Predicted band-gap pressure coefficients of all diamond and zinc-blende semiconductors: Chemical trends

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We have studied systematically the chemical trends of the band-gap pressure coefficients of all group IV, III-V, and II-VI semiconductors using first-principles band-structure method. We have also calculated the individual ''absolute'' deformation potentials of the valence-band maximum ~VBM! and conduction-band minimum ~CBM!. We find that ~1! the volume deformation potentials of the Γ_{6c} CBM are usually large and always negative, while ~2! the volume deformation potentials of the Γ_{8v} VBM state are usually small and negative for compounds containing occupied valence d state but positive for compounds without occupied valence d orbitals. Regarding the chemical trends of the band-gap pressure coefficients, we find that ~3! $a_p^{\Gamma-\Gamma}$

efficients by systematically calculating the pressure coefficients for all group IV, III-V, and II-VI semiconductors. We also calculate the ''absolute'' deformation potentials of the VBM and conduction-band maximum ~CBM!. We show that ~1! the volume deformation potentials a_v^{CBM} of the conduction-band minimum ~CBM! state Γ_{6c} are usually large and always negative ~energy increases with pressure!, while ~2! the volume deformation potentials a_v^{VBM} of the VBM Γ_{8v} state are usually small and negative for zinc-blende compounds containing occupied valence d state ~e.g., GaAs, InAs! but positive for compounds without occupied valence d orbitals ~e.g., AlAs!. Regarding the chemical trends of the band-gap pressure coefficients, we find that ~3! $a_p^{\Gamma-\Gamma}$ decreases as the ionicity increases, ~4! $a_p^{\Gamma-\Gamma}$ increases significantly as anion atomic number increases, ~5! $a_p^{\Gamma-\Gamma}$ decreases sf681 -1.5852 T 1 Tf 14.4r (sf681 -103 5tj 6.9857f-1.2131 TD (a)Tj 6.9/F11ses,)]TJ.9/F11 Tf 19.4024 0 TD (~)Tj /31 l0epresTm [!.

coefficients for all the compounds. However, the stable crystal structures for the nitrides and some of the II-VI compounds ~CdS, CdSe! are wurtzite ~WZ!. It appears reasonable to assume that compounds in the WZ structure will have similar pressure coefficients as in the ZB structure, since the nearest-neighbor tetrahedral environment is similar in both structures. However, a recent calculation of Christensen *et al.*[32] using linearized muffin-tin orbital ~LMTO! method found that for InN $a_p^{G-G}=3.1$ meV/kbar in the WZ structure, but only 1.9 meV/kbar in the ZB structure. The difference was attributed to the extra structural degrees of freedom available in the WZ structure: the variation of E_g due to the change in the $h=c/a$ ratio ~where c and a are the hexagonal lattice constants parallel and perpendicular to the @0001# direction!, and the internal structural parameter u. To test their results, we have repeated their calculation for InN. In the WZ structure

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$$\frac{dE_g}{d \ln v} = \frac{]E_g}{] \ln v} + \frac{]E_g}{}$$

ale,

~C, AIN, GaN, InN, etc.!. In the following, we will analyze the chemical trends of the volume deformation potentials and pressure coefficients in terms of simple models, including the $s-s$, $p-p$, and $p-d$ couplings and level repulsions.

IV. EXPLANATION OF TRENDS USING SIMPLE MODELS

Since the deformation potential $a_v^{\Gamma-\Gamma}=a_v^{CBM}-a_v^{VBM}$, where $a_v^{CBM}=dE^{CBM}/d\ln v$ is the deformation potential of the CBM (Γ_{6c}) and $a_v^{VBM}=dE^{VBM}/d\ln v$ is the deformation potential of VBM (Γ_{8v}), we will first analyze individually the chemical trends of the CBM and VBM volume deformation potentials ~Table IV! and the volume dependence of the bulk moduli ~Table II!:

A. Volume deformation potential of the Γ_{6c} state

Under pressure, the antibonding Γ_{6c} state moves upward in energy due to ~a! increase in the kinetic energy, which is proportional to k^2 or $1/l^2$, where k is the reciprocal lattice vector ~in the extended Brillouin zone! and l is the anion-cation bond length, and ~b! $s-s$ level repulsion. The two effects add up for this antibonding state, so a_v^{CBM} is always

positive and mostly3 1 Tf2131rgemoshc355gy,~level repulsion(b) [(9spul Tm 0.00010 032.7(defos -1.2497 TDD (a)Tj -188f27/F6 1 Tf 10.

lated results of $a_v^{\text{VBM}}(\text{GaAs}) = -1.21$ eV and $a_v^{\text{VBM}}(\text{InP}) = -$

where the bowing coefficient b_p^{G-G} of the pressure coefficient is found to be 3.8 meV/kbar for $Al_xGa_{1-x}As$. Since b_p^{G-G} is larger than the difference ~0.6 meV/kbar! between the band-gap pressure coefficients of AlAs and GaAs, a_p^{G-G} will decrease initially as AlAs composition increases. *Linear* extrapolation from the Al-poor samples has the tendency of underestimating a_p^{G-G}(AlAs), thus, partially explains the experimental observation.[19] Bowing of the band-gap pressure coefficient has also been noticed in[3] $Ga_{0.5}In_{0.5}P$ and in[41] GaN_xAs_{1-x} alloys. In fact, due to wave function mixing at the band edge, we expect that bowing of the pressure coefficient should be a common phenomena, especially for alloys whose constituents has large valence-band offset ~e.g., MgSe and ZnSe! and/or large size mismatch ~e.g., GaAs and GaN!.

VI. LDA CORRECTED BAND-GAP PRESSURE COEFFICIENTS

LDA calculation underestimates the band-gap pressure coefficient, as seen in Table III and other first-principles calculations.[42] To corrected the LDA error, we have adopted a simple method by adding an external potential[42,43] to the LDA potential in solving the self-consistent LDA Schrodinger equations, so that the corrected band gaps are similar to experimental data[6] or quasiparticle results.[44,45] The LDA corrected band-gap deformation potentials and pressure coefficients for the group-IV, III-V, and II-VI compounds are given in Table V. The pressure coefficients are obtained using Eq. ~3! and experimental bulk moduli given in Table II. The uncertainty of our predicted values is about 0.5 meV/kbar, mainly due to the uncertainty in fitting the external potentials and uncertainty of the experimental bulk moduli used to derive the pressure coefficients. We see that after correcting the LDA error in the band structure, the predicted values of a_p^a are in better agreement with experimental data ~Table III!. But the chemical trends are the same as in the LDA calculations.

VII. CONCLUSION

In summary, we have tested the validity of the ''empirical rule'' and studied the *chemical trends* of the band-gap pressure coefficients of all group IV, III-V and II-VI semiconductors. We also calculate the absolute deformation potentials of the VBM and CBM. We find that the volume deformation potentials a_v^{VBM} are small and negative for compounds containing occupied valence d state but positive for compounds without occupied valence d orbitals. Regarding the chemical trends of the band-gap pressure coefficients, we find that ~i! a_p^{G-G} decreases as the ionicity increases, ~ii! a_p^{G-G} increases significantly as anion atomic number increases, ~iii! a_p^{G-G} decreases slightly as cation-atomic number increases, ~iv! the variation of a_p^{G-L} are relatively small and follow similar trends as a_p^{G-G}, and ~v! the magnitude of a_p^{G-X} are small; a_p^{G-X} are usually negative, but are positive for compounds containing first-row elements ~C, AlN, GaN, and InN!. We suggest that the ''empirical rule'' [1,2] of the pressure coefficients should be modified and that one should be cautious in using the absolute deformation potentials from previous calculations.[15,16]

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