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Band structure of ternary-compound semiconductors using a modified tight-binding method

Seong Jae Lee, Hahn Soo Chung, Kyun Nahm, and Chul Koo Kim
Department of Physics, Yonsei University, Seoul 120-749, Korea

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A tight-binding scheme, which incorporates the compositional disorder as an effective potential, is proposed for calculation of the band structure of ternary-compound semiconductors. It is shown that the present theory, which is free from additional adjustable parameters, satisfactorily produces the correct band-gap bowings and, in addition, provides a physical explanation for the empirical theory of Porod and Ferry [Phys. Rev. B **27**, 2587 (1983)].

It is known that the virtual-crystal approximation (VCA) for semiconductor alloys leads to bowing parameters of the main gaps that are too small to account for experiment. This failure of VCA is generally attributed to the compositional disorder and the lattice distortion of the alloy system. Recently, a modified tight-binding (TB) scheme has been proposed by Porod and Ferry, in which the compositional disorder interaction of the alloy $A_xB_{1-x}C$ is represented by an empirical term proportional to $x(1-x)$.[1] Although their scheme has been successful in explaining the energy-gap bowing of ternary and quaternary alloys, it suffers from being a phenomenological theory. It does not provide any physical basis for the $x(1-x)$ term and requires adjustable parameters. In this Brief Report, we propose a novel TB scheme in which the compositional disorder is incorporated as an effective potential. In our theory, the lattice distortion is also included approximately.

We consider a mixed crystal $(AC)_x(BC)_{1-x}$. Here, we assume that all C atoms occupy the proper positions. The potential of the alloy is given by

$$V(r)=V_{\mathrm{VC}}(r)+V_{\mathrm{dis}}(r) , \tag{1}$$

where V_{VC} is the periodic virtual-crystal potential and V_{dis} the nonperiodic potential fluctuation due to the compositional disorder. V_{dis} for a particular distribution is given by[2]

$$V_{\mathrm{dis}}(r)=(1-x)\sum_{j_A}\Delta(r-R_j)-x\sum_{j_B}\Delta(r-R_j) , \tag{2}$$

where $\Delta(r)=V_{AC}(r)-V_{BC}(r)$. Here, j_A (j_B) indicates that the summation on j is carried out on AC (BC) molecular sites only.

The conventional VCA makes the following approximation:

$$\sum_{j_A}\Delta(r-R_j)=x\sum_{j}\Delta(r-R_j) ,$$

$$\sum_{j_B}\Delta(r-R_j)=(1-x)\sum_{j}\Delta(r-R_j) .$$

This approximation makes V_{dis} disappear and $V(r)$ becomes equal to $V_{\mathrm{VC}}(r)$. In order to go beyond VCA, we introduce the disorder effect by assuming that $\sum_{j_A}\Delta(r-R_j)=\alpha x\sum_j\Delta(r-R_j)$ and $\sum_{j_B}\Delta(r-R_j)=\beta(1-x)\sum_j\Delta(r-R_j)$, where α and β are disorder functions and are dependent on the concentration x and the potential energy. With this approximation, the disorder potential is given by

$$V_{\mathrm{dis}}(r)=(\alpha-\beta)x(1-x)\sum_{j}\Delta(r-R_j) . \tag{3}$$

This approximation is analogous to the single-site approximation of the self-energy in the coherent-potential approximation and replaces the random fluctuating potential by a periodic effective disorder potential.[3] A simple way of utilizing Eq. (3) is to neglect the concentration dependence of $(\alpha-\beta)$ and treat it as an adjustable parameter. This approximation makes our V_{dis} identical to the empirical term introduced by Porod and Ferry,[1] thus providing a physical rationale for their method.

The concentration dependence of $(\alpha-\beta)$ can be evaluated by considering an ensemble average of the potential-energy deviation from the VCA value. This has been done by the authors in connection with an empirical pseudopotential scheme.[4] However, the TB scheme appears to provide a more natural theoretical framework than the pseudopotential scheme, because the disorder potential and the lattice distortion are more easily handled in the real space than in the reciprocal space. Since the details of the calculation on the concentration dependence have been reported in Ref. 4, we simply use the result

$$\alpha-\beta=-[x(1-x)N]^{-1/2} , \tag{4}$$

where N is the number of the nearest neighbors, which is 12 for fcc. Following the convention of Slater and Koster,[5] the TB parameters are now expressed as follows:

$$P_i^{\mathrm{alloy}}=xP_i^{AC}+(1-x)P_i^{BC}-\left[\frac{x(1-x)}{N}\right]^{1/2}(P_i^{AC}-P_i^{BC}) . \tag{5}$$

The P_i ($i=1-23$) defined and listed for elemental compounds in Table I is taken from Ref. 6.

However, for the TB parameters, P_5-P_9, we need a

TABLE I. Tight-binding parameters (in units of eV) employed in the present work for GaAs, InAs, and AlAs crystals.

Interaction integral	GaAs	InAs	AlAs
$P_1=E_{s,s}(0,0,0)_0$	−6.7236	−7.1793	−6.1517
$P_2=E_{s,s}(0,0,0)_1$	−3.9783	−4.4868	−1.9922
$P_3=E_{x,x}(0,0,0)_0$	0.6410	1.6600	1.2107
$P_4=E_{x,x}(0,0,0)_1$	2.8741	2.3356	2.3318
$P_5=4E_{s,s}(0.5,0.5,0.5)$	−6.9000	−6.4000	−7.1600
$P_6=4E_{s,x}(0.5,0.5,0.5)_{01}$	5.2400	5.4000	5.2520
$P_7=4E_{s,x}(0.5,0.5,0.5)_{10}$	4.3210	4.0000	4.0500
$P_8=4E_{x,x}(0.5,0.5,0.5)$	2.0000	2.0000	2.0080
$P_9=4E_{x,y}(0.5,0.5,0.5)$	5.5000	5.4600	4.8500
$P_{10}=4E_{x,x}(0,1,1)_0$	−0.3391	−0.8241	−1.1206
$P_{11}=4E_{x,x}(0,1,1)_1$	−1.7563	−1.2025	−1.1670
$P_{12}=4E_{x,y}(1,1,0)_0$	0.6000	0.5500	0.7600
$P_{13}=4E_{x,y}(1,1,0)_1$	0.9600	0.8800	1.3300
$P_{14}=4E_{x,y}(1,1,0)_0$	0.4445	0.2274	0.5522
$P_{15}=4E_{x,x}(1,1,0)_1$	1.1208	0.9831	1.1054
$P_{16}=4E_{s,x}(1,1,0)_0$	0.0452	0.0560	0.0400
$P_{17}=4E_{s,x}(1,1,0)_1$	0.0964	0.0860	0.0730
$P_{18}=4E_{s,s}(1,1,0)_0$	−0.0474	−0.0924	−0.0258
$P_{19}=4E_{s,s}(1,1,0)_1$	−0.0653	−0.1256	−0.0765
$P_{20}=4E_{s,x}(0,1,1)_0$	0.7800	0.8400	0.5400
$P_{21}=4E_{s,x}(0,1,1)_1$	−0.0800	−0.0800	−0.1200
$P_{22}=4E_{x,y}(0,1,1)_0$	0	0	0
$P_{23}=4E_{x,y}(0,1,1)_1$	0	0	0

more careful interpolation scheme, because these parameters represent the nearest-neighbor interaction, and, thus, are expected to be most sensitive to the lattice relaxation due to alloying. It is known that the anion-cation bond does not follow the simple interpolation rule, $xd_{AC}+(1-x)d_{BC}$. For example, the bond lengths of pure elements of GaAs and InAs are 2.448 and 2.623 Å, respectively, but, in $Ga_{1-x}In_xAs$, they vary as $2.448+0.075x$ and $2.623-0.055x$.[7] In order to incorporate this lattice relaxation effect in our calculation, we follow the prescription proposed by Harrison and Ciraci,[8] in which the off-diagonal TB parameters are scaled inversely proportional to the square of the bond length:

$$d_{\text{alloy}}^2 P_i^{\text{alloy}} = x d_{AC}^2 P_i^{AC} + (1-x) d_{BC}^2 P_i^{BC} - \left[\frac{x(1-x)}{N}\right]^{1/2} (P_i^{AC} - P_i^{BC}) \,, \tag{6}$$

for $i=5$–9. Here, for d_{alloy} we use the weighted average. For example, in $Ga_{1-x}In_xAs$

$$d_{\text{alloy}} = x(2.623-0.055x) + (1-x)(2.448+0.075x) \,.$$

We have evaluated the band structure of $Ga_{1-x}In_xAs$ and $Al_xGa_{1-x}As$ using the above formulation. We find that the lattice relaxation effect within our approximation scheme gives almost negligible bowing parameters. Therefore, we conclude that the main contribution to the bowing effect comes from the compositional disorder. The calculated result of $Ga_{1-x}In_xAs$ (Fig. 1) is compared with the experimental result of Van Vechten *et al.*[9] However, for $Al_xGa_{1-x}As$ (Fig. 2) there exist several different experimental data with a substantial spread among them.[10–13] Recently, Fu *et al.* showed that a significant spread of data can arise from the different processes of the preparation of samples in addition to the known limitations in the accuracies of the evaluated gaps and compositions.[14] Therefore, at present, it is not clear which result is best to be compared with the ensemble-

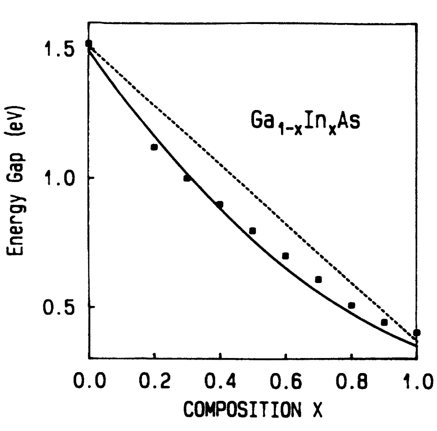

FIG. 1. Calculated values of E_0 gap of $Ga_{1-x}In_xAs$ are compared with experiment: ■, Ref. 9; solid line, present theory; dotted line, VCA.

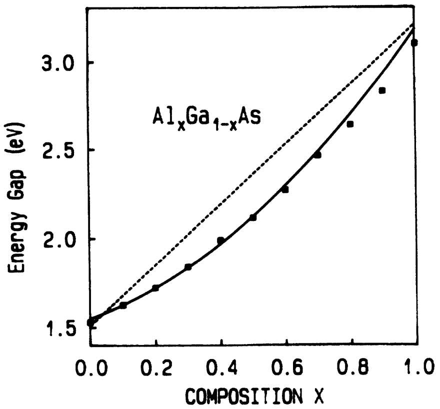

FIG. 2. Calculated values of E_0 gap of $Al_xGa_{1-x}As$ are compared with experiment: ■, Ref. 10; solid line, present theory; dotted line, VCA.

averaged theoretical value, and further experimental study appears necessary. In this Brief Report, we choose the earlier result of Dingle *et al.*,[10] because it exhibits the substantial downward bowing, which is prevalent in other ternary compounds. As can be seen from the figures, the calculations are in excellent agreement with the experiments, particularly considering the fact that our theory does not have any additional adjustable parameters. In the case that other data, such as those of Bosio *et al.*,[13] are to be believed, then the agreement between the theory and the experiment becomes less satisfactory. This may indicate that the nearest-neighbor approximation we used for Eq. (5) is not sufficient and should go beyond the situation discussed in Ref. 4.

In conclusion, a simple TB scheme, which incorporates the compositional disorder as an effective potential and includes the lattice relaxation effect in an approximate fashion, is presented. It is shown that this theory, which does not employ any additional adjustable parameters, satisfactorily accounts for the band-gap bowings found in ternary semiconductor alloys. Also in the process, a physical rationale for the empirical theory of Porod and Ferry[1] is provided.

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