Solid State Mater. Sci. **14**, 1 (1988).

[8] D. N. Talwar and C. S. Ting, Phys. Rev. B **25**, 2660 (1982).

[9] K. Hass, H. Ehrenreich, and B. Velicky, Phys. Rev. B **27**, 1088 (1983).

[10] S. Krishnamurthy and J. A. Moriarty, Phys. Rev. B **32**, 1027 (1985).

[11] A.-B. Chen, Y.-M. Lai-Hsu, and W. Chen, Phys. Rev. B **39**, 923 (1989).

[12] M. A. Berding, S. Krishnamurthy, A. Sher, and A.-B. Chen (to be published).

[13] K. C. Pandey, Phys. Rev. Lett. **49**, 223 (1982).

[14] G.-X. Qian, R. M. Martin, and D. J. Chadi, Phys. Rev. B **38**, 7649 (1988).

[15] J. E. Northrup, Phys. Rev. Lett. **57**, 154 (1986).

[16] D. J. Chadi, Phys. Rev. Lett. **52**, 1911 (1984).

[17] S. Y. Tong, G. Xu, and W. N. Mei, Phys. Rev. Lett. **52**, 1693 (1984).