PHYSICAL REVIEW B VOLUME 36, NUMBER 18 15 DECEMBER 1987-II

Bonds in III-V quaternary alloy semiconductors of $A^{\mathrm{III}}_{1-x}B^{\mathrm{III}}_{x}C^{\mathrm{V}}_{1-y}D^{\mathrm{V}}_{y}$ type

Masaya Ichimura and Akio Sasaki
Department of Electrical Engineering, Kyoto University, Kyoto 606, Japan

(Received 8 June 1987)

Relative numbers or statistics of bonds in III-V quaternary alloy semiconductors of $A^{\mathrm{III}}_{1-x}B^{\mathrm{III}}_{x}C^{\mathrm{V}}_{1-y}D^{\mathrm{V}}_{y}$ type are uniquely determined through a thermodynamical approach in which the cohesive and the strain energies of bonds are taken as the enthalpy in the analysis. The valence-force-field model is used for calculating the strain energy, and the effect of local environment on the bond strain is considered. The analysis is applied to nine different quaternary alloy semiconductors composed of two elements of Al, Ga, or In as the group-III elements and two elements of P, As, or Sb as the group-V elements. The strain energy is a predominant factor in $\mathrm{In}_{1-x}\mathrm{Ga}_{x}C^{\mathrm{V}}_{1-y}D^{\mathrm{V}}_{y}$ ($C^{\mathrm{V}},D^{\mathrm{V}}=\mathrm{P,As,Sb}$), the cohesive energy is a predominant factor in $\mathrm{Ga}_{1-x}\mathrm{Al}_{x}C^{\mathrm{V}}_{1-y}D^{\mathrm{V}}_{y}$, and both factors compensate each other almost completely in $\mathrm{In}_{1-x}\mathrm{Al}_{x}C^{\mathrm{V}}_{1-y}D^{\mathrm{V}}_{y}$. The results are interpreted on the basis of the bond-length dependence of each energy.

I. INTRODUCTION

The lattice constant and band gap of a III-V quaternary alloy semiconductor can be changed independently, and thus layers with different compositions can be grown on a certain substrate with lattice matching. This makes quaternary alloys indispensable for many electrical and optical devices. However, fundamental properties of quaternary alloys such as the composition dependence of the energy gap have not been fully understood: They were experimentally determined or often estimated by interpolation from relevant binary compounds and ternary alloys. However, for quaternary alloys of $A^{\mathrm{III}}_{1-x}B^{\mathrm{III}}_{x}C^{\mathrm{V}}_{1-y}D^{\mathrm{V}}_{y}$ type, the approach based on interpolation cannot avoid some ambiguity.[1] For example, one can regard the $\mathrm{In}_{0.5}\mathrm{Ga}_{0.5}\mathrm{As}_{0.5}\mathrm{P}_{0.5}$ alloy as a 1:1 mixture of either InP and GaAs or InAs and GaP. It arises from the ambiguity in the statistics of bonds that the relative numbers of each bond cannot be uniquely determined from a global atomic composition.[2,3] It will be easy to see that various ratios of bonds yield the same atomic composition. For III-V ternary alloys, there is no such ambiguity; for example, the relative number of In—As bonds in $\mathrm{In}_{1-x}\mathrm{Ga}_{x}\mathrm{As}$ is always $1-x$. This holds for quaternary alloys of $A^{\mathrm{III}}_{1-x-y}B^{\mathrm{III}}_{x}C^{\mathrm{III}}_{y}D^{\mathrm{V}}$ and $D^{\mathrm{III}}A^{\mathrm{V}}_{1-x-y}B^{\mathrm{V}}_{x}C^{\mathrm{V}}_{y}$ type, too. In quaternary alloys of $A^{\mathrm{III}}_{1-x}B^{\mathrm{III}}_{x}C^{\mathrm{V}}_{1-y}D^{\mathrm{V}}_{y}$ type, two species of atoms are distributed on each of group-III and group-V sublattices. Thus the statistics of bonds, formed between group-III and group-V atoms, depend on the distribution of atoms in the sublattices. The ambiguity in the statistics of bonds would cause difficulties in predicting various material parameters, since properties of III-V semiconductors are mainly determined by characters of bonds.[4] Thus it is a fundamental and important task to investigate the statistics of bonds in quaternary alloy semiconductors of $A^{\mathrm{III}}_{1-x}B^{\mathrm{III}}_{x}C^{\mathrm{V}}_{1-y}D^{\mathrm{V}}_{y}$ type.

The relative number of bonds at the thermal equilibrium state can be derived through thermodynamical consideration. However, most of thermodynamical analyses on quaternary alloy systems are based on the regular solution approximation,[5] i.e., taking an atom as a basic figure. Thus it gives no information on the statistics of bonds. A few theories which take a bond as a basic figure have been proposed.[2,3] Our approach also takes a bond as a basic figure but is different from them in the estimation of the enthalpy; we consider the strain energy as the major portion of the mixing enthalpy and take into account the effect of the local environment on the strain of each bond.

For both ternary[6–9] and quaternary alloys,[10] the calculated strain energy was found to be comparable to the experimentally determined mixing enthalpy. This indicates that the strain energy is the main energetical interaction among constituent compounds in III-V alloys. In previous papers we showed that the strain energy can influence the atom arrangement in III-V ternary alloys.[9,11] Since the strain energy of quaternary alloys is no less than those of the relevant ternary alloys,[10] it would influence the atom arrangement of $A^{\mathrm{III}}_{1-x}B^{\mathrm{III}}_{x}C^{\mathrm{V}}_{1-y}D^{\mathrm{V}}_{y}$ quaternary alloys, too.

In order to calculate the strain energy, the atomic scale structure is necessary to be considered. Recently, the results of fluorescence-detected extended x-ray-absorption fine-structure (EXAFS) measurement on $\mathrm{In}_{1-x}\mathrm{Ga}_{x}\mathrm{As}_{1-y}\mathrm{P}_{y}$ were reported.[12] It shows that, as in ternary alloys,[13] each bond length in $\mathrm{In}_{1-x}\mathrm{Ga}_{x}\mathrm{As}_{1-y}\mathrm{P}_{y}$ tends to preserve that in the constituent binary compound. Thus the virtual-crystal approximation (VCA), which assumes an undistorted zinc-blende structure, is not a good approximation for bond lengths in III-V quaternary alloys: The lattice tends to relax for the reduction in the strain energy of bonds. We found[14] that the bond lengths in $\mathrm{In}_{1-x}\mathrm{Ga}_{x}\mathrm{As}_{1-y}\mathrm{P}_{y}$ can be correctly estimated by using the valence-force-field (VFF) model. In this work, too, we use the VFF model to calculate the strain energy taking into account the deviation of atoms from the VCA atom sites. In addition, we take into account effects of local environment on the strain of bonds: The strain of a bond is expected to depend on what bonds are its neighbors, and various local arrangements are possible around a single kind of bond because of the randomness in the atom arrangement.

In Sec. II we qualitatively discuss the factors which determine the statistics of bonds, and then the calculation procedure of the free energy including the mixing entropy and enthalpy is described in Sec. III in detail. Calculation results are given in Sec. IV for nine quaternary alloy systems, and then we interpret the results in Sec. V.

II. ENERGETICAL INTERACTION IN QUATERNARY ALLOYS

Statistics of bonds must be consistent with the atomic composition. For example, the sum of the relative numbers of A—C and A—D bonds should not contradict the composition ratio of the A atom in the $A^{\mathrm{III}}_{1-x}B^{\mathrm{III}}_{x}C^{\mathrm{V}}_{1-y}D^{\mathrm{V}}_{y}$ alloy. Because of these constraints, the statistics of bonds are expressed by a single variable ξ which is defined in Sec. III. Here, we shall note that A—C and B—D bonds simultaneously increase or decrease by the same amount, and so do A—D and B—C bonds.[2,3]

To determine the relative numbers of bonds, we take into account the following two factors: (i) cohesive energy and (ii) strain energy of each bond. The strain energy here corresponds to a change in the cohesive energy of a bond. Thus, in fact, we consider only one kind of interaction, i.e., cohesive energy of bonds. This can be justified by the fact that the cohesion of the III-V crystal is mainly due to the formation of bonds.[4] In factor (i) we consider cohesive energy in unstrained bonds, and then the strain energy is included in factor (ii). Since the strain energy was found to be comparable to the mixing enthalpy for quaternary alloys,[10] the strain energy would be dominant as compared with other interactions, e.g., chemical interaction between the second nearest-neighbor pair. We will discuss it in Sec. V.

The effect of factor (i) on the statistics of bonds is easily understood: The number of bonds with large cohesive energy tends to increase at the thermal equilibrium. Since the numbers of two kinds of bonds increase or decrease simultaneously, the sum of cohesive energy of these two bonds determines whether they will increase or decrease. For example, A—C bonds and thus B—D bonds increase if the sum of cohesive energy of them is larger than that of A—D and B—C bonds.

Next, we turn to factor (ii), i.e., the strain energy. In the following consideration and analysis, we assume that the lattice coherency is retained throughout a whole crystal. This assumption is crucial for the discussion about the effect of the strain energy on the atom arrangement. If the lattice coherency is broken, for example, with the generation of many dislocations, the strain is relaxed, and then the amount of the strain energy is significantly reduced. However, this is not the case with high-quality materials used for device applications. In addition, a quaternary alloy is usually grown epitaxially onto a lattice-matched substrate, and the lattice coherency would be retained quite well. Thus it is necessary to consider the strain energy.

Before discussing the effect of strain energy for quaternary alloys, we briefly describe it for ternary alloys.[7,8] When an alloy $A^{\mathrm{III}}_{0.5}B^{\mathrm{III}}_{0.5}C^{\mathrm{V}}$ is decomposed into two separate alloy crystals, e.g., $A^{\mathrm{III}}_{0.7}B^{\mathrm{III}}_{0.3}C^{\mathrm{V}}$ and $A^{\mathrm{III}}_{0.3}B^{\mathrm{III}}_{0.7}C^{\mathrm{V}}$, then the strain energy in each alloy decreases because the strain energy of ternary alloys is maximum at the composition $x=0.5$.[8,9] However, if the lattice coherency is retained between these two crystals, they strain each other because of their different lattice constants. The amount of this strain would depend on the shape and size of each decomposed region or on whether they are on a substrate. In all cases, the coexistence of two or more different composition regions or the composition fluctuations in lattice-coherent semiconductors causes some excess strain energy. This would imply that the strain energy does not simply cause the creation of the composition fluctuation.

Such a mechanism cannot be applied to quaternary alloys, because the different composition regions can have an equal lattice constant. For example, if $\mathrm{In}_{0.6}\mathrm{Ga}_{0.4}\mathrm{As}_{0.9}\mathrm{P}_{0.1}$ is decomposed into $\mathrm{In}_{0.74}\mathrm{Ga}_{0.26}\mathrm{As}_{0.58}\mathrm{P}_{0.42}$ and $\mathrm{In}_{0.53}\mathrm{Ga}_{0.47}\mathrm{As}$, all of which are lattice-matched to InP, no excess strain is caused between these two regions.

Consider an alloy system $A^{\mathrm{III}}_{1-x}B^{\mathrm{III}}_{x}C^{\mathrm{V}}_{1-y}D^{\mathrm{V}}_{y}$ in which the lattice constant of binary compound AD is equal to that of BC but there is a large difference in lattice constant between AC and BD. Although such an alloy system is hypothetical, it is very similar to $\mathrm{In}_{1-x}\mathrm{Ga}_{x}\mathrm{Sb}_{1-y}\mathrm{As}_{y}$: The lattice mismatch between InAs and GaSb is 0.76%, while that between GaAs and InSb is 14%. If the atom arrangement is random, an alloy $A^{\mathrm{III}}_{0.5}B^{\mathrm{III}}_{0.5}C^{\mathrm{V}}_{0.5}D^{\mathrm{V}}_{0.5}$ is composed of four kinds of bonds. Then, large strain energy is stored in this alloy because of the difference in length among three of four bonds. Assume that it is decomposed into two regions AD and BC. Then, the crystal is composed of A—D and B—C bonds only. Since their lengths are the same, they do not strain each other. Thus the strain energy is decreased down to zero by such decomposition, even if the lattice coherency is retained between two regions.

Noting that bonds increase or decrease in pairs, we could generalize the above effect as follows: The strain energy would decrease with increasing the pair of smaller length difference, such as A—D and B—C bond pairs in the above case. If, on the contrary, the pair of larger length difference increases, the strain energy would increase because these two bonds largely strained each other. This tendency is confirmed by the calculation described in later sections.

Therefore, we should consider the following two factors to determine the statistics of bonds: (i) cohesive energy of bonds and (ii) strain energy. In a general case, A—C bonds and thus B—D bonds may increase when

(i) the sum of cohesive energy of A—C and B—D bonds is larger than that of A—D and B—C bonds, and/or (ii) the length difference between A—C and B—D bonds is smaller than that between A—D and B—C bonds. The effects of these two factors are investigated more quantatively in the next two sections.

III. FREE ENERGY OF QUATERNARY ALLOY

The free energy is expressed by

$$F=H_b+H_s-TS \ , \tag{1}$$

where H_b is the enthalpy due to the cohesive energy of bond, i.e., factor (i) in the last section, H_s the strain energy, i.e., factor (ii), and TS the product of the entropy S and the temperature T. The statistics of bonds at the equilibrium state are obtained by minimizing F with respect to relative numbers of bonds.

A. Relative numbers of bonds and the entropy

Not all of the relative numbers of bonds are independent variables for a given atomic composition. They are conveniently expressed by using a single variable ξ as follows:[3]

$$\begin{aligned} x_{AC}&=x_Ax_C+\xi, \quad x_{BC}=x_Bx_C-\xi \ , \\ x_{AD}&=x_Ax_D-\xi, \quad x_{BD}=x_Bx_D+\xi \ , \end{aligned} \tag{2}$$

where x_{pq} is the relative number of the p—q bond, and x_p is the composition of atom p and satisfies the relation $x_A+x_B=1$ or $x_C+x_D=1$. It is easy to see that the statistics of bonds given by Eq. (2) is always consistent with the atomic composition. The ξ becomes zero if the atom arrangement is completely random.

The approximate entropy of mixing S was derived as follows:[2]

$$S=Nk_B\left[-4\sum_{pq}x_{pq}\ln x_{pq}+3\sum_{p}x_p\ln x_p\right] \ , \tag{3}$$

where N is the number of group-III (V) atoms and k_B the Boltzmann constant.

B. Cohesive energy

The enthalpy due to the cohesion of bonds, H_b, is written as

$$H_b=4N\sum_{p,q}x_{pq}h_{pq} \ , \tag{4}$$

where h_{pq} is the enthalpy due to the cohesion of an unstrained p—q bond. As noted earlier, the strain energy is taken separately into account by the term H_s. $4N$ is the total number of bonds. It should be noted that the bond is less stable with the smaller value of $|h_{pq}|$ since h_{pq} is the enthalpy. h_{pq} is a negative value, and its absolute value corresponds to the amount of cohesive energy.

With the use of Eq. (2), H_b can be rewritten as follows:

$$\begin{aligned} H_b&=H_0+\xi\omega_b \ , \\ H_0&=4N\sum_{p,q}x_px_qh_{pq} \ , \\ \omega_b&=4N[(h_{AC}+h_{BD})-(h_{AD}+h_{BC})] \ . \end{aligned} \tag{5}$$

If the quaternary alloy system $A^{\rm III}_{1-x}B^{\rm III}_xC^{\rm V}_{1-y}D^{\rm V}_y$ is an ideal solution, there is no strain energy in the alloy and the atom arrangement is completely random. Then the total enthalpy becomes H_0. Since H_0 is uniquely determined by the composition, only $\xi\omega_b$ is necessary to consider for the determination of statistics of bonds.

Since h_{pq} is defined as the enthalpy for the unstrained p—q bond, we can derive it from the thermodynamical properties of the binary compound pq, which consists of unstrained bonds. The entropy of mixing is zero for a binary compound, and the cohesion of crystal is considered to be solely due to bonds in our model. Thus $4Nh_{pq}=\mu_{pq}$ corresponds to the free energy or chemical potential of the binary compound pq. ω_b can be calculated by

$$\omega_b=(\mu_{AC}+\mu_{BD})-(\mu_{AD}+\mu_{BC}) \ . \tag{6}$$

The values of the equivalent of ω_b have already been obtained for nine III-V quaternary alloy systems in Ref. 15.

C. Strain energy

The strain of each bond is affected by what kinds of bonds surround it; for example, the bond tends to be greatly compressed when surrounded by bonds longer than the average bond length. In our model the strain energy of a bond is calculated in each tetrahedron cell. We have assumed for ternary alloy that the strain of a bond is determined in various types of tetrahedra where a central site is occupied by a common element and surrounding sites by mixed elements.[9,11] For quaternary alloys, we need to consider both the group-III and the group-V tetrahedra; for example, the B—C bond represented by the double line in Fig. 1 is simultaneously contained in an $A(3)B(1)$ (group III) tetrahedron and a $C(2)D(2)$ (group V) tetrahedron. In general, a B—C bond can be contained in $A(4-i)B(i)$ for $i=1$–4 and

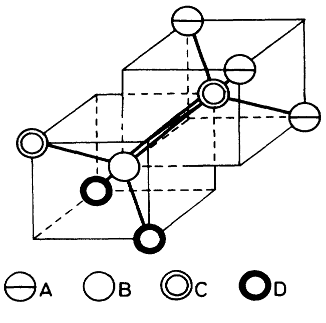

FIG. 1. Tetrahedra in the quaternary alloy $A_{1-x}B_xC_{1-y}D_y$. The B—C bond represented by a double line is included in $A(3)B(1)$ (group III) and $C(2)D(2)$ (group V) tetrahedra.

$C(4-k)D(k)$ for $k=0$–3 tetrahedra. Note that tetrahedra without either B or C atoms cannot contain the B—C bond. Thus there are 16 kinds of local environments for B—C bonds in an alloy, and the B—C bond can have 16 different amounts of strain energy, one for each local environment.

Another factor influencing the bond strain is the total average bond length of the crystal within which the tetrahedra are embedded; for example, a bond length in a certain type of tetrahedron would decrease when the averaged lattice constant of the crystal decreases. Therefore, in our model, the strain energy of a bond is determined from (a) the type of group-III tetrahedron, (b) the type of group-V tetrahedron, and (c) the average bond length.

In calculating the strain energy in quaternary alloys, we consider the unit cell such as shown in Fig. 2. It should be noted that the crystal represented by this unit cell consists of only $A(3)B(1)$ and $C(2)D(2)$ tetrahedra. Thus the B—C bond (double line) in Fig. 1 and that in Fig. 2 are surrounded by the same tetrahedra. Although some other $A(3)B(1)$ and $C(2)D(2)$ unit cells are possible, they are all obtained by symmetric operations from the cell in Fig. 2, and thus all of them are equivalent. Let the size of the unit cell be equal to the lattice constant of the alloy in which the tetrahedra shown in Fig. 1 are embedded. Then, with respect to the above (a), (b), and (c), the environment around the B—C bond in Fig. 1 is the same as that in Fig. 2, and thus the strain energy is considered equal for both B—C bonds in our model. The lattice constant of the alloy is calculated from the atomic compositions by using the Vegard law.

The strain calculation in the unit cell was carried out by the same procedure as in the previous work,[14] i.e., the VFF model by Martin[16] was used, and the deviation from VCA structure was taken into account for both sublattices. First, calculation was done for the case where the size of the unit cell is equal to the average lattice constant weighted by the composition of that cell. The amounts of bond angle distortion and/or length deviation are quite different among unit cells. Then, we calculated the strain for several unit cells varying the size of the cell. The results show that the angles between bonds depend little on the size of the cell. This indicates that the angle distortion energy depends weakly on the size of the cell. Thus we can assume that the change in the cell size does not much influence the angle distortion energy. It does influence the length deviation energy: If the size of the unit cell changes by Δa, each bond within it changes by $(\sqrt{3}/4)\Delta a$. The strain energy of, for example, a B—C bond in the $A(4-l)B(i)C(4-k)D(k)$ unit cell is expressed as

$$\varepsilon_{BC}(i,k)=\tfrac{1}{2}\varepsilon^{a}_{BC}(i,k)+\tfrac{3}{2}\alpha_{BC}\{d^{0}_{BC}-d_{BC}(i,k)\}^{2}\ , \tag{7}$$

where $\varepsilon^{a}_{BC}(i,k)$ is the strain energy stored in the angles between the B—C bond and its neighbors. The factor $\frac{1}{2}$ appears because the strain energy of each angle will be counted twice when the strain energy for all bonds is summed up. The second term is the length deviation energy of the B—C bond.[16] Here, d^{0}_{BC} and α_{BC} are the unstrained bond length and the elastic constant of length deviation of the B—C bond, respectively, and $d_{BC}(i,k)$ is the length of the B—C bond in the $A(4-i)B(i)C(4-k)D(k)$ unit cell. It was assumed that the size of a unit cell does not influence $\varepsilon^{a}_{BC}(i,k)$ but $d_{BC}(i,k)$, as discussed above.

The strain energy of all B—C bonds in an alloy is given by

$$H_s^{BC}=4N\sum_{i,k}P_{BC}(i,k,\xi)\varepsilon_{BC}(i,k)\ , \tag{8}$$

where $P_{BC}(i,k,\xi)$ is the relative number of B—C bonds contained in $A(4-i)B(i)$ and $C(4-k)D(k)$ tetrahedra, and given by

$$P_{BC}(i,k,\xi)={}_3C_{i-1}\,{}_3C_k\,\frac{x_{AC}^{4-i}x_{BC}^{i+4-k}x_{BD}^{k}}{x_B^3x_C^3}\ , \tag{9}$$

where ${}_3C_m$ is the combination number and zero when $m=0,4$. For other bonds, i and $4-i$ (k and $4-k$) can be exchanged according to the exchange between A and B (C and D). $P_{pq}(i,k,\xi)$ satisfies

$$\sum_{i,k}P_{pq}(i,k,\xi)=x_{pq}\ . \tag{10}$$

The total strain energy is expressed by

$$H_s=\sum_{p,q}H_s^{pq}=4N\sum_{p,q}\sum_{i,k}P_{pq}(i,k,\xi)\varepsilon_{pq}(i,k)\ . \tag{11}$$

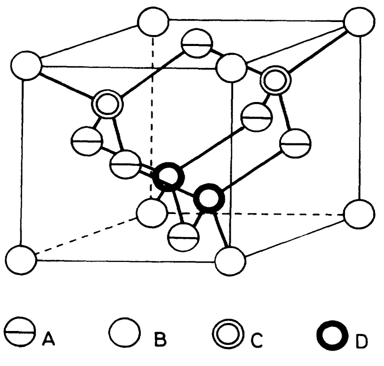

FIG. 2. Zinc-blende-like unit cell which consists of $A(3)B(1)$ and $C(2)D(2)$ tetrahedra.

IV. CALCULATION RESULTS

A. $In_{1-x}Ga_xAs_{1-y}P_y$

First, we show the results of the $In_{1-x}Ga_xAs_{1-y}P_y$ system and describe how each term influences the equilibrium value of ξ. Figure 3 shows H_s, $\omega_b\xi$, and TS as functions of ξ for the composition $x=0.5$ and $y=0.5$ at the temperature $T=1000$ K. The mixing free energy F_m is the sum of these three terms and differs from the total free energy F by H_0, which is independent of ξ. ξ_0 represents the equilibrium value of ξ at which F_m is minimum. As seen from Fig. 3, H_s increases with ξ, while $\omega_b\xi$ decreases. Thus their effects compensate each other to some extent, and ξ_0 is close to zero because of

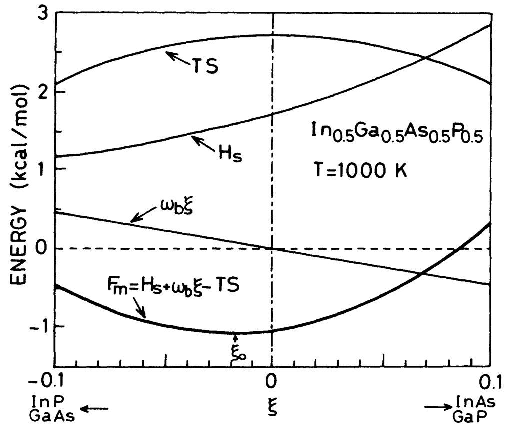

FIG. 3. Strain energy H_s, cohesive energy term $\omega_b\xi$, entropy term TS, and the mixing free energy $F_m = H_s + \omega_b\xi - TS$ as functions of ξ for $\mathrm{In_{0.5}Ga_{0.5}As_{0.5}P_{0.5}}$ at $T = 1000$ K. Positive (negative) ξ indicates more In—As and Ga—P (Ga—As and In—P) bonds. F_m is minimum at $\xi = -0.018$.

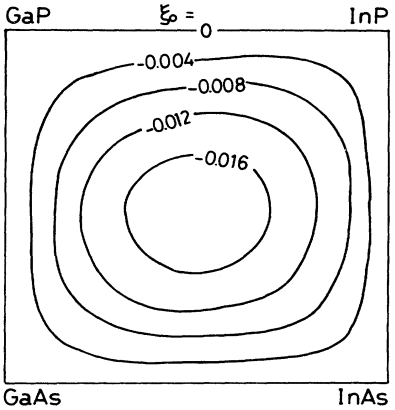

FIG. 5. Composition dependence of the equilibrium value of ξ for $\mathrm{In}_{1-x}\mathrm{Ga}_x\mathrm{As}_{1-y}\mathrm{P}_y$ at $T = 1000$ K.

TS being maximum at $\xi = 0$. However, because the slope of H_s near $\xi = 0$ is somewhat larger than that of $\omega_b\xi$, ξ_0 becomes negative (-0.018). The dependence of H_s on ξ is in accordance with our prediction that H_s will decrease if the pair of bonds with the smaller length difference increases. In the $\mathrm{In}_{1-x}\mathrm{Ga}_x\mathrm{As}_{1-y}\mathrm{P}_y$ system, $d_{\mathrm{InP}} - d_{\mathrm{GaAs}} = 0.093$ Å and $d_{\mathrm{InAs}} - d_{\mathrm{GaP}} = 0.263$ Å.

Figure 4 shows the temperature dependence of ξ_0 for $x = 0.5$ and $y = 0.5$. At low temperatures, TS is negligible, and thus $H_s + \omega_b\xi$ determines ξ_0. The result near $T = 0$ K indicates that $H_s + \omega_b\xi$ is minimum at $\xi = -0.09$. As T increases, the entropy term begins to dominate, and ξ_0 is close to zero at temperatures of usual crystal growth.

The composition dependence of ξ_0 at 1000 K is shown in Fig. 5. ω_b is independent of the composition as seen in Eq. (5). The value of H_s depends on the composition rather strongly, but the slope of H_s at $\xi = 0$ depends weakly; the slope varies within ±15% from that at $x = 0.5$ and $y = 0.5$. Thus the dependence in Fig. 5 is mainly influenced by change in the entropy. A certain amount of deviation of ξ from zero causes a larger decrease in S, as x or y approaches zero or unity. In addition, the variable range of ξ diminishes:

$$-\min\{(1-x)(1-y), xy\} < \xi < \min\{(1-x)y, x(1-y)\}\ , \qquad (12)$$

since $x_{pq} > 0$. [Refer to Eq. (2).] For ternary alloys and binary compounds, there is no freedom in the statistics of bonds, i.e., ξ is always zero.

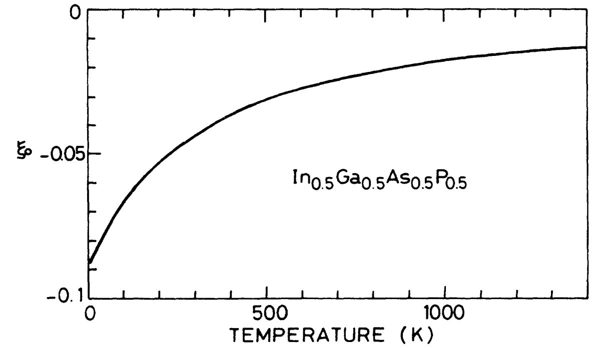

FIG. 4. Temperature dependence of the equilibrium value of ξ for $\mathrm{In_{0.5}Ga_{0.5}As_{0.5}P_{0.5}}$.

B. Other quaternary alloy systems

Next we show the results for the other eight quaternary alloy systems at $x = 0.5$, $y = 0.5$, and $T = 1000$ K. When assigning the element to the symbol, A, B, C, or D, we put the heavier element to A(C), as in $\mathrm{In}_{1-x}\mathrm{Ga}_x\mathrm{As}_{1-y}\mathrm{P}_y$.

The results are shown in Fig. 6. On the basis of qualitative features of the results, we can classify the alloy systems into the following three groups.

(1) $\mathrm{In}_{1-x}\mathrm{Ga}_x C^{\mathrm{V}}_{1-y} D^{\mathrm{V}}_y$ [C^{V}, D^{V}=Sb, As, P; Figs. 3, 6(a) and 6(b)]: $\omega_b\xi$ decreases and H_s increases with ξ. However, the slope of H_s at $\xi = 0$ is larger than $|\omega_b|$. Thus, ξ_0 becomes negative. In the alloy of $\mathrm{In_{0.5}Ga_{0.5}Sb_{0.5}As_{0.5}}$, H_s decreases down to a very small value, 0.03 kcal/mol at the lower limit of ξ ($\xi = -0.25$) because the length difference between InAs and GaSb is very small, as mentioned in Sec. II.

(2) $\mathrm{In}_{1-x}\mathrm{Al}_x C^{\mathrm{V}}_{1-y} D^{\mathrm{V}}_y$ [Figs. 6(c)–6(e)]: The value of H_s is not much different from that in the corresponding $\mathrm{In}_{1-x}\mathrm{Ga}_x C^{\mathrm{V}}_{1-y} D^{\mathrm{V}}_y$ systems, because the elastic properties of Ga—C^{V} and Al—C^{V} bonds are very similar. However, $|\omega_b|$ is larger than that in $\mathrm{In}_{1-x}\mathrm{Ga}_x C^{\mathrm{V}}_{1-y} D^{\mathrm{V}}_y$. Thus though H_s dominates over $\omega_b\xi$ in $\mathrm{In}_{1-x}\mathrm{Ga}_x C^{\mathrm{V}}_{1-y} D^{\mathrm{V}}_y$, the variations of H_s and $\omega_b\xi$ compensate each other almost completely in $\mathrm{In}_{1-x}\mathrm{Al}_x C^{\mathrm{V}}_{1-y} D^{\mathrm{V}}_y$, and thus ξ_0 is very close to zero.

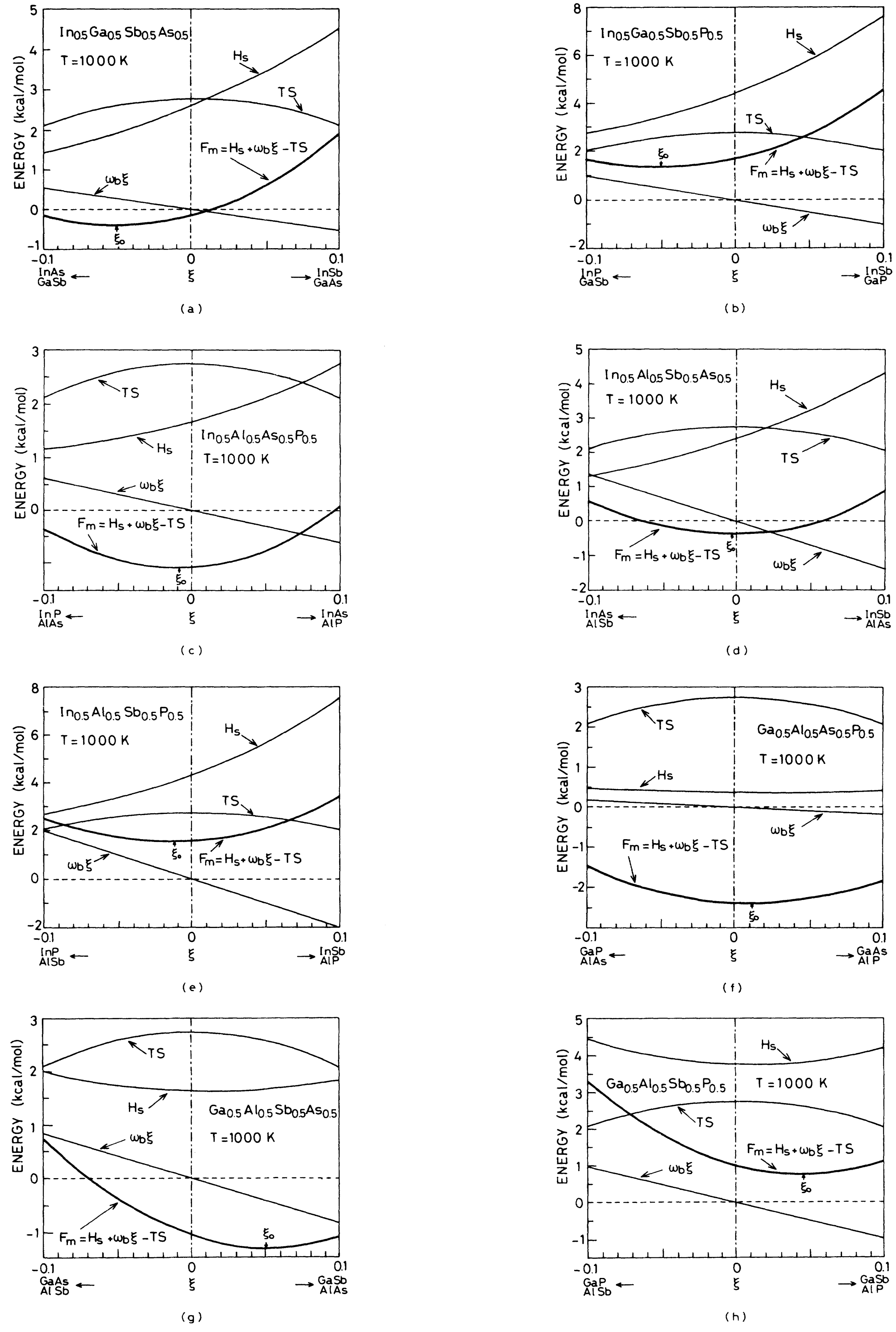

FIG. 6. Figures similar to Fig. 3 for quaternary alloys other than $In_{1-x}Ga_xAs_{1-y}P_y$ at $x=0.5$, $y=0.5$, and $T=1000$ K.

TABLE I. Equilibrium value of ξ, i.e., ξ_0 for nine $A^{\rm III}_{1-x}B^{\rm III}_x C^{\rm V}_{1-y}D^{\rm V}_y$ systems at $x, y = 0.5$, $T = 1000$ K.

	Material A-B-C-D	ξ_0
In-Ga-$C^{\rm V}$-$D^{\rm V}$	In-Ga-As-P	−0.018
	In-Ga-Sb-As	−0.050
	In-Ga-Sb-P	−0.050
In-Al-$C^{\rm V}$-$D^{\rm V}$	In-Al-As-P	−0.009
	In-Al-Sb-As	−0.003
	In-Al-Sb-P	−0.012
Ga-Al-$C^{\rm V}$-$D^{\rm V}$	Ga-Al-As-P	0.012
	Ga-Al-Sb-As	0.051
	Ga-Al-Sb-P	0.046

(3) $\mathrm{Ga}_{1-x}\mathrm{Al}_x C^{\rm V}_{1-y}D^{\rm V}_y$ [Figs. 6(f)–6(h)]: $\omega_b\xi$ decreases with ξ, while H_s weakly depends on ξ and is nearly symmetric with respect to the line of $\xi = 0$. Thus, ξ_0 is positive owing to the variation of $\omega_b\xi$. The even-function-like dependence of H_s on ξ is due to the fact that $d_{\mathrm{Ga}C^{\rm V}} \simeq d_{\mathrm{Al}C^{\rm V}}$; for example, in $\mathrm{Ga}_{1-x}\mathrm{Al}_x\mathrm{As}_{1-y}\mathrm{P}_y$, $d_{\rm GaP} \simeq d_{\rm AlP}$ and $d_{\rm GaAs} \simeq d_{\rm AlAs}$, and thus, as concerns the elastic properties, the increase of Ga—P and Al—As bonds is almost equivalent to the increase of Al—P and Ga—As bonds. On the other hand, the chemical properties of Ga—$C^{\rm V}$ and Al—$C^{\rm V}$ bonds are quite different. Thus ω_b can be a large negative value relative to the variation of H_s.

The values of ξ_0 are listed in Table I. A more detailed interpretation of these results is given in the next section.

V. DISCUSSIONS

The following features are commonly observed from the results for all quaternary alloy systems: ω_b is negative and H_s increases with ξ except for $\mathrm{Ga}_{1-x}\mathrm{Al}_x C^{\rm V}_{1-y}D^{\rm V}_y$ systems where H_s weakly depends on ξ. This is not accidental but can be interpreted as follows.

Consider the covalent radius r_p for each atom. The p—q bond length d_{pq} is approximately given by $r_p + r_q$ (or the covalent radii are defined so that $r_p + r_q = d_{pq}$). We assume $r_A > r_B$ and $r_C > r_D$ for the $A^{\rm III}_{1-x}B^{\rm III}_x C^{\rm V}_{1-y}D^{\rm V}_y$ system. Then,

$$(r_A + r_C) - (r_B + r_D) > |(r_A + r_D) - (r_B + r_C)| \ . \tag{13}$$

According to the consideration in Sec. II, H_s becomes large with the increase of the numbers of A—C and B—D bonds, because the pair of A—C and B—D strain each other more largely than A—D and B—C pair. Since the heavier atom usually has larger covalent radius and is assigned to $A(C)$, the relations $r_A > r_B$, and $r_C > r_D$ are satisfied except $\mathrm{Ga}_{1-x}\mathrm{Al}_x C^{\rm V}_{1-y}D^{\rm V}_y$ systems. Thus, H_s increases with more A—C and B—D bonds, i.e., with positive ξ for all $\mathrm{In}_{1-x}\mathrm{Ga}_x C^{\rm V}_{1-y}D^{\rm V}_y$ and $\mathrm{In}_{1-x}\mathrm{Al}_x C^{\rm V}_{1-y}D^{\rm V}_y$ systems. We have $r_{\rm Al} \simeq r_{\rm Ga}$ for $\mathrm{Ga}_{1-x}\mathrm{Al}_x C^{\rm V}_{1-y}D^{\rm V}_y$, since $d_{\mathrm{Al}C^{\rm V}} \simeq d_{\mathrm{Ga}C^{\rm V}}$ and thus

$$\begin{aligned} |(r_{\rm Ga} + r_{C^{\rm V}}) - (r_{\rm Al} + r_{D^{\rm V}})| - |(r_{\rm Ga} + r_{D^{\rm V}}) - (r_{\rm Al} + r_{C^{\rm V}})| &= (r_{\rm Ga} + r_{C^{\rm V}} - r_{\rm Al} - r_{D^{\rm V}}) - (r_{\rm Al} + r_{C^{\rm V}} - r_{\rm Ga} - r_{D^{\rm V}}) \\ &= 2(r_{\rm Ga} - r_{\rm Al}) \\ &\simeq 0 \ . \end{aligned} \tag{14}$$

Therefore, H_s depends weakly on ξ for $\mathrm{Ga}_{1-x}\mathrm{Al}_x C^{\rm V}_{1-y}D^{\rm V}_y$ systems.

The sign of ω_b can also be understood by considering covalent radii. The negative ω_b indicates that the sum of the cohesive energy of A—C and B—D bonds is larger than that of A—D and B—C bonds. The cohesive energy of the covalent crystal is considered to be approximately proportional to $d^{-2.5}$,[17] and under the conditions of $r_A > r_B$ and $r_C > r_D$, the following relation is satisfied:

$$\begin{aligned} &(r_A + r_C)^{-2.5} + (r_B + r_D)^{-2.5} \\ &\qquad > (r_A + r_D)^{-2.5} + (r_B + r_C)^{-2.5} \ . \end{aligned} \tag{15}$$

This indicates that the sum of the cohesive energy of A—C and B—D bonds is larger than that of A—D and B—C bonds, i.e., $\omega_b < 0$, under the above conditions. As mentioned earlier, these conditions are satisfied for all quaternary alloy systems except for $\mathrm{Ga}_{1-x}\mathrm{Al}_x C^{\rm V}_{1-y}D^{\rm V}_y$. For Al$C^{\rm V}$ compounds, the cohesive energy is larger than that expected from the $d^{-2.5}$ dependence; for example, although the bond lengths of AlAs and GaAs are almost the same, the melting point of AlAs is significantly higher than that of GaAs, which implies that the cohesive energy of Al-As is larger than that of Ga-As. Thus we should regard $d_{\mathrm{Al}C^{\rm V}}$ and thus $r_{\rm Al}$ as smaller than the crystallographic one when the $d^{-2.5}$ dependence of cohesive energy is assumed. Such an effective bond length was found to be useful to predict some electronic properties of Al$C^{\rm V}$, although its physical basis is not clear.[18] Then, as concerns the cohesive energy, we can expect that Eq. (15) is satisfied for all quaternary alloy systems discussed here. Thus ω_b is negative for all quaternary alloy systems.

As described in the last section, the qualitative features of the results depend on the group-III elements. This is ascribed to the fact that the cohesive energy of the Al—$C^{\rm V}$ bond is larger than that expected from its crystallographic length: The effect of $\omega_b\xi$ becomes relatively large as compared with that of H_s when the alloy includes Al.

For binary or ternary $A_{1-x}B_xC$ alloys, the atom arrangement is described in term of order (preference for unlike neighbor pair) or cluster (preference for like neighbor pair). However, it is difficult to relate the value of ξ to order or cluster in quaternary alloys. For example, if ξ becomes positive, i.e., the A—C bond increases, then the triplet A—C—A increases, but A—D—A decreases because of the decrease of the A—D bond. Then, in general, one cannot conclude whether the like pair A—A increases or not. Rather, ξ is the measure for the uniformity in an alloy. If A—C and B—D bonds increase, the region including both A and C atoms more than the average composition increases, and the region with more B and D atoms also increases. Thus there would be two types of regions with different compositions in the alloy, i.e., the alloy would become nonuniform. The alloy is most uniform at $\xi=0$, and the value of $|\xi_0|$ represents the degree of nonuniformity.

At $x=0.5$ and $y=0.5$, like pairs necessarily increase, i.e., clustering occurs with the increase of $|\xi|$, because $(0.25+\xi)^2+(0.25-\xi)^2=0.25+2\xi^2$, where the two terms in LHS are the probabilities of appearance of two different triplets including the same like pair, such as A—C—A and A—D—A. The increase of H_s at nonzero ξ in $\mathrm{Ga}_{1-x}\mathrm{Al}_xC^{\mathrm{V}}_{1-y}D^{\mathrm{V}}_y$ is due to the cluster; the strain energy tends to increase by the clustering as discussed in previous works.[9]

The pairwise interaction model (PIM) has been used for discussion about the atom arrangement of III-V quaternary alloys[2] as well as ternary alloys.[19] In the approach, the second-nearest-neighbor interaction is assumed to contribute to mixing enthalpy, and the strain energy is neglected. For ternary alloys, the PIM predicts clustering, whereas our model, which accounts for the strain energy, predicts ordering. It occurs also in quaternary alloys. Both models give very different results; for example, according to the PIM, the enthalpy due to the second-nearest interaction decreases with ξ for $\mathrm{In}_{1-x}\mathrm{Ga}_x\mathrm{As}_{1-y}\mathrm{P}_y$, and thus ξ_0 is relatively a large positive value. However, the assumption of PIM has not been justified, yet. Moreover, the approach neglecting the strain energy is inappropriate for III-V alloys, since the strain of the bond is experimentally confirmed by EXAFS (Ref. 12) and the calculated strain energy is no less than the mixing enthalpy obtained from thermodynamical experiments.[6–10] The strain energy cannot be neglected for the enthalpy in III-V alloy semiconductors. Thus our approach can be understood to be more appropriate than that based on the PIM. The second-nearest interaction would be necessary in order to take into account a more accurate discussion in addition to, but not instead of, the strain energy.

The statistics of bonds could be experimentally determined from the lattice vibration spectra. For some alloys, there appears several phonon modes corresponding to bonds, for example, In—As, Ga—As, In—P, and Ga—P like phonon modes appear within a certain composition range for $\mathrm{In}_{1-x}\mathrm{Ga}_x\mathrm{As}_{1-y}\mathrm{P}_y$, and the intensity of the signal of each mode is considered to represent the number of the oscillator, i.e., the corresponding bond. It was reported that results of infrared reflectivity measurements on $\mathrm{In}_{1-x}\mathrm{Ga}_x\mathrm{As}_{1-y}\mathrm{P}_y$ can be explained well by assuming $x_{pq}=x_px_q$, i.e., $\xi_0=0$.[20] This would be consistent with our results that ξ_0 is close to zero for $\mathrm{In}_{1-x}\mathrm{Ga}_x\mathrm{As}_{1-y}\mathrm{P}_y$. However, the accuracy of such experimental approach would not be good enough to estimate a small deviation from $\xi=0$. It seems that the experimental technique for determining the statistics of bonds is yet to be developed.

In the model proposed here, we choose a bond as a basic figure of the thermodynamical analysis, and thus the correlation among atoms is considered only to the lowest order: the single variable ξ is not enough to describe the atom arrangement of quaternary alloys. For example, the probability of the appearance of a tetrahedron in fact cannot be uniquely determined from the relative numbers of bonds but should be treated as another independent variable; in deriving Eq. (9), we assume that there is no excess correlation among bonds. Equation (9) is reduced to a simple binodal distribution for tetrahedra in ternary alloys. This does not mean that the arrangement of bonds is completely random: the unphysical situations, such as an A—D bond sharing an atom with a B—C bond, are excluded in deriving the entropy.[2] For a more accurate analysis, we need to choose a tetrahedron as a basic figure, as we did for ternary alloys,[9] since the short-range order on a sublattice influences the strain energy. However, this effect is rather small; for example, the decrease of the strain energy due to the short-range order is about 10% for $\mathrm{In}_{1-x}\mathrm{Ga}_x\mathrm{As}$ at $T=1000$ K.[9] Thus we believe that the qualitative features of the results given here are not affected by neglect of the short-range order.

So far, we pay attention only to the value of ξ. However, the value of the free energy at $\xi=\xi_0$ is also important; one can discuss the phase equilibrium and the miscibility of the alloy system. It can be seen from Figs. 3 and 6 that the alloy system with a large immiscibility region, such as $\mathrm{In}_{1-x}\mathrm{Ga}_x\mathrm{Sb}_{1-y}\mathrm{P}_y$, tends to have large free energy. For a further study on the quaternary alloy systems, these problems will be discussed by extending the model proposed here.

VI. CONCLUSION

The relative numbers of bonds in the III-V quaternary alloys have been derived by a thermodynamical analysis. The strain energy of bonds is taken into account as the enthalpy, in addition to the cohesive energy. Considering that the bonds increase or decrease in pairs, we discussed how these two factors influence the statistics of bonds, and it has been shown that the strain energy decreases when the pair of bonds with the small difference in length increases. The calculation results show that, in $\mathrm{In}_{1-x}\mathrm{Ga}_x\mathrm{As}_{1-y}\mathrm{P}_y$, Ga—As and In—P bonds slightly increase from the value of complete random atom arrangement owing to the effect of the strain energy, although the sum of cohesive energy of Ga—P and In—As is larger than that of Ga—As and In—P. The same tendency is commonly observed for other $\mathrm{In}_{1-x}\mathrm{Ga}_xC^{\mathrm{V}}_{1-y}D^{\mathrm{V}}_y$ systems. For $\mathrm{Ga}_{1-x}\mathrm{Al}_xC^{\mathrm{V}}_{1-y}D^{\mathrm{V}}_y$, the effect of the cohesive energy is predominant, and the effects of both energies compensate each other almost completely for $\mathrm{In}_{1-x}\mathrm{Al}_x C^{\mathrm{V}}_{1-y} D^{\mathrm{V}}_y$ systems. The difference among nine alloy systems can be explained by considering the covalent radius of each atom.

Since the properties of a covalent crystal are predominantly determined by the properties of the bond, the statistics of the bonds would greatly influence various material parameters of quaternary alloy semiconductors. Thus the effects of the statistics of bonds on electrical and optical properties are suggested to be investigated.

ACKNOWLEDGMENTS

We would like to thank Dr. Y. Takeda and Mr. Sz. Fujita for stimulating discussions. This work was partly supported by the Scientific Research Grant-in-Aid No. 62104005 for Special Project Research on "Alloy Semiconductor Physics and Electronics" from the Ministry of Education, Science and Culture, and by Hattori Hokokai Foundation.

---

[1] H. Sonomura, H. Horinaka, and T. Miyauchi, Jpn. J. Appl. Phys. **22**, L689 (1983).

[2] K. Onabe, J. Phys. Chem. Solids **43**, 1071 (1982).

[3] T. Onda and R. Ito, Jpn. J. Appl. Phys. **26**, 1241 (1987).

[4] For example, J. C. Phillips, *Bond and Bands in Semiconductors* (Academic, New York, 1973), and W. A. Harrison, *Electronic Structure and the Properties of Solids* (Freeman, San Francisco, 1980).

[5] For example, A. S. Jordan and M. Ilegems, J. Phys. Chem. Solids **36**, 329 (1975).

[6] J. C. Mikkelsen, Jr., Electrochem. Soc. **132**, 500 (1985).

[7] T. Fukui, J. Appl. Phys. **57**, 5188 (1985).

[8] P. A. Fedder and M. W. Muller, J. Phys. Chem. Solids **45**, 685 (1984).

[9] M. Ichimura and A. Sasaki, J. Appl. Phys. **60**, 3850 (1986), and Jpn. J. Appl. Phys. **25**, 976 (1986).

[10] H. Sonomura, J. Appl. Phys. **59**, 739 (1986).

[11] M. Ichimura and A. Sasaki, Jpn. J. Appl. Phys. **26**, 1296 (1987).

[12] H. Oyanagi, Y. Takeda, T. Matsushita, T. Ishiguro, and A. Sasaki, *Proceedings of the International Symposium on GaAs and Related Compounds, 1985,* IOP Conf. Ser. No. 79 (Adam Hilger, 1986), p. 295.

[13] For example, J. C. Mikkelsen, Jr. and J. B. Boyce, Phys. Rev. B **28**, 7130 (1983).

[14] M. Ichimura and A. Sasaki, Jpn. J. Appl. Phys. **26**, 246 (1987).

[15] K. Onabe, Jpn. J. Appl. Phys. **21**, L323 (1982).

[16] R. M. Martin, Phys. Rev. B **1**, 4005 (1970).

[17] G. B. Stringfellow, J. Cryst. Growth **27**, 21 (1974).

[18] S. Gonda, Solid State Commun. **60**, 249 (1986).

[19] For example, G. B. Stringfellow and P. E. Green, J. Phys. Chem. Solids **30**, 1779 (1969), and P. A. Jones, W. Porod, and D. K. Ferry, *ibid.* **44**, 107 (1983).

[20] C. Pickering, J. Electron. Mater. **10**, 901 (1981).