Ab initio calculation of hydrostatic absolute deformation potential of semiconductors

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The hydrostatic absolute deformation potential (ADP) of the valence-band maximum state is one of the most important properties of semiconductors. Yet, it has been calculated in the past only using assumptions that have not been rigorously approved. In this letter, we present an approach to calculate the hydrostatic ADP of Si, GaAs, and ZnSe using an *ab initio* all-electron method and lattice harmonic expansions. We show that the calculated ADP is independent of the selection of the reference energy levels. The calculated ADPs are all positive for the three systems. However, as the *p-d* coupling increases in the II-VI compounds, the ADP decreases. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2168254]

The deformation potential is an important physical property introduced to describe the electron-phonon interaction and the strain-induced energy level shift in a crystal.[1,2] It has been studied extensively in the past for a large variety of semiconductors because it contains important information on the wavefunction characters of the energy levels.[3] It is now well accepted that the difference of the volume deformation potentials, e.g., for the band gap, evaluated with *ab initio* methods are generally in good agreement with experimental values.[4] However the value and the sign of the individual volume deformation potential $a_v^i = dE^i/d \ln v$ for state i, such as the valence-band maximum (VBM), is still under debate.[4–10] This is a serious issue in semiconductor physics because these so-called absolute deformation potentials (ADPs) are important factors in assessing quantum confinement for holes, and separately for electrons in heterostructure quantum wells and nanocrystals;[11–13] thus, it is crucial to have a reliable method to obtain the ADPs accurately, and to understand their general chemical trends.

The difficulty in theoretical calculation of the hydrostatic ADP is that the absolute position of an energy level in an infinity periodic crystal is not well defined. To overcome this problem, various approximations have been assumed. For example, using the model-solid pseudopotential theory, which assumes that the crystal potential is a direct superposition of the neutral atomic pseudopotential, Van de Walle[7] finds that the hydrostatic ADP of the VBM a_v^{VBM} is always *positive*. On the other hand, using the dielectric midgap energy level as a constant reference, Cardona and Christensen[5] find that a_v^{VBM} is always *negative*. Wei and Zunger[4] have assumed that the energy level of the deep core state is not sensitive to the volume deformation, thus, it could be used as a reference to obtain the ADP of the band edge states. Both positive and negative values have been obtained in their calculations. However, the assumption seems to be problematic because the calculated hydrostatic ADPs depend on the reference core levels. For example, for Si, the ADPs differ by about 1 eV if the 1*s* or 2*s* core levels are used as references.

From the theoretical point of view, the change of the VBM energy under volume deformation is due to the following effects:[4] (i) *The anion-cation p-p coupling*. In the simple tight-binding model, the VBM is a bonding state of the anion *p* and cation *p* orbitals,[14] so its energy level decreases as the volume or the bond length decrease. (ii) *The kinetic energy-induced band broadening*. When the volume decreases, the bandwidth increases. At the top of the valence band, the energy of the VBM thus increases with decreasing volume. (iii) For compounds with active *d* valence bands (e.g., most of the II-VI compounds), there is also a *p-d coupling effect*, which moves the energy of the VBM higher when the volume decreases, because the VBM is a *p-d* antibonding state. Effects (i) to (iii) can have similar magnitude and partially cancel each other, so a_v^{VBM} are usually small, and it is difficult to determine its sign in priori.

A significant advancement in the determination of the ADP in semiconductors is proposed by Van de Walle and Martin,[6] who point out that the uniaxial ADP of an energy level in a semiconductor can be obtained using the band offset of a superlattice with a homojunction of different strained regions. This approach has been shown to be valid by Resta *et al.*[8] for nonpolar material. Using this approach, Franceschetti *et al.*[9] calculated the core level ADP of Si under (001) uniaxial strain and showed that the core-level deformation potentials of Si are not negligible and differ by about 1 eV between the 1*s* and 2*s* core levels.

So far, this approach has been used only to calculate the ADP of nonpolar systems under uniaxial strains. In this paper, using the first-principles all-electron band structure method and lattice harmonic expansion, we show that the hydrastatic ADP of nonpolar, as well as polar, semiconductors can be obtained using a similar approach if a proper average of the supercell calculations is carried out. We find that: (a) The calculated hydrostatic ADP of VBM is a well-defined bulk property, independent of the reference core levels; and (b) The hydrostatic ADP of Si, GaAs, and ZnSe are all positive, as expected from simple tight-binding picture, but the value for ZnSe is much smaller than that for Si and GaAs due to the larger *p-d* coupling in the II-VI compounds.[4]

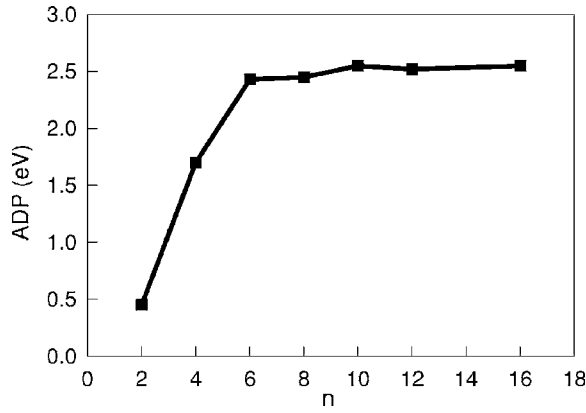a)Electronic mail: swei@nrel.gov

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FIG. 1. Calculated uniaxial absolute deformation potentials of Si along the (110) direction as a function of the supercell layer thickness. We find that the ADP is relatively converged when $n \geq 10$.

TABLE I. Calculated uniaxial ADP of VBM of Si, GaAs, and ZnSe along (100), (110), and (111) directions. All values are in eV. For Si, the results are compared with previous calculations.

Semiconductor	Reference	p_{100}	p_{110}	p_{111}
Si	This work	1.50	2.60	2.83
	Van de Walle et al.[a]	1.3	0.4	3.1
	Resta et al.[b]	1.5	2.6	3.0
	Franceschetti et al.[c]	1.5	1.7	2.7
	Experiment[d]	1.8±0.7		
GaAs		1.20	2.55	3.06
ZnSe		0.19	1.49	1.74

[a]See Ref. 6.
[b]See Ref. 8.
[c]See Ref. 9.
[d]See Ref. 20.

The calculation is performed at the experimental lattice constants[4,15] using the local density approximation of density functional theory as implemented in the WIEN2K linearized augmented plane-wave code.[16] Local orbitals[17] are used for Ga and Zn $3d$ states to improve the flexibility of the basis functions. High convergence in the cutoff energy, k-point sampling, and self-consistent charge density are achieved. To obtain the absolute deformation potential of the VBM, we first calculate the deformation potential of the energy difference between the VBM and a core level (e.g., the cation or anion $1s$ core level) by expanding and compressing the lattice constant separately by about 1%. Then we calculate the uniaxial core-level ADP by constructing a $(n \times n)$ homojunction superlattice along certain directions such as [100], [110], and [111]. One side of these superlattices is compressed along the superlattice direction by 1%, and the other side is expanded by 1%. The atoms at the interfaces between the expanded and compressed region are fixed at their ideal zinc-blende (ZB) position, whereas the internal structural parameters are relaxed by the valance force field method.[18] For the polar orientations, such as [100] and [111], the superlattices with anion-terminated and cation-terminated interfaces are inequivalent, and there exists an electric field in each separate layer. In this case, we average over both cation- and anion-terminated superlattices and anion and cation core levels to remove the electric field. To reduce the interface effects, we have checked the convergence of the calculated core-level ADP with respect to the superlattice layer thickness n. For the [110] superlattice, the calculated ADP as a function of the layer thickness n for Si is shown in Fig. 1. We find that the results are relatively converged when $n=10$. The corresponding superlattices with similar layer thickness for [100] and [111] directions are $n=6$. We estimate that the uncertainty in our calculated ADP is about 0.1 eV.

To calculate the hydrostatic ADP, we take the definition that it is the angular averaged value of the uniaxial ADPs. To facilitate the angular average, we first expand the uniaxial ADPs $p(\hat{r})$ for direction $\hat{r}$ in terms of lattice harmonics K_ν,[19] which are symmetry-adapted linear combinations of spherical harmonic functions:

$$p(\hat{r}) = a + \sum_\nu c_\nu K_\nu(\hat{r}). \tag{1}$$

Using the orthonormal relations of the lattice harmonics, the angular averaged value $\bar{p}$ is given simply by a. For ZB compounds with $l_{max}=4$, the lattice harmonic expansion for the ADP can be written as

$$p(\hat{r}) = a + b\left(x^4 + y^4 + z^4 - \frac{3}{5}r^4\right)/r^4. \tag{2}$$

The coefficients of a and b can be obtained by least square fitting of the directly calculated value along some low index directions. For example, using p_{100}, p_{110}, and p_{111}, from Eq. (2), we have

$$\bar{p} = a = (4p_{110} + p_{100})/5 \pm |(4p_{110} - p_{100} - 3p_{111})|/5. \tag{3}$$

Similarly, for $l_{max}=6$, the lattice harmonic expansion can be written as

$$p(\hat{r}) = a + b\left(x^4 + y^4 + z^4 - \frac{3}{5}r^4\right)/r^4 + c\left[x^2y^2z^2 + \frac{1}{22}\left(x^4 + y^4 + z^4 - \frac{3}{5}r^4\right)r^2 - \frac{1}{105}r^6\right]/r^6, \tag{4}$$

and

$$\bar{p} = a = (10p_{100} + 16p_{110} + 9p_{111})/35. \tag{5}$$

The convergence of the lattice harmonic expansion can be tested by comparing the values obtained from Eq. (3) and Eq. (5).

We first test the dependence of the calculated uniaxial ADP of the VBM on the reference core levels. For Si, if we choose the $1s$ core level as reference, the relative deformation potential of the VBM to the $1s$ core level is 2.46 eV, whereas the ADP of the $1s$ core level along the [100] direction is −0.96 eV; therefore, the VBM ADP is 1.50 eV. If we choose the $2s$ core level as reference, the relative deformation potential of the VBM to the $2s$ core level is 1.47 eV, whereas the ADP of $2s$ core level along the [100] direction is 0.00 eV; therefore, the VBM ADP is 1.47 eV, very close to the value obtained using the $1s$ core level as reference. Similar tests have been done for GaAs and ZnSe. We find that when the calculated results are averaged over anion- and cation-terminated supercells, the result is also independent of the reference core levels. We conclude that within our calculation accuracy, the calculated ADP of the VBM is independent of the reference core levels; therefore, it is a well-defined bulk property.

Table I gives our calculated ADP of the VBM of Si, GaAs, and ZnSe for (100), (110), and (111) uniaxial strains.

TABLE II. Calculated hydrostatic ADP of VBM of Si, GaAs, and ZnSe using the harmonic expansion with $l_{max}=4$ or $l_{max}=6$. All values are in eV. The results are compared with previous calculations.

Reference	Si	GaAs	ZnSe
This work ($l_{max}=4$)	2.38 ± 0.08	2.28 ± 0.04	1.23 ± 0.11
This work ($l_{max}=6$)	2.34	2.30	1.18
Van de Walle[a]	2.46	1.16	1.65
Cardona et al.[b]	−1.6	−1.6	−0.7
Wei and Zunger[c]	2.05	−1.21	−1.97

[a]See Ref. 7.
[b]See Ref. 5.
[c]See Ref. 4.

For Si, our results are compared with previous calculations and experimental results. We find that our results are close to previously calculated values except for p_{110}, where we find that our result agrees with that of Resta et al.,[8] obtained from linear response theory, but is significantly larger than results obtained by Van de Walle et al.[6] and Franceschetti et al.,[9] both using supercell approach as in the present calculation. We believe that the difference is due to small supercells used in the previous calculations. As seen in Fig. 1, using a small cell can significantly underestimate the ADP in the (110) direction.

Table II shows the hydrostatic ADP obtained from the harmonic expansion using $l_{max}=4$ [Eq. (3)] and $l_{max}=6$ [Eq. (5)]. Comparing the results obtained for $l_{max}=4$ and $l_{max}=6$, we find that the $l_{max}=4$ results are converged to within 0.1 eV for the ADP, which is within the numerical uncertainty in our calculation. In this case, the anisotropy parameter b in Eq. (2) can be obtained by $b=2(p_{100}-p_{110})$, and the uniaxial ADP along an arbitrary direction $\hat{r}$ can be easily obtained through Eq. (2).

We find that the calculated hydrostatic ADP for Si, GaAs, and ZnSe are all *positive*. This is consistent with the simple tight-binding model, which treats the VBM as a bonding state of cation p and anion p orbitals,[14] but does not agree with the dielectric midgap model of Cardona and Christensen,[5] which finds that the ADPs are all negative. The results obtained by Van de Walle[7] using the model-solid theory also show that the hydrostatic ADP are all positive. However, they find that the ADP of ZnSe is larger than that of GaAs, opposite to our finding. As pointed out by Wei and Zunger,[4] the reason that ZnSe has smaller ADP is due to the large p-d coupling in the II-VI compounds, which has a negative contribution to the ADP. This p-d coupling effect is not explicitly included in the model-solid theory, which could explain why the model-solid theory got the opposite trend. The results of Wei and Zunger were obtained by as-

suming that the core-level ADPs are negligible.[4] However, our calculations show that the ADP for the core states are significant, around 3 eV for GaAs and ZnSe. This explains why the signs of the VBM ADPs for GaAs and ZnSe are reversed after the ADP of the core levels are correctly included in the present calculation.

In summary, we have proposed an approach to calculate accurately the hydrostatic ADP of semiconductor compounds using the *ab initio* all-electron method and lattice harmonic expansion. We find that the ADPs of the VBM are all positive for Si, GaAs, and ZnSe, but increased p-d coupling in ZnSe reduces its VBM ADP. We would also like to point out that using lattice harmonic expansion to obtain angular-averaged properties as described in this letter can also be applied, in principle, to many other physical properties such as effective mass, etc.

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