Energy-band gap of monolayer superlattices calculated by a modified tight-binding method with electronegativity

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The tight-binding method is modified successfully to calculate the energy-band gap at the Γ point for monolayer superlattices in which each monolayer comprises a binary and ternary compound semiconductor. In the case of $(InAs)_1/(GaAs)_1$ monolayer superlattices, the energy-band gap is 5% smaller than that of $In_{0.5}Ga_{0.5}As$ ternary compound semiconductors. The energy-band gap of $(InAs)_1/(GaAs)_1$ monolayer superlattices increases nonlinearly to that of the ternary compound semiconductors as the degree of alloying between In and Ga atoms is increased.

INTRODUCTION

Recently, progress has been made in the growth techniques for semiconductor thin layers.[1–5] Short period superlattices (SSL's) such as monolayer superlattices[6] have been grown successfully, and it is especially encouraging that excess atoms on the top of the surface can be desorbed by annealing, and a surface without steps can be obtained over a wafer.[3,4] Attempts have been made to develop devices using SSL's.[7] Although the growth techniques have improved, the conventional theoretical calculation methods are not sufficient to obtain good correspondence with the experimental results for the various compound semiconductors. The Kronig-Penney model is not available because of the impossibility of carrier confinements in the thin layers of the SSL's. Energy-band gaps have been calculated from first-principles[8–10] and tight-binding theories.[11–13] Although various methods of modification have been suggested, no simple method has emerged in which calculated values are coincident with the experimental values of the energy-band gap for various binary and ternary bulk semiconductors. The dependence of the energy-band gap on the temperature or the static pressure should also be explained by the same simple method. Reliable energy-band gap values of monolayer superlattices, in which each monolayer comprises a binary (MSLB) or ternary (MSLT) compound, can be calculated using the modified method.

In this paper, we show a modified method for the tight-binding approximation and the results of a calculation of the energy-band gap of $(InAs)_1/(GaAs)_1$, $(AlAs)_1/(GaAs)_1$, and $(Ga_xIn_{1-x}As)_1/(Ga_{1-x}In_xAs)_1$ monolayer superlattices.

CALCULATIONAL DETAILS

The Hamiltonian matrix used in our calculations is simple and is composed of 16×16 elements. The diagonal elements are the energy values of the $1s$ orbital and $3p$ orbitals in each ion of two anions and two cations. The orbital interaction parameters, which are the nondiagonal elements, are considered between the first- or the second-nearest-neighbor ions.

For calculations on binary compound semiconductors, the orbital energy values shown by Herman and Skillman[14] are used as the original energy values of the diagonal elements, ε_0, and the original values ε_0, are modified using the electronegativity given by Sanderson.[15] The nine binary compound semiconductors are classified according to three kinds of cations into three groups. In each group, β values can be defined such that

$$\beta=\frac{S_{b'}}{S_b}\ , \tag{1}$$

where S_b and $S_{b'}$ stand for the electronegativity values of GaAs, InAs, or AlAs, and the electronegativity values of binary compound semiconductors in each group, respectively. The values of S_b and $S_{b'}$, as shown by Sanderson[15] for various compounds, are defined as the geometric averages of the electronegativity values of the relevant atoms. The orbital energy values of cations ε_{bc} and anions ε_{ba} of the binary compounds in each group are defined as $\beta\varepsilon_0$ and ε_0/β, respectively. The interaction parameters between the orbitals, which are the functions of the lattice constant, are estimated from the equation of Froyen and Harrison.[16]

In the case of ternary compound semiconductor alloys, the original values of the orbital energy are defined as

$$\varepsilon_{tc0}=x\varepsilon_{bc}+(1-x)\varepsilon_{b'c}\ , \tag{2}$$

$$\varepsilon_{ta0}=x\varepsilon_{ba}+(1-x)\varepsilon_{b'a}\ , \tag{3}$$

where ε_b and $\varepsilon_{b'}$ are the modified energy values of the binary compounds which correspond to alloy contents $x=1$ and 0, respectively, and the subscripts c and a refer to the cation and the anion, respectively. The original values ε_{tc0} and ε_{ta0} are modified by relative values of the electronegativity as follows. The nonlinearity of the electronegativity is taken into account to explain the nonlinear relations between the energy-band gap and the alloy content. The nonlinear function used in our method is the same as the quadratic functions shown in Vechten

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and Bergstrasser,[17] such that

$$S_{tn}=1S_t^2+mS_t+n \ , \tag{4}$$

$$S_t=xS_b+(1-x)S_{b'} \ . \tag{5}$$

The three coefficients l, m, and n of the quadratic function are determined by fitting our theoretical values to experimental values at alloy contents of $x=0$, 0.5, and 1.0. In addition, we define the values of the quadratic function for $x=0$ and 1.0 always to be 1.0, and this means that the value S_{tn} can be regarded as the nonlinearly relative values of the electronegativity. The coefficient values of l, m, and n, as the result, are -0.347, 2.263, and -2.654 for $Ga_xAl_{1-x}As$ ternary alloys, and -1.295, 8.942, and -14.416 for $In_xGa_{1-x}As$, respectively. For the orbital energy values of cations ε_{tc} and anions ε_{ta}, the values of $S_{tn}\varepsilon_{tc0}$, and ε_{ta0}/S_{tn}, respectively, are used. The first- and second-nearest-neighbor interaction parameters are estimated using the lattice constants based on Vegard's law.

For monolayer superlattices in which each monolayer comprises a binary (MSLB) or ternary (MSLT) compound semiconductor, the orbital energy values can also be determined as follows. The original values of orbital energy $\varepsilon_{sbc0}, \varepsilon_{sba0}$ for the MSLB and $\varepsilon_{stc0}, \varepsilon_{sta0}$ for the MSLT are the same as the modified values $\varepsilon_{bc}, \varepsilon_{ba}$ used for the binary compounds and the modified values $\varepsilon_{tc}, \varepsilon_{ta}$ used for the ternary alloys. The electronegativity values of the MSLB and MSLT, the same as the binary compounds, are defined such that

$$S(\text{MSLB})=\sqrt{S_bS_{b'}} \ , \tag{6}$$

$$S(\text{MSLT})=\sqrt{S_{tn}S_{tn'}} \ , \tag{7}$$

where $S_b, S_{b'}$ and $S_{tn}, S_{tn'}$ are the electronegativity values in each monolayer forming the MSLB and MSLT, respectively. This means that the monolayer superlattices are considered as the new compounds composed of each monolayer. The ratio of the electronegativity value is defined such that

$$\alpha=\frac{S(\text{MSLB or MSLT})}{S_t} \ , \tag{8}$$

where S_t are the modified electronegativity values of the ternary compound alloys, of which the alloy contents are the same as the entirely averaged contents of MSLB or MSLT. Like the orbital energy values of cations ε_{sbc} and anions ε_{sba}, the values of $\alpha S_{tn}\varepsilon_{sbc0}$ and $\varepsilon_{sba0}/(\alpha S_{tn})$ are used respectively in the case of the MSLB. The orbital energy values, in the case of the MSLT, are defined by a similar procedure. The first-nearest-neighbor parameters of the MSLB and MSLT are the same as the parameters of the relevant binary compounds or ternary alloys. The second-nearest-neighbor parameters of the MSLB and MSLT are the arithmetic averages of the second-nearest-neighbor parameters of the relevant binary compounds or ternary alloys.

RESULTS AND DISCUSSION

In this work, we consider the energy-band gap of the Γ point at a temperature of 300 K.

Our results of theoretical calculations for energy-band gaps of various binary compound semiconductors before and after modification with electronegativity are shown in Figs. 1(a) and 1(b), respectively. The correspondence between calculated and experimental values is improved by the modification.

The electronegativity can be considered as the effective force between the atomic nucleus and the electron in the orbital of the outermost shell. The compound semiconductors are composed of atoms which have different degrees of electronegativity from one another. The local density of charge, therefore, is shifted from the atom with a small degree of electronegativity (cation) to the atom with a large degree of electronegativity (anion). This means that the orbital energy of the outermost shell is modified spontaneously in the compound semiconductor and, therefore, that the original values of Herman and Skillman should be modified to calculate the energy-band gap of compound semiconductors. The absolute values of s- and p-orbital energies of cations should be increased because the local density of the charge is reduced and the effective Coulomb interaction between the atomic nucleus and the electron of the outermost shell increases due to the decrease of the screening effect. In the case of cations, therefore, the absolute orbital energy values are multiplied by the relative electronegativity values in our method. In the case of anions, on the other hand, the local density of the charge is added and the effective Coulomb interaction decreases due to the increase of the screening effect. The absolute orbital energy values, therefore, are divided by the relative electronegativity values in our method.

The temperature dependence of the energy-band gap, as shown in Fig. 2, is estimated in the case of GaAs to evaluate the accuracy of our modification method. The dependence on the temperature should be investigated from the factors of lattice expansion and electron-phonon interaction, as shown by Fan.[18] Each factor can be calculated independently using Fan's equation. The contribution of the lattice expansion calculated from Fan's equation is shown in Fig. 2, in addition to the experimental results[19] for the temperature dependence of the energy-band gap. In our calculations for the contribution of the lattice expansion, only the temperature dependence of the lattice constant is considered, and a value of 6.40×10^{-6} (1/K) is used as the thermal expansion coefficient of GaAs. The results of our calculation, which are also shown in Fig. 2, are in good agreement with the results of Fan's equation.

The dependence of the energy-band gap on the hydrostatic pressure is also estimated compared with the experimental results shown in Fig. 3. The experimental results are based on the experimental equation of Blakemore,[19] and the elastic volume coefficient (7.55×10^{11} dyn/cm^2) of GaAs. In our calculations, only the first- and second-nearest-neighbor interaction parameters depend on the lattice constant, as in the case of the temperature depen-

dence. It is notable that the results of our calculation are coincident with the experimental results shown in Fig. 3.

In considering nonlinearity, the energy-band gaps of ternary compound semiconductor alloys are also calculated. The results of our calculation for $Al_xGa_{1-x}As$ and $Ga_xIn_{1-x}As$ alloys are shown in Figs. 4 and 5, respectively. The experimental results for $Al_xGa_{1-x}As$ (Refs. 20 and 21) and $Ga_xIn_{1-x}As$ alloys[22–24] are also shown in Figs. 4 and 5, respectively. Our results are almost coincident with experimental results for alloy contents from $x=0$ to 1.0.

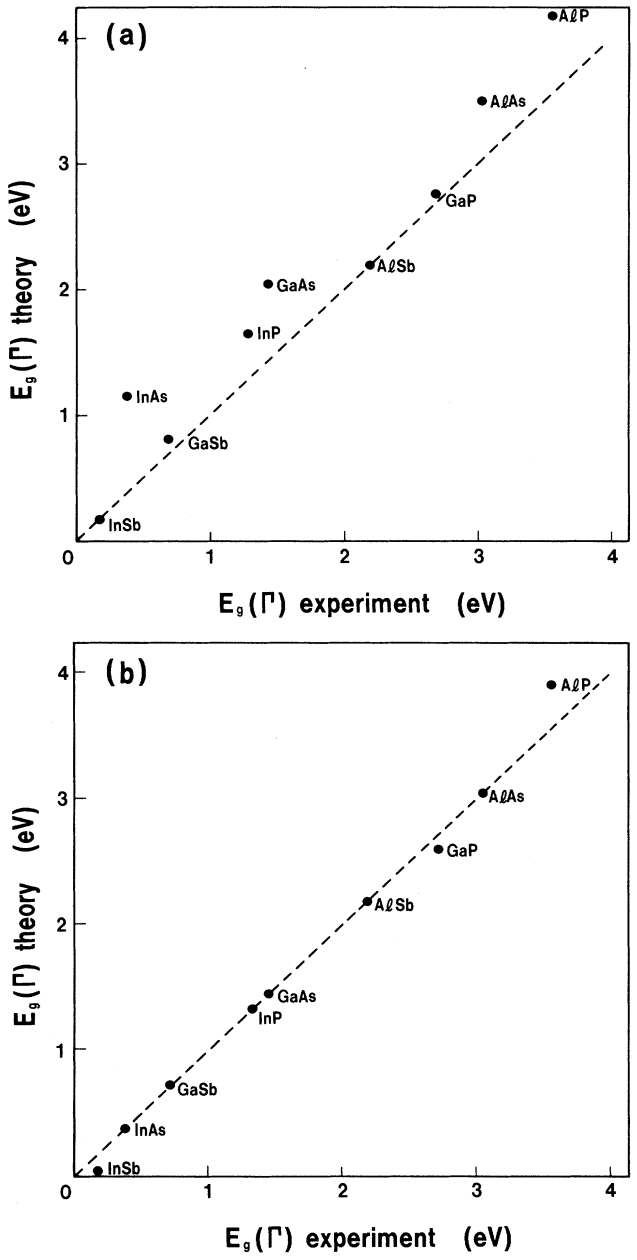

FIG. 1. The theoretical values of the energy-band gap at 300 K plotted vs the experimental values for various binary compound semiconductors. The theoretical values are obtained by the tight-binding method, (a) without and (b) with the modification using electronegativity values. It should be noted that the correspondence improves with the modification of the electronegativity. On the broken lines, the theoretical values are equal to the experimental values.

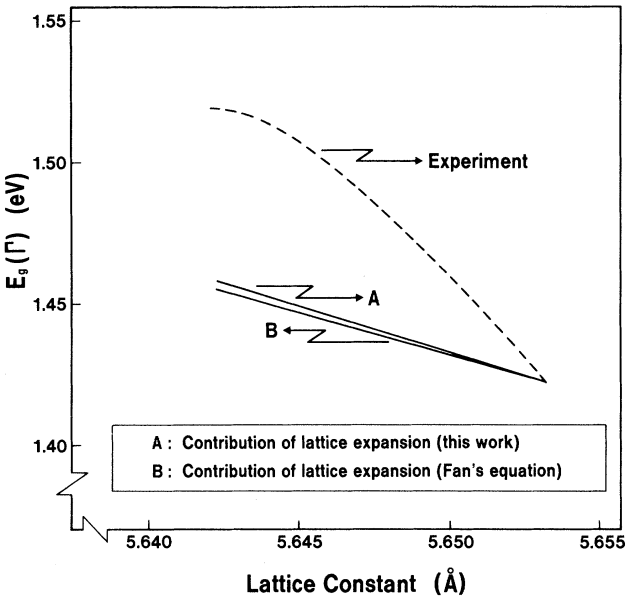

FIG. 2. The experimental temperature dependence of the energy-band gap of GaAs (broken line, Ref. 19), and the contributions of the lattice expansion to the temperature dependence. The temperature is converted into the lattice constant by using the thermal expansion coefficient 6.40×10^{-6} (1/K) of GaAs. The contribution level calculated by our method using electronegativity (solid line *A*) is coincident with that calculated from Fan's equation (solid line *B*, Ref. 18).

On the basis of the successful coincidence with the experimental results mentioned above, it is possible to calculate the reliable energy-band gap of monolayer superlattices in which each monolayer comprises a binary (MSLB) or ternary compound semiconductor (MSLT). The (001)-oriented superlattices are considered in this work. The results of our calculation are shown in Figs. 4 and 5 in the cases of $(AlAs)_1/(GaAs)_1$ and $(InAs)_1/(GaAs)_1$ monolayer superlattices, respectively. It should be noted that the energy-band gap of $(InAs)_1/(GaAs)_1$ superlattices (0.72 eV) is 5% smaller than that of $In_{0.5}Ga_{0.5}As$ alloys (0.76 eV), although the energy-band gap of $(AlAs)_1/(GaAs)_1$ superlattices (2.00 eV) is in agreement with that of $Al_{0.5}Ga_{0.5}As$ alloys (2.00 eV). This can be attributed to the large lattice mismatch between GaAs and InAs (7.4%) compared with that between GaAs and AlAs (0.3%). We can consider our results compared with energy-band gaps calculated from first principles for monolayer superlattices.[8–10] As shown by Zhang *et al.*,[8] the energy-band gap of the $(AlAs)_1/(GaAs)_1$ superlattice calculated from first principles is 0.21 eV smaller at low temperature than the energy-band gap calculated from the virtual-crystal approximations, in which the energy-band gap is defined as

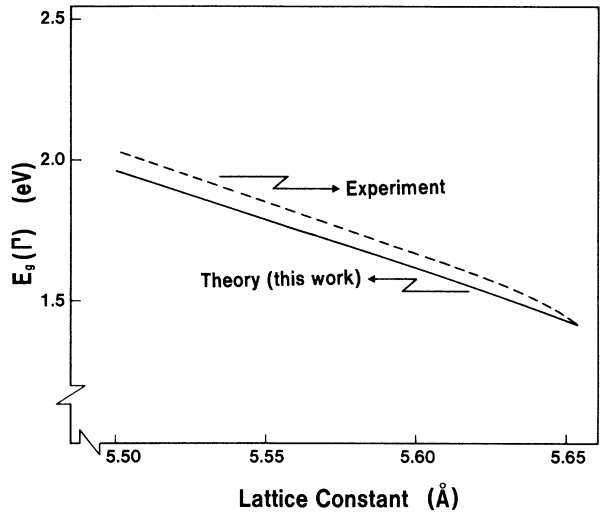

FIG. 3. The dependence of the energy-band gap of GaAs on the hydrostatic pressure. The hydrostatic pressure is converted into the lattice constant by using the elastic volume coefficient 7.55×10^{11} (dyn/cm^2) of GaAs. The dependence calculated by our method using electronegativity is similar.

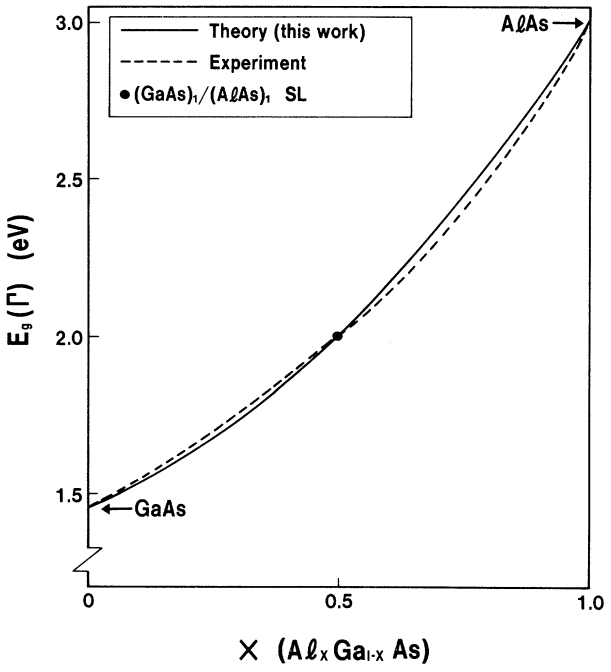

FIG. 4. The energy-band gap of $Al_xGa_{1-x}As$ ternary alloys and $(AlAs)_1/(GaAs)_1$ monolayer superlattices at 300 K. The dependence of the energy-band gap on the Al content X for ternary alloys is calculated by our method using the electronegativity (solid line), and obtained experimentally (broken line, Refs. 20 and 21). The energy-band gap of $(AlAs)_1/(GaAs)_1$ monolayer superlattices (solid circle) calculated by our method is almost the same as that of $Al_{0.5}Ga_{0.5}As$ ternary alloys.

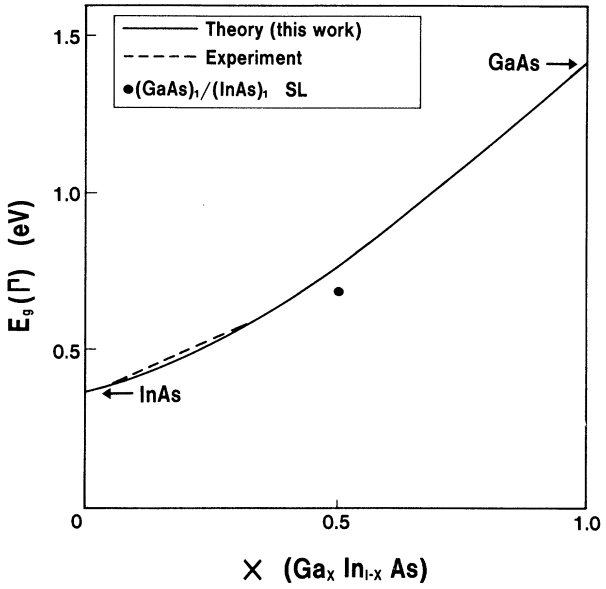

FIG. 5. The energy-band gap of $Ga_xIn_{1-x}As$ ternary alloys and $(GaAs)_1/(InAs)_1$ monolayer superlattices at 300 K. The dependence of the energy-band gap on the Ga content X for ternary alloys is calculated by our method using the electronegativity (solid line), and obtained experimentally (broken line, Refs. 22–24). The energy-band gap of $(GaAs)_1/(InAs)_1$ monolayer superlattices (solid circle) calculated by our method is about 5% smaller than that of $Ga_{0.5}In_{0.5}As$ ternary alloys.

the arithmetic average of the relevant bulk energy levels of GaAs and AlAs. The difference of energy-band gaps is considered as resulting from a bowing effect for conduction-band states (0.1–0.15 eV) in $Al_{0.5}Ga_{0.5}As$ alloys.[8] By considering the bowing effect and the uncertainty of the calculations (0.1 eV),[8] the energy-band gap of $Al_{0.5}Ga_{0.5}As$ is nearly equal to that of $(AlAs)_1/(GaAs)_1$ superlattices, the same as in our results. In addition, the energy-band-gap value of $(AlAs)_1/(GaAs)_1$ superlattices in Fig. 4 is in good agreement with the value obtained from the photoluminescence spectra at room temperature by Kobayashi.[25] In the case of $(InAs)_1/(GaAs)_1$ superlattices, the band-gap narrowing to the alloys calculated from first principles is 0.04 eV (5%), as shown by Wei.[9] This value is coincident with our result in Fig. 5. The exact values of the lattice constants, however, cannot be determined simply in the case of strained-layer superlattices such as InAs/GaAs superlattices. As mentioned above, in this work we use approximations for the superlattices in which the first-nearest-neighbor parameters are the same as the values of the relevant binary compounds, and the second-nearest-neighbor parameters are the arithmetic averages of the values of the relevant binary compounds. This means that the effects of the shift of the As atom to the Ga-atom side, which is observed experimentally,[26] are considered only in first-nearest-neighbor parameters. In order to obtain a more precise coincidence between calculated and experimental values, it may be necessary to modify our assumptions concern-

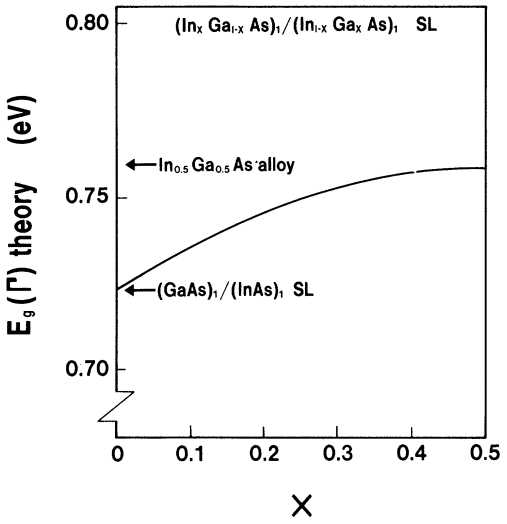

FIG. 6. The energy-band gap of $(Ga_xIn_{1-x}As)_1/(Ga_{1-x}In_xAs)_1$ monolayer superlattices in which the macroscopic compositions are constant. It should be noted that the relation between the energy-band gap and the alloy composition X of each monolayer is nonlinear.

ing the lattice deformation in a real state of the superlattice. The inhomogeneous lattice deformations, for example, which are caused in the growth direction by the lattice mismatch with the substrate, are important factors in obtaining the precise coincidence with the experimental results. According to this problem, the dependence of the energy-band gap on the lattice constant of the substrates has been calculated by Dandrea[10] considering only the effects of homogeneous deformations. The energy-band gap of $(GaAs)_1/(GaP)_1$ on the GaAs substrate is 0.25 eV smaller than that on the substrate having a lattice constant of $GaAs_{0.5}P_{0.5}$.[10] The lattice mismatch between GaAs and $GaAs_{0.5}P_{0.5}$ is about 1.7%. The lattice mismatch between $(InAs)_1/(GaAs)_1$ and the InP substrate, which is often used in the growth experiments, is about 0.3%, and not negligible to a calculation of precise values which are coincident with the experimental results. In addition, in the case of superlattices, the lattice mismatch to the substrate is accommodated more by the elastic lattice deformation than the misfit dislocations. In the case of alloys, on the other hand, the misfit dislocations can be introduced easily, and the elastic lattice deformation can decrease after the introduction of misfit dislocations. This is supported by the phenomenon by which mirror surfaces of layers grown on the lattice-mismatched substrate can be obtained more easily in superlattices than those in the alloys.[1] The effect of the lattice mismatch to the substrate, therefore, is more important in the superlattices than the alloys. We need more experimental results for the inhomogeneous deformation, which may be the graded deformation in the growth direction, to perform more precise calculations.

The energy-band gap, as shown in Fig. 6, is also calculated in the case of $(Ga_xIn_{1-x}As)_1/(Ga_{1-x}In_xAs)_1$ monolayer superlattices, in which each monolayer comprises a ternary compound semiconductor alloy. The lattice mismatch of superlattices to the substrate is constant in this case because the average content of the superlattices is constant. It should be noted that the energy-band gap is dependent nonlinearly on the alloy content of each monolayer. That is, the energy-band gap of $(InAs)_1/(GaAs)_1$ monolayer superlattices increases nonlinearly with that of $In_{0.5}Ga_{0.5}As$ ternary alloys as the alloying at the interfaces between InAs and GaAs monolayers is enhanced. The experimental results at a temperature of 77 K are shown by Fukui.[27] The results of our calculation are coincident with the experimental results converted at 300 K.

CONCLUSIONS

We have successfully developed a method of determining the parameters for theoretical calculations of energy-band gaps for monolayer superlattice semiconductors, in addition to binary and ternary bulk semiconductors. By considering the electronegativity, the correspondence of our calculated values with experimental values has improved for the energy-band gap of the binary and ternary bulk semiconductors. In the dependence of the energy-band gap on the temperature and the hydrostatic pressure, the correspondence between our calculated results and experimental results are sufficient to us. By our simple modified method, we can calculate the reliable energy-band gap of monolayer superlattice semiconductors. As to the results, the energy-band gap of $(InAs)_1/(GaAs)_1$ monolayer superlattices is 5% smaller than that of $In_{0.5}Ga_{0.5}As$ ternary alloys, although the energy-band gap of $(AlAs)_1/(GaAs)_1$ monolayer superlattices is the same as that of $Al_{0.5}Ga_{0.5}As$ ternary alloys. In addition, the energy-band gap of $(InAs)_1/(GaAs)_1$ monolayer superlattices increases nonlinearly to that of $In_{0.5}Ga_{0.5}As$ ternary alloys as the alloying is enhanced between InAs and GaAs monolayer superlattices.

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