J Mater Sci (2006) 41:5323–5328
DOI 10.1007/s10853-006-0314-2

Optoelectronic and dielectric properties of $GaAs_xSb_{1-x}$ ternary alloys

F. Mezrag · N. Y. Aouina · N. Bouarissa

Received: 22 December 2004 / Accepted: 5 October 2005 / Published online: 6 June 2006
© Springer Science+Business Media, LLC 2006

Abstract Based on the pseudopotential scheme under the virtual crystal approximation in which the effect of compositional disorder is involved, the dependence of optoelectronic properties of $GaAs_xSb_{1-x}$ on alloy composition x have been studied. Our results showed generally good agreement with the available experimental data. The material of interest is found to exhibit features of both direct and indirect band-gap semiconductor depending on the alloy composition x. The method used has been combined with the Harrison bond-orbital model and employed to calculate the dielectric constants and their composition dependence.

Introduction

III–V binary compound semiconductors are being investigated for possible applications in various electronic and photonic devices. Solid solutions between III–V compounds have become increasingly important for microelectronical applications, giving the possibility to choose the energy range e.g for optoelectronic or laser applications more appropriate than with the binary compounds [1, 2].

Using GaSb with GaAs (both components are direct gap semiconductors), the gallium arsenide antimonide ($GaAs_xSb_{1-x}$) ternary semiconductor alloys can be obtained. The latter is most often encountered with the $x = 0.5$ composition that matches the lattice constant of InP, although it should also be noted that at $x = 0.91$ is lattice matched to InAs [2].

The energy band-gaps and optical and dielectric constants are important parameters that are required to model quantum structures. A precise knowledge of the band structure of the material of interest is necessary to evaluate its expectable domain of application, and the direct–indirect transition crossover composition value is particularly of prime importance. Moreover, to design and fabricate wave-guide devices, the refractive index has to be precisely known as a function of wavelength and composition. Although several experimental and theoretical investigations of optoelectronic and dielectric properties of III–V ternary semiconductor alloys have been reported [2, 3], so far, to the best of our knowledge, there has been relatively little work on the properties of $GaAs_xSb_{1-x}$. For that, further studies of the properties of $GaAs_xSb_{1-x}$ system are required.

In the present paper we have investigated the composition dependence of the energy band-gaps of $GaAs_xSb_{1-x}$ ternary alloys using the empirical pseudopotential method (EPM) within the virtual crystal approximation (VCA) which takes into account the effect of compositional disorder. The knowledge of the energy gaps has allowed us to obtain the refractive index and its composition dependence using three different models, namely, the modified Moss relation [4] based on an atomic model, the relation of Ravindra et al. [5] which governs the linear variation of refractive index with energy gap in semiconductors and the empirical relation of Hervé and Vandamme [6]. Attention has also been given to the behavior of the refractive index with respect to the photon energy using the analytical expression based on the simplified model of interband transitions reported by Adachi [7]. Combining the used method with the Harrison bond-orbital model, we have

F. Mezrag · N. Y. Aouina · N. Bouarissa (✉)
Physics Department, Faculty of Science and Engineering,
University of M'sila, 28000 M'sila, Algeria
e-mail: N_Bouarissa@yahoo.fr

calculated the dielectric constant and studied its variation versus arsenide concentration x.

Calculations

The local model empirical pseudopotential method (EPM) has been used so as to calculate the electronic structure of the material under investigation. The EPM is based on adjusting the pseudopotential form factors in order to reproduce measured band gap energies at selected points in the Brillouin zone. For that, we have used the non-linear least squares method [8] for the optimization of the empirical pseudopotential parameters. The experimental band gap energies for GaSb and GaAs binary compounds used in the fitting procedure are shown in Table 1. The dimension of our eigenvalue problem is a (136×136) matrix. However, 59 plane waves give generally a good convergence.

The alloy potential is calculated within the virtual crystal approximation (VCA), where a non-periodic potential due to the compositional disorder [12, 13] has been included. Thus, the potential of the alloy is taken as,

$$V_{\text{alloy}}(r) = V_{\text{VCA}}(r) + V_{\text{dis}}(r) \tag{1}$$

where $V_{\text{VCA}}(r)$ is the periodic virtual crystal potential and $V_{\text{dis}}(r)$ is the non-periodic potential due to the compositional disorder. Hence, the final expression for the pseudopotential form factors was,

$$V_{\text{alloy}}(G) = (1-x)V_{\text{GaSb}}(G) + xV_{\text{GaAs}}(G) - p[x(1-x)]^{\frac{1}{2}}[V_{\text{GaAs}}(G) - V_{\text{GaSb}}(G)] \tag{2}$$

where p is an adjustable parameter. When the VCA is used alone (without taking into account the disorder effect), p equals to zero. However, when the compositional disorder is included, the value of p is found to be 0.71, which gives a E_g^{Γ} band gap bowing parameter of 1.2 eV in agreement with the experimental one reported in ref. [1].

The lattice constant of the alloy of interest is obtained according to Vegard's rule [14],

$$a_{\text{alloy}}(x) = (1-x)a_{\text{GaSb}} + x\,a_{\text{GaAs}} \tag{3}$$

The refractive index (n) has been calculated using three different models that are related directly to the energy band-gap E_g as follows,

(i) The Moss formula [4] based on an atomic model,

$$E_g n^4 = k \tag{4}$$

where E_g is the energy band gap and k is a constant with a value of 108 eV [4].

(ii) The Ravindra et al. [5] relation,

$$n = \alpha + \beta E_g \tag{5}$$

with $\alpha = 4.084$ and $\beta = -0.62$ eV^{-1}

(iii) The Hervé and Vandamme [6] empirical expression,

$$n = \sqrt{1 + \left(\frac{A}{E_g + B}\right)^2} \tag{6}$$

for $\omega << \omega_0$, where ω_0 is the ultratviolet resonance frequency, $A = 13.6$ eV and $B = 3.4$ eV

In order to show the variation of the refractive index as a function of the photon energy for a given values of the composition x, we have adopted the same model used by Adachi [7],

$$n(\omega) \approx \varepsilon_1(\omega)^{0.5} \tag{7}$$

where $\varepsilon_1(\omega)$ is the real part of the dielectric function given by,

$$\varepsilon_1(\omega) = A\left[f(\chi_0) + \frac{1}{2}\left[\frac{E_0}{E_0 + \Delta_0}\right]^{1.5} f(\chi_{0s})\right] + B \tag{8}$$

with

$$f(\chi_0) = \chi_0^{-2}\left[2 - (1+\chi_0)^{0.5} - (1-\chi_0)^{0.5} H(1-\chi_0)\right] \tag{9a}$$

$$f(\chi_{0s}) = \chi_{0s}^{-2}\left[2 - (1+\chi_{0s})^{0.5} - (1-\chi_{0s})^{0.5} H(1-\chi_{0s})\right] \tag{9b}$$

Table 1 Band-gap energies of GaSb and GaAs

Compound	Band-gap energy (eV)					
	E_g^{Γ}		E_g^{X}		E_g^{L}	
	Exp	Cal	Exp	Cal	Exp	Cal
GaSb	0.725[a,b]	0.72 [c]	1.03[b]	1.02[c]	0.761[b]	0.78 [c]
GaAs	1.42[d]	1.42 [c]	1.81[d]	1.81[c]	1.72[d]	1.72[c]

[a] Ref. [9]
[b] Ref. [10]
[c] Present calculations
[d] Ref. [11]

$$\chi_0 = \frac{\hbar\omega}{E_0} \tag{10a}$$

$$\chi_{0s} = \frac{\hbar\omega}{E_0 + \Delta_0} \tag{10b}$$

where $\hbar\omega$ is the photon energy and

$$H(y) = \begin{cases} 1 & \text{for} \quad y \geqslant 0 \\ 0 & \text{for} \quad y < 0 \end{cases} \tag{11}$$

where A and B are parameters obtained by fitting Eq. (8) to the experimental III–V binary data[7].

The static dielectric constant (ε_0) has been calculated for each composition x in the range 0 to 1 using the relation which holds between ε_0 and high-frequency dielectric constant (ε_∞) within the Harrison model [15],

$$\frac{\varepsilon_0 - 1}{\varepsilon_\infty - 1} = 1 + \vartheta \tag{12}$$

where ϑ is given by [15],

$$\vartheta = \frac{\alpha_p^2 \left(1 + 2\alpha_c^2\right)}{2\alpha_c^4} \tag{13}$$

α_p is the polarity which was determined using the Vogl [16] definition,

$$\alpha_p = -\frac{V_A(3)}{V_S(3)} \tag{14}$$

V_S (3) and V_A (3) are the symmetric and antisymmetric form factors for a given composition x at G(111), respectively.

α_c is the covalency of the material of interest defined as,

$$\alpha_c^2 = 1 - \alpha_p^2 \tag{15}$$

Note that the high-frequency dielectric constant (ε_∞) has been estimated using the relation [17],

$$\varepsilon_\infty = n^2 \tag{16}$$

Results

The final local adjusted symmetric V_S and antisymmetric V_A pseudopotential form factors and used lattice constants for binary compounds GaSb and GaAs are listed in Table 2.

Figure 1 shows the composition dependence of band-gap energies, namely the direct band-gap E_0 (taken as the transition $\Gamma_v \rightarrow \Gamma_c$) and the indirect ones E_g^X (taken as the transition $\Gamma_v \rightarrow X_c$) and E_g^L (taken as the transition $\Gamma_v \rightarrow L_c$) for the ternary alloy $GaAs_xSb_{1-x}$. The solid and dashed lines are fitting curves to $E = a + bx + cx(x-1)$, where c is the band-gap bowing parameter. The analytical expressions are as follows:

$$E_0 = 0.68 + 0.51x - 1.21x^2 \tag{17}$$

$$E_g^X = 0.94 - 1.51x + 2.31x^2 \tag{18}$$

$$E_g^L = 0.72 - 1.07x + 2.02x^2 \tag{19}$$

The unit of the energy is eV. Accordingly, all band-gap energies increase non-linearly on going from GaSb to GaAs. The system transition between the direct and indirect structures occurred twice. Firstly, at the composition $x \cong 0.048$ which corresponds to an estimated crossover band-gap of 0.62 eV. This transition is originated by L-conduction band. The second transition occurred at $x \cong 0.59$corresponding to a crossover band-gap of 0.82 eV and is originated by Γ-conduction band. Thus, our results suggest that the material of interest is a direct band-gap ($\Gamma_v \rightarrow \Gamma_c$) semiconductor for the composition $0 \leq x < 0.048$ and $0.59 < x \leq 1$ and is an indirect band-gap ($\Gamma_v \rightarrow L_c$) semiconductor for $0.048 < x < 0.59$.

Table 3 gives some resulting energy band-gaps in the alloy being studied here for different concentrations x ($0 < x < 1$). At $x = 0.5$, the material of interest is an indirect ($\Gamma_v \rightarrow L_c$) band-gap with $E_g^L = 0.73$ eV. $GaAs_xSb_{1-x}$ is most often encountered with this composition that matches the lattice constant of InP [2]. Another interesting composition is x=0.91 at which the alloy under investigation is lattice matched to InAs [2]. Our results show that at this composition, $GaAs_xSb_{1-x}$ is a direct ($\Gamma_v \rightarrow \Gamma_c$) semiconductor band-gap with $E_g^\Gamma = E_0 = 1.17$ eV.

The composition dependence of the refractive index has been calculated according to the relations (4–6) given in the section ‘Calculations’. Our results together with known data [18] are plotted in Fig. 2. Accordingly, a non-linear behavior of the refractive index can be clearly noticed for all three used models. A similar behavior has been reported for the refractive index in the Al_xGa_{1-x} As ternary alloy system [19]. Unlike this non- linear behavior, the known data of the refractive index exhibit linearity with respect to composition x. This discrepancy is mainly attributed to the fact that our results are obtained from the calculation of the refractive index for each composition x taking into account

Table 2 Pseudopotential form factors and lattice constants for GaSb and GaAs

Compound	Form factors (Ryd)						Lattice constant (Å)
	$V_S(3)$	$V_S(8)$	$V_S(11)$	$V_A(3)$	$V_A(4)$	$V_A(11)$	
GaSb	–0.191206	0.005	0.043533	0.04534	0.03	0	6.118
GaAs	–0.239833	0.0126	0.059625	0.060536	0.05	0.01	5.653

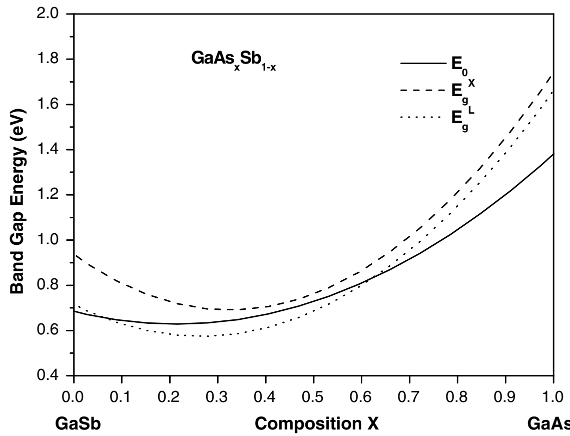

Fig. 1 Direct and indirect band-gap energies in $GaAs_xSb_{1-x}$ as a function of As content x

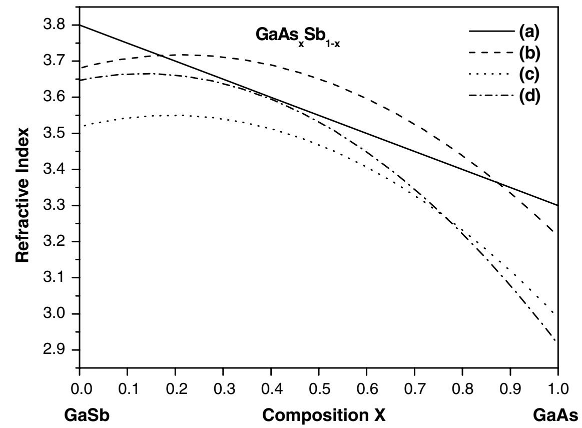

Fig. 2 Refractive index as a function of As content x, in $GaAs_xSb_{1-x}$ calculated from: (**a**) known data from the literature [18]. The refractive index is obtained using: (**b**) Ravindra et al.'s relation; (**c**) Hervé and Vandamme relation; and (**d**) Moss relation

the effect of compositional disorder, while the known data for the alloy of interest are just an interpolation between binary parent compounds GaSb and GaAs. The non-linearity with respect to x obtained in our results arises from the effects of alloy disorder. Thus, we are more convident to our results. We do believe however, that the Ravindra et al. model [5] gives better values of the refractive index than the other used models. This is because the values of the refractive index for GaSb and GaAs are closer to experiment when using the expression (5) as clearly seen in Table 4. The lines (b), (c) and (d) in Fig. 2 correspond to the best fit of our results to the expression,

$$n(x) = a + bx + cx^2 \quad (20)$$

The resulting values of a, b and c using the different models are listed in Table 5.

Using the analytical relation [7] based on the simplified model of interband transitions, the refractive index of the alloy of interest has been calculated as a function of the photon energy for $x = 0.02$, $x = 0.3$ and $x = 0.7$. Our results are shown in Fig. 3. The solid lines give our best fit to the calculated data. Accordingly, for all values of x, the refractive index exhibit non-linearity with respect to the photon energy showing however different refractive index bowing parameters for different values of alloy composition x. This arises from the effects of compositional alloy disorder on the refractive index which depend on the alloy concentration x. However, it should be noted that the refractive index decreases with increasing the photon energy on going from $\hbar\omega = 1.2$ to 3.2 eV, whatever the x value used in our calculations. Thus, the change of the arsenide concentration does not have an effect on the behavior of the refractive index with respect to the photon energy. This is not the case for $Al_xGa_{1-x}As$ where it has been reported that the change of the aluminum composition may strongly affect the behavior of the refractive index with respect to the photon energy [19].

Table 3 Calculated band-gap energies of $GaAs_xSb_{1-x}$ for different concentrations x

Ternary alloy	Band-gap energy (eV)		
	E_g^Γ	E_g^X	E_g^L
$GaAs_{0.10}Sb_{0.90}$	0.60	0.70	0.55
$GaAs_{0.30}Sb_{0.70}$	0.64	0.70	0.58
$GaAs_{0.50}Sb_{0.50}$	0.75	0.81	0.73
$GaAs_{0.70}Sb_{0.30}$	0.92	1.02	0.96
$GaAs_{0.91}Sb_{0.09}$	1.17	1.39	1.33

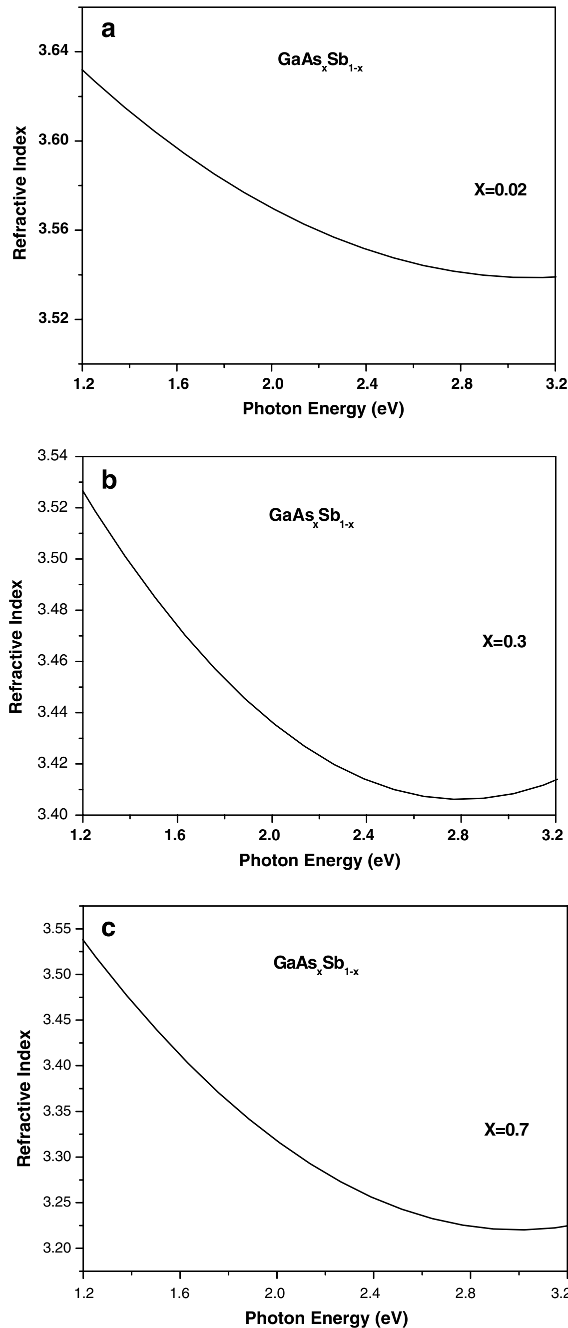

Fig. 3 (**a**) Refractive index as a function of the photon energy, in $GaAs_xSb_{1-x}$ for $x = 0.02$. (**b**) Refractive index as a function of the photon energy, in $GaAs_xSb_{1-x}$ for $x = 0.3$. (**c**) Refractive index as a function of the photon energy, in $GaAs_xSb_{1-x}$ for $x = 0.7$

The composition dependence of the static dielectric constant (ε_0) has been obtained according to the expression (12) using different models for the calculation of the high-frequency dielectric constant (ε_∞) that was directly deduced from the relation (16). Our results are displayed in Fig. 4. For comparison, known data [18] are also plotted. In view of Fig. 4, one can note that ε_0 decreases with increasing x on going from GaSb to GaAs showing a strong non-linear

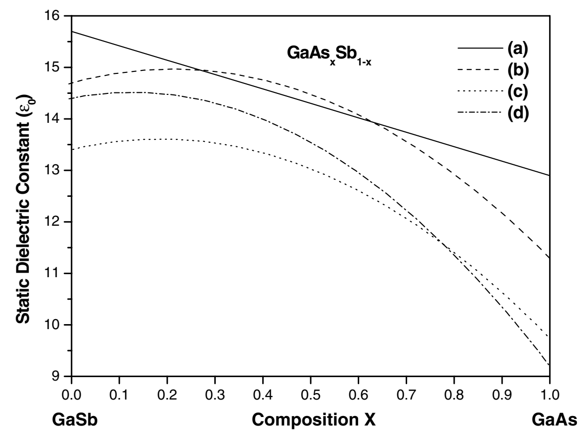

Fig. 4 Static dielectric constant as a function of As content x, in $GaAs_xSb_{1-x}$. (*a*) Known data from the literature [18]. The refractive index is obtained using (**b**) Ravindra et al.'s relation; (**c**). Hervé and Vandamme relation~; and (**d**). Moss relation

behavior for all used models in contrast to the linear behavior exhibited by the known data reported in ref. [18]. This is an expected result since our results are related to the refractive index discussed previously in the present work (Fig. 2). Once again we are convident to our results since those reported in ref. [18] were just an interpolation between the ε_0 of GaSb and GaAs. It seems as well that the Ravindra et al. model [5] leads to the obtention of values for ε_0 that are closer to experiment than the other used models. This is clearly seen in Table 6 for GaSb and GaAs binary parent compounds. The lines (b), (c) and (d) in Fig. 4 are the best fit of our calculated data by a least squares procedure. The analytical expressions are as follow:

$$\varepsilon_0(x) = 14.4 + 1.77x - 6.97x^2 \quad (21)$$

$$\varepsilon_0(x) = 14.7 + 2.52x - 5.92x^2 \quad (22)$$

$$\varepsilon_0(x) = 13.41 + 2.17x - 5.84x^2 \quad (23)$$

The expressions (21–23), correspond to the Moss [4] Ravindra et al. [5] and Hervé and Vandamme [6] models, respectively.

Summary

In summary, the composition dependence of energy band-gaps and optical and dielectric constants of $GaAs_xSb_{1-x}$ ternary semiconductor alloys has been

Table 4 Refractive indices of $GaAs_xSb_{1-x}$ for different compositions x

Material	n (calculated using relation (4))	n (calculated using relation (5))	n (calculated using relation (6))	n (known)
GaSb	3.5	3.64	3.45	3.8[a]
$GaAS_{0.10}Sb_{0.90}$	3.74	3.74	3.58	3.75[b]
$GaAs_{0.50}Sb_{0.50}$	3.49	3.63	3.44	3.55[b]
$GaAs_{0.90}Sb_{0.10}$	3.11	3.37	3.15	3.35[b]
GaAs	2.95	3.2	2.99	3.3[a]

[a]Ref. [20].

[b]Known data for $0 < x < 1$ are estimated from the linear relation suggested in ref. [18]

Table 5 Values of the parameters a, b, and c obtained by fitting the dependence of the refractive index of $GaAs_xSb_{1-x}$ on x to $n = a + bx + cx^2$

Model	a	b	c
Moss [4]	3.65	0.27	–1
Ravindra et al. [5]	3.68	0.36	–0.83
Hervé and Vandamme [6]	3.52	0.33	–0.86

Table 6 Static dielectric constants of $GaAs_xSb_{1-x}$ for different compositions x

Material	ε_0 calculated using relation (4) for n	ε_0 calculated using relation (5) for n	ε_0 calculated using relation (6) for n	ε_0 known
GaSb	13.28	14.34	12.89	15.70[a]
$GaAs_{0.10}Sb_{0.90}$	15.17	15.17	13.91	15.42[b]
$GaAs_{0.50}Sb_{0.50}$	13.20	14.33	12.85	14.30[b]
$GaAs_{0.90}Sb_{0.10}$	10.57	12.40	10.83	13.18[b]
GaAs	9.53	11.23	9.79	12.90[a]

[a]Ref. [18].

[b]Known data for $0 < x < 1$ are estimated from the linear relation suggested in ref. [18]

investigated. Our calculations are based on the EPM within the VCA which takes into account the effect of compositional disorder. The scheme used was combined with the Harrison bond-orbital model and employed for the calculation of the static dielectric constants. The agreement between our results and the available experimental data is found to be generally satisfactory. The material under study is found to be a direct band-gap semiconductor in the composition range $0 \leq x < 0.048$ and $0.59 < x \leq 1$, and an indirect band-gap semiconductor in the composition range $0.048 < x < 0.59$. Unlike, the linear behavior suggested in the literature for the refractive index with respect to alloy composition x, our results for all used models showed that the refractive index varies non-linearly with respect to x exhibiting a strong bowing parameter that is believed to be due to the effect of alloy disorder. It should be noted, however, that the Ravindra et al. model gives better values of the refractive index with respect to experiment as compared to other used models. The behavior of the refractive index with respect to the photon energy is found to be independent of the arsenide concentration. The composition dependence of the static dielectric constant showed as well a non-linear behavior and suggested that the use of the values of the refractive index obtained according to Ravindra et al. model for calculating the static dielectric constant gives better results.

References

1. Madelung O (eds) (1996) Semiconductors—basic data. Springer, Berlin
2. Vurgaftman I, Meyer JR, Ram-Mohan LR (2001) J Appl Phys 89:5815
3. Bouarissa N (2001) Mater Sci Eng B 86:53
4. Gupta VP, Ravindra NM (1980) Phys Stat Sol (b) 100:715
5. Ravindra NM, Auluck S, Srivastava VK (1979) Phys Stat Sol (b) 93:K155
6. Hervé PJL, Vandamme LKJ (1994) Infrared Phys Technol 35:609
7. Adachi S (1987) J Appl Phys 61:4869
8. Kobayasi T, Nara H (1993) Bull Coll Med Sci Tohoku Univ 2:7
9. Zollner S, Garriga M, Humlicek J, Gopalan S, Cardona M (1991) Phys Rev B 43:4349
10. Alibert C, Joullie A, Joullie AM, Ance C (1983) Phys Rev B 27:4946
11. Aspnes DE, Olson CG, Lynch DW (1976) Phys Rev Lett 37:766
12. Lee SJ, Kwon TS, Nahm K, Kim CK (1990) J Phys Condens Matter 2:3253
13. Bouarissa N (1998) Phys Lett A 245:285
14. Vegard L (1921) Z Phys 5:17
15. Davydov SYu, Tikhonov SK (1998) Semiconductors 32:947 and references cited therein
16. Vogl P (1978) J Phys C 11:251
17. Samara GA (1983) Phys Rev B 27:3494
18. Levinshtein M, Rumyantsev S, Shur M (eds) (1999) Handbook series on semiconductor parameters, vol 2. World Scientific, Singapore
19. Bouarissa N (2001) Matter Chem Phys 72:387
20. Levinshtein M, Rumyantsev S, Shur M (eds) (1996) Handbook series on semiconductor parameters, vol 1. World Scientific, Singapore