Effects of covalency, *p-d* coupling, and epitaxial strain on the band offsets of II-VI semiconductors

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Using the first-principles all-electrons method, we have systematically studied the natural band offsets among zinc blende BeX, MgX, and ZnX ($X=$S, Se, Te). We show that ZnX, which has large anion *p*-cation *d* repulsion, always has higher natural valence band maximum (VBM) than BeX and MgX, whereas BeX, which shows strong covalency, has higher natural VBM than MgX due to kinetic-energy-induced valence band broadening. However, epitaxial strain could reverse these trends. We found that for these isovalent semiconductors, the band offset is not sensitive to interface atomic compositions.

Extensive experimental and theoretical studies have been carried out to understand the nature of the band offsets between two semiconductor compounds forming heterostructure.[1,2] The band offset is one of the most important parameters in device modeling[1] and in determining the dopability of semiconductor compounds.[3] For *conventional* II-VI as well as III-V semiconductors, it is shown[2] that (i) for common-cation systems (e.g., ZnS, ZnSe, and ZnTe), the valence band maximum (VBM) increases as the anion atomic number increases, whereas the valence band offset ΔE_v decreases as the cation atomic number increases, e.g., from ZnX to CdX to HgX ($X=$S, Se, and Te). (ii) For common-anion system, the compound with shallow occupied cation *d* orbitals (e.g., ZnSe) always has higher VBM than the one without it (e.g., MgSe). The valence band offset ΔE_v decreases when the anion atomic number increases, e.g., from sulphides to selenides to tellurides. It has been shown that coupling between the anion *p* and cation *d* states plays a decisive role in determining these chemical trends of valence band offsets.[2] Furthermore, previous studies[4,5] have shown that, for isovalent semiconductors, the band offset is not sensitive to the interface atomic structures.

Recently, considerable interest has arisen for using BeX, MgX, and their alloys with the conventional II-VI semiconductor ZnX as materials for light-emitting and laser diodes in the blue/green region.[6] In addition to the technological importance, these unconventional II-VI compounds also show some interesting, but unexplained, physical phenomena. For example, recent photoelectron spectroscopy measurements of Nagelstrasser *et al.*[7] show that ΔE_v at the BeTe/ZnSe interface is highly dependent on the interface composition and can vary by as much as 0.8 eV. Subsequent *ab initio* pseudopotential calculations of Bernardini *et al.*[8] show that the experimentally proposed valence band offset cannot occur in the nominal BeTe/ZnSe interface. Instead, other types of interfaces, such as BeSe/ZnSe or ZnTe/ZnSe may form, which could explain the scattering of the experimental data. However, their theoretical study does not include the spin-orbital coupling. Furthermore, they only presented the band offset for strained interfaces and show that BeSe, which does not have an active cation *d* orbital, has a higher VBM than that for ZnSe, which does have an active Zn 3*d* orbital, in contrast to the general understanding.[2] It is not clear whether this reversal of chemical trend is caused by epitaxial strain, and

why BeX has much higher VBM than other common-anion IIA-VI compounds such as MgX.

In this paper, we study systematically the *natural* valence band offsets between isovalent semiconductors MX, with $M=$ Be, Mg, Zn and $X=$ S, Se, Te. We find that the band offset between the nearly lattice-matched ZnSe and BeTe is independent of the interface composition, which is consistent with a recent theoretical study,[8] but in contrast with previous reported data.[7] Furthermore, we show that ZnX always has higher natural VBM than BeX and MgX due to anion *p*-cation *d* repulsion, which is consistent with previous understanding of the general chemical trends of the band offset in semiconductors.[2] However, epitaxial strain could reverse the sign of the band offset. Moreover, we show that BeX is strongly covalent. The large unexpected BeX/MgX valence band offsets are due to kinetic energy effects, which also play an important role in explaining chemical trends of band offsets in semiconductors.

We used the self-consistent, first-principles all-electron full-potential linearized augmented plane wave (LAPW) method[9] within the local-density approximation (LDA).[10,11] The Ceperley-Alder exchange correlation potential[10] as parametrized by Perdew and Zunger[11] has been used in our calculations. Spin-orbit (SO) coupling has been included in the calculations in a second variational procedure. The band offset is calculated following the same approach as used in photoemission core level spectroscopy,[12] i.e.,

$$\Delta E_v(AX/BY) = \Delta E_{C',v}^{BY} - \Delta E_{C,v}^{AX} + \Delta E_{C,C'}^{AX/BY}, \qquad (1)$$

where

$$\Delta E_{C,v}^{AX} = E_v^{AX} - E_C^{AX} \qquad (2)$$

(and similarly $\Delta E_{C',v}^{BY}$) are the core (*C*) level to VBM energy separations for pure AX (and similarly for pure BY), and

$$\Delta E_{C,C'}^{AX/BY} = E_{C'}^{BY} - E_C^{AX} \qquad (3)$$

is the difference in core-level binding energy between AX and BY at the AX/BY interface.

For natural band offset, the core level to VBM energy separations is calculated for binary compounds AX and BY at their experimental zinc blende lattice constant.[13,14] Table I presents our calculated lattice constants and bulk moduli for

TABLE I. Calculated lattice constants a_{eq} and bulk moduli B for Be, Mg, and Zn compounds. The available experimental results are shown in parentheses for comparison (Ref. 14).

		S	Se	Te
Be	a_{eq} (Å)	4.81 (4.865)	5.09 (5.139)	5.57 (5.625)
	B (GPa)	104 (105)	85 (92.2)	64 (66.8)
Mg	a_{eq} (Å)	5.62 (5.622)	5.89 (5.89)	6.38 (6.414)
	B (GPa)	63	51	38 (60.6)
Zn	a_{eq} (Å)	5.33 (5.41)	5.61 (5.668)	6.03 (6.089)
	B (GPa)	89 (77.1)	73 (62.4)	57 (51.0)

the compounds considered compared with available experimental data. We find a good agreement between our results and experimental data, and the relatively small difference between the calculated and the experimental lattice constants has no significant effect on the reported results below. The difference in core-level binding energy between AX and BY is obtained from $(AX)_n/(BY)_n$ superlattices with (001) orientation and an in-plane lattice constants equal to the average of the experimental bulk lattice parameters of the two binaries AX and BY. The atomic positions along the superlattice direction are fully relaxed. The calculation for strained valence band offsets for some of the Be-based and Zn-based II-VI semiconductors are performed at ZnSe substrate lattice constant, and all the structural parameters perpendicular to the substrate are, again, fully relaxed. The uncertainty in our calculated band offsets is estimated to be 0.1 eV.

To study the effect of interface composition on the band offset, we have considered ZnSe/BeTe with three kind of possible interfaces, namely the Zn-Te, Be-Se, and mixed Zn-Te+Be-Se interfaces. We found that the band offset for single-type and mixed-type interfaces are very similar, and in good agreement with previous studies,[4,5] which show that for isovalent semiconductors interfaces, the band offset is not sensitive to the local atomic arrangement. Our calculated value of ΔE_v(ZnSe/BeTe)$= 0.70$ eV (we use the convention that positive ΔE_v indicates that the compound on the right-hand side has higher VBM) is also consistent with recent *ab initio* pseudopotential calculations[8] that gave a value of 0.52 eV. The difference is attributed mostly to the neglect of SO coupling in the pseudopotential study.

The results for the natural valence band offsets for ZnX, BeX, and MgX are given in Fig. 1. The general chemical trend observed in this system is similar to that observed in conventional semiconductors.[2] For example, we find that the VBM of common-cation compounds increases as the anion atomic number increases. This is because the VBM is mainly an anion p state and the energy of the anion p orbital increases from -7.11, -6.66, to -6.11 eV, for S, Se, and Te, respectively. For common-anion systems, we find that ZnX always has higher VBM than BeX and MgX compounds. This trend is explained by the p-d coupling in a zinc blende structure with T_d symmetry: ZnX has a shallow occupied 3d orbital, and the p-d repulsion leads to an upward shift of the
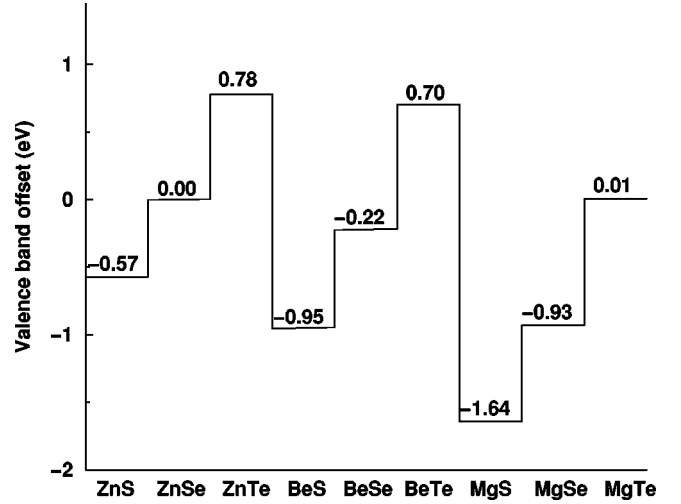

FIG. 1. Calculated natural valence band offsets ΔE_v(ZnSe/BY) (in eV) of Be-, Mg-, and Zn-based II-VI semiconductors, for Y = S, Se, and Te.

VBM.[2] Since Be and Mg have only unoccupied d orbitals, the VBMs of BeX and MgX are lower than the corresponding Zn compounds.

Another interesting feature revealed from our results is the higher VBM of BeX compared to the corresponding MgX compounds (see Fig. 1). This result is at first puzzling because, in the past, the failure of the common-anion rule, which states that for common-anion semiconductor pairs the valence band offset is small because the VBM is mainly an anion p state, has been attributed to the large difference in the repulsion between anion p and cation d states on the semiconductor pairs (e.g., in CdTe/HgTe and AlAs/GaAs).[2,15] However, p-d repulsion is weak in both BeX and MgX, which do not have active occupied cation d orbitals. Furthermore, in the two-level tight-binding model,[16] the Γ_{15v} VBM state has an energy

$$\epsilon_v = \frac{\epsilon_p^c + \epsilon_p^a}{2} - \left\{ \left(\frac{\epsilon_p^c - \epsilon_p^a}{2} \right)^2 + V_{pp}^2 \right\}^{1/2}, \qquad (4)$$

where ϵ_p^c and ϵ_p^a are the cation and anion p atomic orbital energies, and V_{pp} is the coupling potential, given by[16] $9.7536/d^2$ eV, where d is the cation-anion bond length in Å. Table II gives the calculated valence band offsets of BeX/MgX systems obtained from Eq. (4) using the LDA

TABLE II. Calculated natural valence band offsets (in eV) using the tight-binding model, with and without corrections (see text for details), for common-anion BeX/MgX systems and for BAs/AlAs. The results are compared with those of direct LAPW calculations.

X	Te	Se	S	BAs/AlAs
$\Delta \epsilon_v$	0.27	0.34	0.40	0.81
$\Delta(\epsilon_v - \overline{\epsilon_h})$	-0.11	-0.03	0.03	0.25
$\Delta(\epsilon_v - \overline{\epsilon_h} + \delta\epsilon_v)$	-0.56	-0.58	-0.60	-0.62
LAPW	-0.69	-0.71	-0.69	-0.39 (Ref. 19)
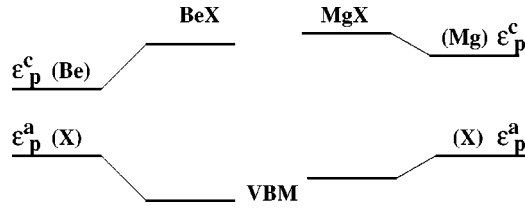
FIG. 2. Schematic plot of the two-level, tight-binding repulsion in Be*X* and Mg*X* compounds.
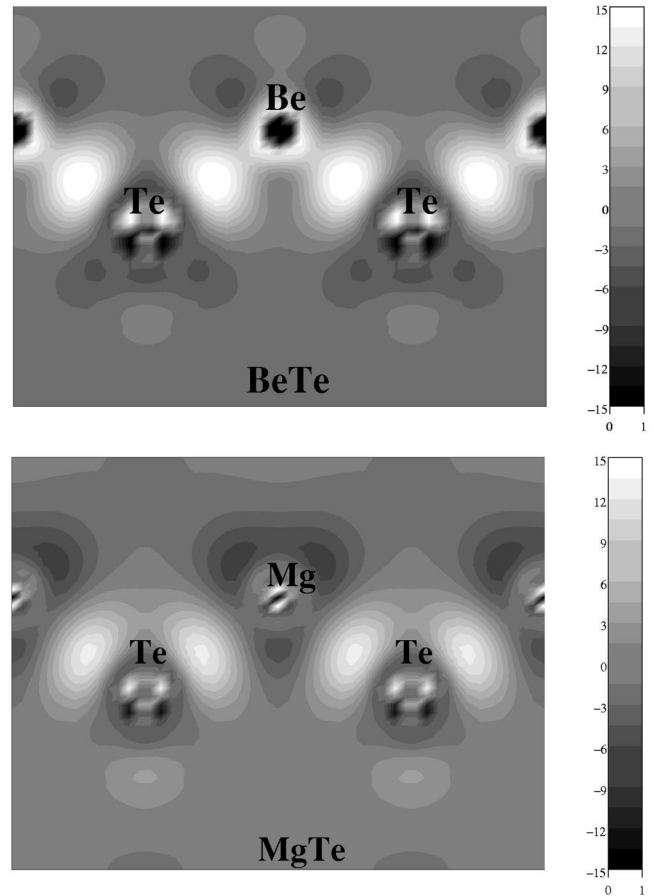

FIG. 3. Difference between the self-consistent crystal charge density and the overlapping atomic charge density in BeTe and MgTe, in units of 10^{-3} e/au^3.

atomic eigenvalues. In this simple tight-binding model, Mg*X* always has higher VBM than Be*X*. This is explained [see Fig. 2 and Eq. (4)] by the smaller atomic energy difference $\epsilon_p^c - \epsilon_p^a$ for Be*X* (5.05, 4.60, and 4.05 eV, respectively, with $X=$ S, Se, and Te) than for Mg*X* (5.73, 5.28, and 4.74 eV, respectively), and by the shorter Be-*X* bond length compared to the corresponding Mg-*X* bond length (see Table I). However, compared with the LAPW results also shown in Table II, the level repulsion model leads to exactly opposite results. Harrison and Tersoff[16] have noticed the failure of Eq. (4) in some semiconductor systems. They proposed a correction term to the simple tight-binding level in which ϵ_v is referred to $\overline{\epsilon_h}$, which is the average of the sp^3 hybrid energies ϵ_h^c and ϵ_h^a of cation and anion, respectively, assuming that $\overline{\epsilon_h}$ lines up at the interface.[16]

The correction term suggests that when ϵ_h^c is closer to ϵ_h^a, i.e., when $\overline{\epsilon_h}$ is closer to ϵ_h^a and the system is more covalent, the compound will have a high VBM due to this "charge sharing" effect. Indeed, we find that the Be compounds are much more covalent compared to the Mg compounds.[17] Figure 3 shows the difference between the self-consistent crystal charge density in BeTe and MgTe and the overlapping atomic charge density. The bright regions show where the charge accumulates, and the dark regions show where the charge is removed when the compound is formed. We can see from the figure that, in both cases, charge is removed from the antibonding direction and put along the bond direction. In MgTe, the maximum in the charge difference is close to the Te atom, which reflects the ionicity of the MgTe bond. In BeTe, however, the usual cation-to-anion charge transfer is not observed. In fact, as can be seen in Fig. 3, BeTe shows a charge distribution very similar to that of covalent Si or Ge. This indicates that there is a large hybridization between the Te *p* and the Be *p* orbitals and, therefore, a significant contribution of the Be *p* orbital to the VBM. Similar results were obtained for BeSe and BeS compared to MgSe and MgS, respectively. Table II shows the band offsets of Be*X*/Mg*X* systems after the correction term $\overline{\epsilon_h}$ is included. Although the agreement with the direct LAPW calculations is improved, we find that the inclusion of the $\overline{\epsilon_h}$ term is still not sufficient.

We argue here that in the tight-binding model described above, the kinetic-energy-induced valence band broadening effect on the VBM is not correctly described. This is reflected by the fact that Eq. (4) significantly overestimates the magnitude of the VBM deformation potential.[18] In reality, the deformation potential at VBM is very close to zero because when the compound is compressed, the *p-p* repulsion,

described by Eq. (4), pushes the VBM down. However, due to kinetic energy effect, the band width of the valence band and the VBM increase. This kinetic energy effect is larger for compounds with smaller bond lengths and that are more covalent. To include this kinetic-energy-induced valence band broadening effect, we assume that ϵ_v of Eq. (4) should also include a correction of the form $\Delta\epsilon_v = \alpha/d^2$. Assuming that the deformation potential at the VBM is negligible, α is determined according to $\delta\epsilon_v/\delta d=0$. This yields

$$\Delta\epsilon_v = \alpha_c V_{pp}, \qquad (5)$$

where α_c is the covalency of a bond defined by[16]

$$\alpha_c = \frac{V_{pp}}{(V_{\mathrm{pol}}^2 + V_{pp}^2)^{1/2}}, \qquad (6)$$

and $V_{\mathrm{pol}}=(\epsilon_p^c - \epsilon_p^a)/2$. Equations (5) and (6) suggest that the upward shift of VBM is larger for compounds with higher covalency (i.e., α_c is large) and with shorter bond lengths (i.e., V_{pp} is large). Because the Be*X* compounds have shorter bond lengths in their ideal zinc blende structure (see Table I) than the corresponding Mg*X* compounds, and are also more covalent than Mg*X*, we expect an increase in the VBM for Be*X* relative to the corresponding Mg*X* compound.

The tight-binding results of the valence band offsets $\Delta\epsilon_v(\text{Be}X/\text{Mg}X)$ between BeX and MgX corrected with the kinetic energy contribution $\Delta\epsilon_v$ and the "charge-transfer term" $\overline{\epsilon_h}$ used by Harrison and Tersoff[16] are shown in Table II. It can be seen that after the corrections are taken into account, the calculated valence band offsets using the tight binding model compare well with our direct LAPW results. Thus, the higher VBM of BeX than MgX is related to the higher covalency of the BeX compounds. It should be mentioned that the same trend in the band offset has been observed also in the III-V BAs/AlAs system.[19] We have calculated the band offset for this system, on the basis of the tight-binding model, corrected with the "charge transfer" term[16] and the kinetic energy contribution [Eq. (5)]. Again, for this system the result obtained from our corrected tight-binding model compares well with the direct LAPW result (see Table II).

These results show that the covalency contributions to the band offset are also an important factor in determining the trend of valence band offset of common-anion semiconductors, especially when the binaries have significantly different covalencies. It is interesting to notice that this covalency effect also applies to systems such as AlAs/GaAs and CdTe/HgTe for which GaAs and HgTe are more covalent pairs.

We have also studied the valence band offsets of the BeX, MgX, and ZnX compounds, strained on ZnSe. The results are summarized in Fig. 4. For $\Delta E_v(\text{ZnSe/Be}X)$, the results are qualitatively in agreement with those reported in Ref. 8. But quantitatively, the difference between our results and those of Ref. 8 are, again, mostly due to the SO coupling, which is not included in their calculations. We find that the effect of the epitaxial strain is to shift upward the VBM's of the strained compounds relative to those at their respective equilibrium lattice constants. The equilibrium lattice constants of BeX, MgS, and ZnS are smaller than that of ZnSe. The in-plane tensile epitaxial strain leads to a negative crystal-field splitting, and the top of the valence band has the Γ_{4v} (Γ_{7v} with SO coupling) character.[20,21] In this case, the increase of the VBM's of BeX, MgS, and ZnS is due mainly to the crystal-field splitting, which is relatively large for BeS and BeSe on ZnSe. On the other hand, ZnTe, MgSe, and MgTe have larger equilibrium lattice constants than ZnSe. Thus, the in-plane compressive epitaxial strain leads to a positive crystal-field splitting, and the top of the valence band has the Γ_{5v} (Γ_{6v} with SO coupling) character. In this case, the increase of the VBM of MgSe and MgTe is due also
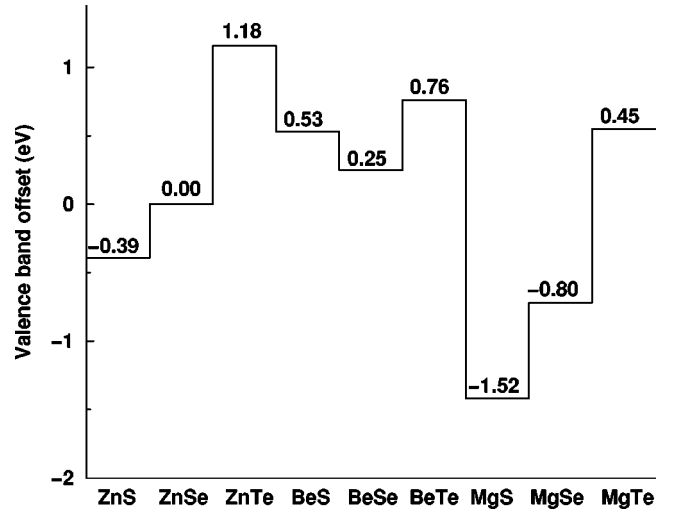

FIG. 4. Calculated strained band offset $\Delta E_v(\text{ZnSe/B}Y)$ (in eV) of Be-, Mg-, and Zn-based II-VI semiconductors on ZnSe substrate, for $Y=$ S, Se, and Te.

to the crystal-field splitting. However, the effect is relatively small because, for the same magnitude of epitaxial strain, the increase of the Γ_{5v} energy is twice as lower as for the Γ_{4v} state.[20] In the case of ZnTe, the compressive strain leads to a larger p-d repulsion and to a higher VBM. For ZnS, the tensile strain reduces the p-d coupling, and thus, the VBM energy, and partially cancels the effect of the crystal field splitting. It is interesting to see from Fig. 4 that epitaxial strain can reverse the order of the VBM between some compounds pairs. For example, ZnSe has higher natural VBM than BeSe at equilibrium, whereas BeSe has higher VBM than ZnSe if it is strained on ZnSe.

In summary, using first-principles all-electrons method, we have systematically studied the band offset of the Be-, Mg-, and Zn-based II-VI semiconductors. We show that they follow the general trend observed previously for other semiconductor systems, however, epitaxial strain could reverse this trend. Most importantly, we find that in addition to the p-d coupling mechanism, the covalency effects also play an important role in understanding the chemical trends of the band offset of semiconductor systems.

[1] E. Yu and T. McGill, in *Solid State Physics*, edited by H. Ehren-reich and D. Turnbull (Academic, Boston, 1992), Vol. 46, p. 1.

[2] S.-H. Wei and A. Zunger, Appl. Phys. Lett. **72**, 2011 (1998).

[3] S.B. Zhang, S.-H Wei, and A. Zunger, J. Appl. Phys. **83**, 3192 (1998).

[4] R.G. Dandrea, C.B. Duke, and A. Zunger, J. Vac. Sci. Technol. B **10**, 1144 (1992).

[5] M. Peressi, N. Binggeli, and A. Baldereshi, J. Phys. D **31**, 1273 (1998).

[6] A. Waag, F. Fisher, H.J. Lugauer, T. Litz, J. Laubender, U. Lunz, U. Zehnder, W. Ossau, T. Gerhardt, M. Möller, and G. Land-wehr, J. Appl. Phys. **80**, 792 (1996).

[7] M. Nagelstrasser, H. Dröge, F. Fisher, T. Litz, A. Waag, G. Land-wehr, and H.P. Steinrück, J. Appl. Phys. **83**, 4253 (1998).

[8] F. Bernardini, M. Peressi, and V. Fiorentini, Phys. Rev. B **62**, R16 302 (2000).

[9] S.-H. Wei and H. Krakauer, Phys. Rev. Lett. **55**, 1200 (1985).

[10] D.M. Ceperley and B.J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

[11] J.P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[12] S.P. Kowalczyk, J.T. Cheung, E.A. Kraut, and R.W. Grant, Phys. Rev. Lett. **56**, 1605 (1986).

[13] *Landolt-Borstein: Numerical Data and Functional Relationships in Science and Technology*, edited by O. Madelung, M. Schultz, and H. Weiss (Springer, Berlin, 1982), Vols. 17 a,b and 22a.

[14] D.J. Chadi, Phys. Rev. Lett. **72**, 534 (1994); D. Wolverson, D.M. Bird, C. Bradford, K.A. Prior, and B.C. Cavenett, Phys. Rev. B **64**, 113203 (2001); C. Narayana, V.J. Nesamony, and A.L. Ruoff, *ibid.* **56**, 14 338 (1997); T. Li, H. Luo, R.G. Greene, A.L. Ruoff, S.S. Trail, and F.J. DiSalvo, Jr., Phys. Rev. Lett. **74**, 5232 (1995).

[15] S.-H Wei and A. Zunger, Phys. Rev. Lett. **59**, 144 (1987).

[16] W.A. Harrison and J. Tersoff, J. Vac. Sci. Technol. B **4**, 1068 (1986).

[17] J.C. Phillips, *Bonds and Bands in Semiconductors*, (Academic Press, New York, 1973); Rev. Mod. Phys. **42**, 317 (1970).

[18] S.-H. Wei and A. Zunger, Phys. Rev. B **60**, 5404 (1999).

[19] G.L.W. Hart and A. Zunger, Phys. Rev. B **62**, 13 522 (2000); R.M. Wentzcovitch and M.L. Cohen, J. Phys. C **19**, 6791 (1986).

[20] S.-H. Wei and A. Zunger, Phys. Rev. B **49**, 14 337 (1994).

[21] C.G. Van de Walle, Phys. Rev. B **39**, 1871 (1994).