

## Systematic approach to developing empirical potentials for compound semiconductors

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A systematic approach to the derivation of empirical potentials for III-V semiconductors is developed. The validity of the approach is confirmed by the calculations of elastic constants for AlAs, GaAs, and InAs, and of excess energies of various monolayer superlattices. The cohesive energy as a function of volume and atomic displacement for AlAs and GaAs is also investigated by introducing the interatomic potentials for cation-cation and anion-anion pairs. Results compare favorably with the available experimental results and *ab initio* pseudopotential calculations. These empirical potentials for III-V semiconductors should be as accurate as those already existing in the literature for elemental semiconductors.

In recent years there have been several studies in modeling the energetics of covalent systems using empirical interatomic potentials.<sup>1-6</sup> This is because such potentials can be useful for investigating complex systems such as microclusters, amorphous systems, alloys, lattice defects, and surfaces. Most of the studies on semiconductors have, however, focused on silicon because of the difficulty of extending the empirical potentials to other materials.

In attempting to explain the universal cohesive-energy curves for various materials, Abell<sup>7</sup> noted that cohesive energies can be modeled by pairwise interactions moderated by the local environment. Using this idea, Khor and Das Sarma (KD) (Ref. 8) have proposed a universal interatomic potential for carbon, silicon, and germanium. Tersoff<sup>9</sup> has also used this idea to obtain potentials for carbon, silicon, germanium, and their binary systems.

Furthermore, Ito, Khor, and Das Sarma<sup>10</sup> extended the KD potential to elemental semiconductors and their binary-alloy systems, which produced good global fits to cohesive energies for various structures, elastic constants, equilibrium lattice parameters, interplanar distances, and excess energies, thus demonstrating the validity of extending these potentials to binary systems. Motivated by this success, we decided to apply similar interatomic potential ideas to binary-compound semiconductor systems.

In this paper, we describe an attempt for systematically developing empirical potentials for III-V semiconductors based on the rules used to obtain the KD potential. We assume that two basic relationships, as noted by KD, also exist for compound semiconductors, that between the equilibrium atomic spacings of various phases and the coordination number  $Z$ , and that between the corresponding cohesive energies and  $Z$ . We adjust the parameters for these relationships to reproduce the relative stability between zinc-blende and rocksalt structures using data from *ab initio* pseudopotential calculations.<sup>11,12</sup> These potentials are tested by the calculation of elastic constants for III-V semiconductors and the equilibrium lattice parameters and excess energies for monolayer superlattices.

For further confirmation of the validity of this approach, the potentials for Al-Al, Ga-Ga, and As-As pairs are similarly determined using data from *ab initio* pseudopotential calculations.<sup>13-16</sup> The cohesive energy for

zinc-blende, rocksalt,  $\beta$ -Sn(I),  $\beta$ -Sn(II), and CsCl structures are calculated for AlAs and GaAs to check the relative stability among these structures. The cohesive energy as functions of atomic displacements from zinc-blende to rocksalt structures and from zinc blende to  $\beta$ -Sn(I) and  $\beta$ -Sn(II) is also investigated. This is related to the cohesive energy as a function of the local environment or the coordination number.

The cohesive energy  $E_{\text{coh}}$  for semiconductors is obtained from the interatomic potential proposed by Ito, Khor, and Das Sarma<sup>10</sup> (IKD). Potential parameters,  $A$ ,  $B_0$ ,  $\theta$ ,  $\lambda$ ,  $\alpha$ ,  $\beta$ , and  $\gamma$  are determined using experimental cohesive energy,<sup>17</sup> bulk modulus,<sup>18</sup> and the relative stability between zinc-blende and rocksalt structures obtained by *ab initio* pseudopotential calculations.<sup>11,12</sup> The bond-bending constant  $\eta$  is optimized to minimize the difference between the experimental and calculated shear moduli  $c_{44}$  and  $C'$  calculated by the homogeneous deformation method.<sup>19</sup>

The values of the potential parameters and elastic constants and their pressure derivatives for III-V semiconductors are listed in Tables I and II, respectively. Our results are in good agreement with the available experimental data.<sup>18,20</sup> This can be compared with the results obtained by Cowley<sup>21</sup> for three other interatomic potentials where the error in  $c_{44}$  even for Si is in the range of 15%–50%.

The applicability of these interatomic potentials to III-V pseudobinary systems is tested by calculating the equilibrium lattice parameters and excess energies for various monolayer superlattices. This is also a good test for these potentials in reproducing the cohesive-energy change induced by lattice and bond angle distortions. In doing the superlattice calculation, we make two assumptions: one is that the axial ratio  $c/a=1$ , and the other presumes that atom  $C$  in  $AC$ - $BC$  monolayer superlattice is displaced in the [001] direction and atoms  $A$  and  $B$  are located on the regular fcc sublattice (i.e., cubic geometry is retained; the error introduced by this constraint is estimated to be, at most, about 0.0003 for the structural parameter  $u$  and 3 meV/atom for the excess energy  $\Delta E$ ).

Table III lists our results for the structural parameter  $u$  (which gives the bond lengths  $r$  as  $r=a(1/8+u^2)^{1/2}$  and  $a[1/8+(u-\frac{1}{2})^2]^{1/2}$ ), the equilibrium lattice parameters

TABLE I. Potential parameters for AlAs, GaAs, InAs, Al-Al, Ga-Ga, and As-As.

	AlAs	GaAs	InAs	Al-Al	Ga-Ga	As-As
$A(\text{eV})$	2705.7318	2477.8329	-709.0028	6512.8912	7005.5649	4634.8038
$B_0$	0.1145868	0.2494045	1.9778563	0.0037074	0.0044236	0.0810363
$\theta (\text{\AA}^{-1})$	2.96983	2.77083	1.79440	3.85634	3.83929	3.16044
$\lambda (\text{\AA}^{-1})$	1.47405	1.75326	2.35475	0.62525	0.81707	1.54759
$\alpha$	0.5773064	0.4648988	-0.3684513	0.7225517	0.6788446	0.6311375
$\beta$	20.50638	18.51165	12.02834	22.20550	21.87022	18.39756
$\gamma$	3.32415	3.28387	3.20203	3.43356	3.43356	3.32921
$\eta$	0.813787	0.755422	0.137927			

$a$ , and excess energies for the superlattices  $\Delta E$ . The results are compared with  $u_{ab}$  and  $\Delta E_{ab}$  obtained by *ab initio* pseudopotential calculations,<sup>22</sup> and with the lattice parameters  $\bar{a}$  derived by Vegard's law and experimental excess energies  $\Delta E_{ex}$  for disordered alloys at  $x=0.5$ , estimated from interaction parameters<sup>23</sup> and the results of the available first-principles calculations.<sup>22,24-26</sup> Clearly, the calculated results agree well with the reference data and give the expected bimodal distribution of bond lengths. Therefore, the interatomic potentials presented in Table I give reasonable cohesive-energy change induced by small angle distortions and are applicable for the thermodynamic study of pseudobinary systems consisting of III-V semiconductors.

For further confirmation of the validity of these potentials we investigate the change in cohesive energy with large lattice and bond distortions. For this calculation interatomic potentials for cation-cation and anion-anion pairs are necessary. In this paper, AlAs and GaAs are regarded as prototypical examples for the calculation of the cohesive energy as functions of volume and atomic displacements because of the particular importance of these materials.

We adopt interatomic potentials for Al-Al, Ga-Ga, and As-As pairs of the IKD form, except that we neglect bond bending. This seems to be reasonable, since it implies that the contribution from the second-nearest neighbors in the bond-bending term is negligible.<sup>8</sup> The potential parameters

are determined using experimental cohesive energy,<sup>27</sup> bulk modulus, and the relative stability between fcc and bcc structures for Al (Ref. 13) and Ga,<sup>14</sup> simple-cubic and bcc structures for As (Refs. 15 and 16) obtained from *ab initio* pseudopotential calculations. The equilibrium lattice constant for fcc Ga is taken to be 3.85 Å.<sup>14</sup> The calculated potential parameter values are listed in Table I.

The results of cohesive energy as a function of volume for AlAs and GaAs are shown in Figs. 1(a) and 1(b), respectively. The volume-energy relationships are displayed for zinc-blende (1), rocksalt (2),  $\beta$ -Sn(I) (3), CsCl (4), and  $\beta$ -Sn(II) (5) structures. We note that cation-cation and anion-anion pairs contribute to the cohesive energy for  $\beta$ -Sn(I), CsCl, and  $\beta$ -Sn(II) structures. Comparing our results with the results from *ab initio* calculations,<sup>11,12,28</sup> the overall agreement for the relative stability among various structures is quite good.

The cohesive-energy behavior as a function of the axial ratio  $c/a$  for GaAs at  $V/V_0=0.73$  (the phase-transition volume) is shown in Fig. 2(a). This corresponds to the cohesive energy as a function of coordination number  $Z$ , which varies from  $Z=4$  (zinc blende) to  $Z \cong 5$  [ $\beta$ -Sn(I)] and  $Z \cong 8$  [ $\beta$ -Sn(II)]. The calculated results in this study (solid line) qualitatively agree with the results of *ab initio* pseudopotential calculations (dotted line).<sup>11</sup> As can be clearly seen, three energy minima such as  $\beta$ -Sn(I) (3), zinc-blende (1), and  $\beta$ -Sn(II) (5) structures are found in this figure. The axial ratio  $c/a$  of  $\beta$ -Sn(I) is equal to 0.43, which is in good agreement with  $c/a \cong 0.41$  obtained by *ab initio* pseudopotential calculations.

Furthermore, the behavior of cohesive energy as the

TABLE II. Elastic constants, in N/m<sup>2</sup>, and their pressure derivatives at atmospheric pressure. The values in parentheses are experimental results.

	AlAs	GaAs	InAs
$c_{11}$	1.249(1.202) <sup>a</sup>	1.228(1.181)	0.837(0.833)
$c_{12}$	0.547(0.570) <sup>a</sup>	0.509(0.532)	0.451(0.453)
$c_{44}$	0.524(0.589) <sup>a</sup>	0.528(0.592)	0.390(0.396)
$C'$	0.351(0.316) <sup>a</sup>	0.360(0.325)	0.193(0.190)
$B$	0.781(0.781) <sup>a</sup>	0.748(0.748)	0.580(0.580)
$dc_{44}/dp$		1.360(1.10)	
$dC'/dp$		0.142(0.055)	
$dB/dp$		4.018(4.56)	

<sup>a</sup>The elastic constants for AlAs are derived from the empirical relationship between elastic constants and lattice parameters for III-V semiconductors [S. Adachi, J. Appl. Phys. **58**, R1 (1985)].

TABLE III. Equilibrium structural parameters  $u$ , equilibrium lattice parameters  $a$  (in Å), and excess energies  $\Delta E$  (in meV) for III-V monolayer superlattices, compared with  $u_{ab}$ ,  $\bar{a}$  (both in parentheses), and  $\Delta E_{ab}$ ,  $\Delta E_{ex}$ , respectively.

	(AlAs) <sub>1</sub> (GaAs) <sub>1</sub>	(GaAs) <sub>1</sub> (InAs) <sub>1</sub>
$u(u_{ab})$	0.251(0.25) <sup>a</sup>	0.262(0.267) <sup>a</sup>
$a(\bar{a})$	5.658(5.658)	5.840(5.845)
$\Delta E$	0.01	21.95
$\Delta E_{ab}$	3.9, <sup>a</sup> 2.7 <sup>b,c</sup>	20.9, <sup>a</sup> 15.0 <sup>d</sup>
$\Delta E_{ex}$	0.00	18.0, 21.7, 32.5

<sup>a</sup>Reference 22.

<sup>b</sup>Reference 24.

<sup>c</sup>Reference 25.

<sup>d</sup>Reference 26.

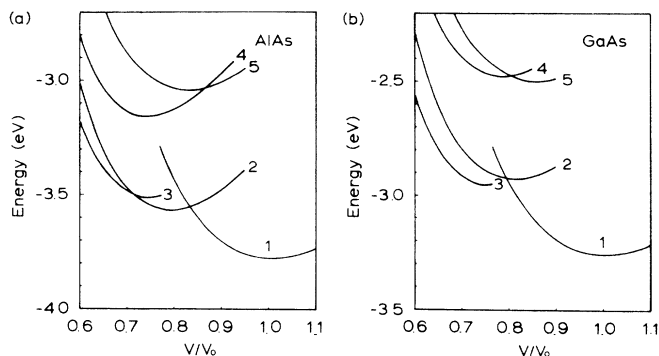


FIG. 1. Calculated cohesive-energy change for (a) AlAs and (b) GaAs for zinc-blende (1), rocksalt (2),  $\beta$ -Sn(I) (3), CsCl (4), and  $\beta$ -Sn(II) (5) structures as a function of volume ratio  $V/V_0$ .

phase varies from zinc-blende ( $Z=4$ ) to rocksalt ( $Z=6$ ) structures is shown in Fig. 2(b). The qualitative agreement between the results in this study (solid line) and in *ab initio* pseudopotential calculations (dotted line) (Ref. 11) is quite good. Based on this we conclude that our interatomic potentials for III-V semiconductors including cation-cation and anion-anion pairs are applicable to situations with large lattice distortion and bond bending, although bond bending should be taken into account to produce the correct activation barrier among various structures.

In conclusion, we have proposed empirical interatomic potentials for III-V semiconductors based on our earlier universal potential.<sup>8,10</sup> We have tested the validity of our proposed potentials by calculating elastic constants, cohesive energy as functions of volume and atomic displacement, and excess energies for various III-V monolayer superlattices. Although the contribution of charge transfer associated with the ionic character of III-V semiconductors, which is left out of our potential, should be taken into account in subsequent improvement of the potential formulation (particularly for the calculation of phonon dispersion), these proposed potentials are as accu-

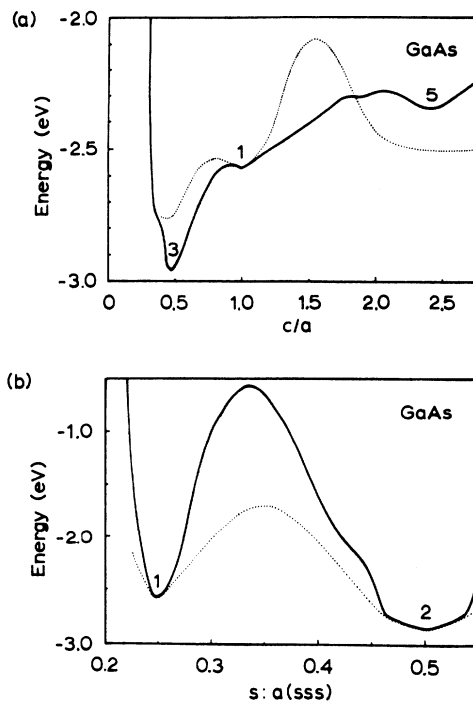


FIG. 2. Calculated cohesive-energy change for GaAs as functions of (a) axial ratio  $c/a$  and (b) atomic position  $s: a(sss)$  for As along the body diagonal in the cubic unit cell.

rate as those currently existing for the elemental semiconductors.<sup>1-6</sup> More detailed numerical results for our potential, including parameters for II-VI materials and calculated defect energies, will be published in a future publication.

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<sup>1</sup>F. Stillinger and T. Weber, Phys. Rev. B **31**, 5262 (1985).

<sup>2</sup>R. Biswas and D. R. Hamann, Phys. Rev. Lett. **55**, 2001 (1985); Phys. Rev. B **36**, 6434 (1987).

<sup>3</sup>J. Tersoff, Phys. Rev. Lett. **56**, 632 (1986).

<sup>4</sup>B. W. Dodson, Phys. Rev. B **35**, 2795 (1987).

<sup>5</sup>M. I. Baskes, Phys. Rev. Lett. **59**, 2666 (1987).

<sup>6</sup>J. R. Chelikowsky, J. C. Phillips, M. Kamal, and M. Strauss, Phys. Rev. Lett. **62**, 292 (1989).

<sup>7</sup>G. C. Abell, Phys. Rev. B **31**, 6184 (1984).

<sup>8</sup>K. E. Khor and S. Das Sarma, Phys. Rev. B **38**, 3318 (1988).

<sup>9</sup>J. Tersoff, Phys. Rev. B **39**, 5566 (1989).

<sup>10</sup>T. Ito, K. E. Khor, and S. Das Sarma, Phys. Rev. B **40**, 9715 (1989).

<sup>11</sup>S. Froyen and M. L. Cohen, Phys. Rev. B **28**, 3258 (1983).

<sup>12</sup>S. B. Zhang and M. L. Cohen, Phys. Rev. B **35**, 7604 (1987).

<sup>13</sup>P. K. Lam and M. L. Cohen, Phys. Rev. B **24**, 4224 (1981); **27**, 5986 (1983).

<sup>14</sup>G. X. Qian, R. M. Martin, and D. J. Chadi, Phys. Rev. B **38**, 7649 (1989); G. X. Qian (private communication). The similarity between Al and Ga is pointed out in this paper. Therefore, we employed the same values of slopes for  $r_e - \ln(Z)$  and  $r_e - \ln(E_{\text{coh}}/Z)$  relationships of Al and cohesive energy for fcc Ga to be 0.2 eV/atom higher than that of orthorhombic Ga in determining the potential parameters for Ga based on the results in this paper.

<sup>15</sup>R. J. Needs, R. M. Martin, and O. H. Nielsen, Phys. Rev. B **33**, 3778 (1986).

<sup>16</sup>T. Sasaki, K. Shindo, and K. Niizeki, Solid State Commun. **67**, 569 (1988).

<sup>17</sup>W. A. Harrison, *Electronic Structure and the Properties of Solids* (Freeman, New York, 1980).

<sup>18</sup>R. M. Martin, Phys. Rev. B **1**, 4005 (1970).

<sup>19</sup>D. C. Wallace, Rev. Mod. Phys. **37**, 57 (1965).

<sup>20</sup>V. K. Garg, D. S. Puri, and M. P. Verma, Phys. Status Solidi

- B 87, 401 (1978).
- <sup>21</sup>E. R. Cowley, *Phys. Rev. Lett.* **60**, 2379 (1988).
- <sup>22</sup>P. Boguslawski and A. Baldereschi, *Phys. Rev. B* **39**, 8055 (1989).
- <sup>23</sup>G. B. Stringfellow, *J. Cryst. Growth* **27**, 21 (1974).
- <sup>24</sup>D. M. Bylander and L. Kleinman, *Phys. Rev. B* **34**, 5280 (1986); **36**, 3229 (1987).
- <sup>25</sup>D. M. Wood, S.-H. Wei, and A. Zunger, *Phys. Rev. Lett.* **58**, 1123 (1987).
- <sup>26</sup>T. Ohno, *Phys. Rev. B* **38**, 13 191 (1988).
- <sup>27</sup>C. Kittel, *Introduction to Solid State Physics*, 5th ed. (Wiley, New York, 1976).
- <sup>28</sup>J. R. Chelikowsky, *Phys. Rev. B* **34**, 5295 (1986).