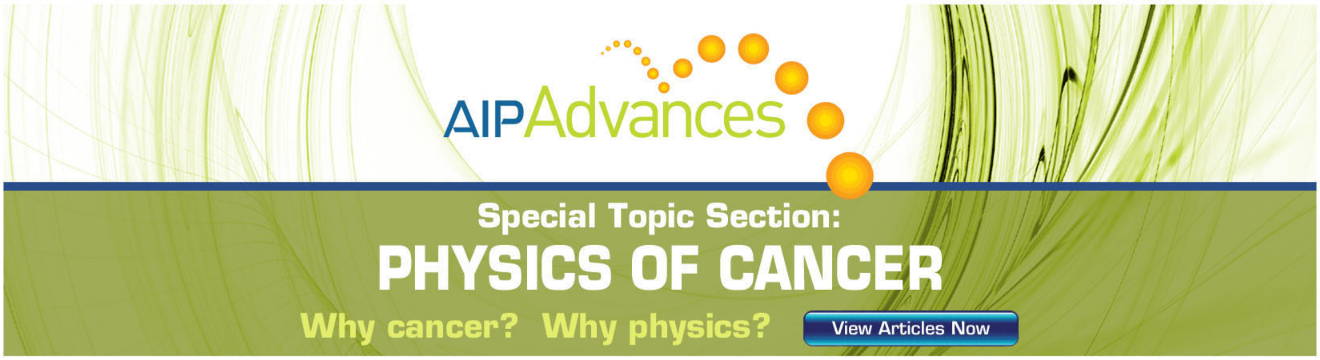
AIP | Journal of Applied Physics

Studies on 0.96 and 0.84 eV photoluminescence emissions in GaAs epilayers grown on Si

Jiachang Liang, Junhua Jiang, Jialong Zhao, and Ying Gao

Citation: J. Appl. Phys. **79**, 7173 (1996); doi: 10.1063/1.361489
View online: http://dx.doi.org/10.1063/1.361489
View Table of Contents: http://jap.aip.org/resource/1/JAPIAU/v79/i9
Published by the American Institute of Physics.



Studies on 0.96 and 0.84 eV photoluminescence emissions in GaAs epilayers grown on Si

Jiachang Liang
Department of Basic Sciences, Civil Aviation Institute of China, Tianjin 300300, People's Republic of China

Junhua Jiang
Department of Basic Sciences, Tianjin University of Light Industry, Tianjin 300222, People's Republic of China

Jialong Zhao and Ying Gao
Laboratory of Excited State Processes, Changchun Institute of Physics, Chinese Academy of Sciences, Changchun 130021, People's Republic of China

(Received 6 June 1995; accepted for publication 10 January 1996)

Studies on the 0.96 and 0.84 eV photoluminescence (PL) emissions at various temperatures in GaAs epilayers grown on Si with [As]/[Ga]=20–50 by metalorganic chemical vapor deposition were made. In terms of an Arrhenius plot and configurational coordinate model, the thermal activation energy and Franck–Condon (FC) shift for the 0.96 eV emission band were obtained by measuring the variations in its PL intensity and full width at half-maximum with temperature, respectively. The dependence on PL intensity versus temperature of the 0.84 eV PL emission could not be fitted with an Arrhenius plot. Instead, it could be fitted with the formula used for amorphous semiconductors or localized states which allowed us to relate this emission with the presence of defects in the heteroepitaxial GaAs layers grown on Si investigated. Taking into account the FC and band-gap shifts, the energy relationships of the transitions from donor to acceptor, from conduction band to acceptor, and from donor to valence band were reformulated. In terms of these transition-energy relationships and experimental data, the 0.96 eV emission was explained as the recombination luminescence of the donor–acceptor pair, composed of an arsenic vacancy and a gallium vacancy, and the 0.84 eV emission as the transition from the localized As interstitial–Ga vacancy complex center to Ga vacancy. © *1996 American Institute of Physics.* [S0021-8979(96)06908-2]

I. INTRODUCTION

It is well known that Si is a favored semiconductor substrate material for optoelectronic integrated circuits and optoelectronics because of its low cost and superior mechanical properties. Therefore, much attention has been paid to the growth of the heteroepilayers on Si. Recently the electrical and optical properties of heteroepitaxial GaAs grown on Si (GaAs/Si) have been studied.[1–4] It has also been reported that the large misfit of lattice constants and the discrepancy of thermal expansion coefficients between GaAs and Si cause the mismatch strain in heteroepilayers, which leads to the band-gap shift and to the creation of charged states of defects in such heteroepitaxial systems.[4–6] Thus, there also exist deep levels originating from charged states of defects in GaAs/Si.

In this work we studied the temperature-dependent near-infrared photoluminescence (NIPL) related to the deep levels present in GaAs/Si grown by metalorganic chemical vapor deposition (MOCVD) with different [As]/[Ga] ratios. Taking Franck–Condon (FC) and band-gap shifts into account, we revised the energy relations for the transitions from donor to acceptor, from conduction band to acceptor, and from donor to valence band and proposed that the 0.96 eV emission could be interpreted as the transition of the donor–acceptor pair (DAP), composed of an arsenic vacancy and a gallium vacancy, and the 0.84 eV emission as the transition from the localized As interstitial–Ga vacancy complex center to Ga vacancy.

II. EXPERIMENTS

The 1.2-μm-thick GaAs epilayers used for the present experiments were grown by MOCVD on n-type (100) Si substrates misorientated 4° toward as $\langle 110 \rangle$ direction using the standard two-step method.[1] The Si substrates were chemically treated in NH_4OH, H_2O_2, H_2O then HCL, H_2O_2, H_2O, and etched in HF for 1 min. In a H_2/AsH_3 ambience, they were heated initially at 950 °C for 10 min, and the temperature was lowered to 450 °C for GaAs buffer growth with thickness of 25 nm. Trimethylgallium and arsine in hydrogen were used as precursor chemicals. Then the temperature was raised to 700 °C, and the top GaAs epilayers were grown with the ratio of [As]/[Ga]=20–50 and with a growth rate of 100 nm/min. The samples were not intentionally doped. The carrier concentration at room temperature is $2\times10^{17}/\mathrm{cm}^3$.

The temperature-dependent NIPL spectra of GaAs/Si epilayer samples were obtained with an ordinary grating monochromator and were detected by a liquid-nitrogen-cooled Ge detector using conventional lock-in techniques. Luminescence was excited with the 632.8 nm line of a He–Ne laser. The measured temperature was 77–300 K and the excitation intensity 1.0 W/cm^2.

III. RESULTS AND DISCUSSION

A. The 0.96 eV PL emission

Figure 1 shows the NIPL spectrum of the GaAs/Si grown with [As]/[Ga]=20 by MOCVD at 77 K and excita-

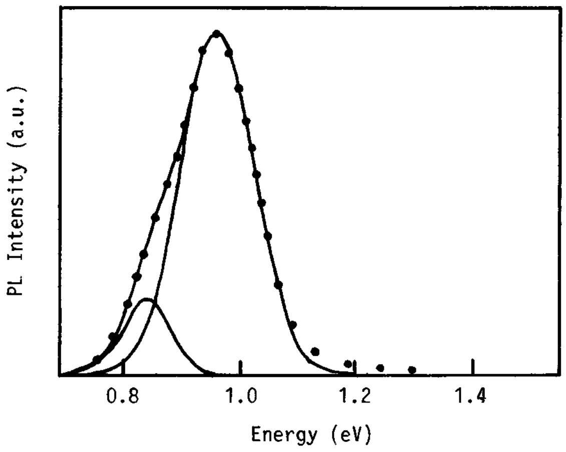


FIG. 1. NIPL spectrum of the GaAs/Si sample grown with [As]/[Ga]=20 by MOCVD at 77 K and excitation intensity of 1.0 W/cm^2. (●)—experimental points.

tion intensity of 1.0 W/cm^2. This NIPL spectrum can be fitted by a sum of two Gauss-type curves, including a main peak of 0.96 eV and a shoulder of 0.84 eV, respectively. The discrepancy at the right tail, as shown in Fig. 1, arises from the presence of an additional weak peak with an energy of 1.13 eV (see Fig. 5), which we have explained as the recombination luminescence of the DAP, composed of a Si shallow donor on Ga site and a Ga vacancy acceptor.[7]

The temperature-dependent PL spectra of this GaAs/Si sample were carried out in the temperature range of 77–300 K. Figure 2 shows the variation of PL intensity with temperature for the 0.96 eV emission band. In terms of experimental data, the thermal activation energy $E=0.10$ eV for this emission was obtained by using an Arrhenius plot

$$I=C\ \exp(\Delta E/kT), \tag{1}$$

where I is the PL intensity and C a constant.

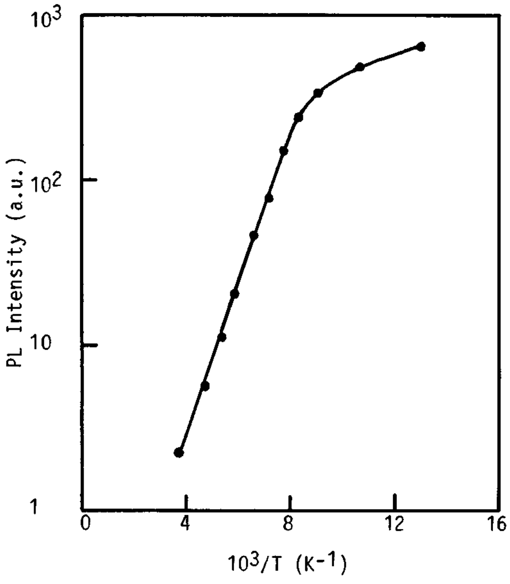


FIG. 2. Temperature dependence of PL intensity for the 0.96 eV emission band in GaAs/Si.

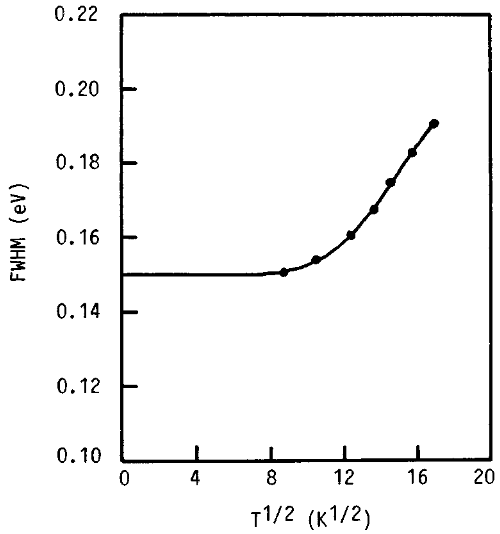


FIG. 3. Variation of FWHM with $T^{1/2}$ for the 0.96 eV emission band.

Figure 3 shows the variation of the full width at half-maximum (FWHM) of the 0.96 eV emission band in this GaAs/Si sample with the square root of temperature. According to the configurational coordinate model,[8] the theoretical temperature dependence of FWHM $W(T)$ is

$$W(T)=(8\ln 2)^{1/2}S^{1/2}\hbar\omega[\coth(\hbar\omega/2kT)]^{1/2}, \tag{2}$$

where $\hbar\omega$ is the phonon energy and S the Huang–Rhys factor. The solid line in Fig. 3 is the fit of Eq. (2) to the experimental data with $\hbar\omega=36$ meV and $S=3.2$. The Huang–Rhys factor $S>1$ indicates that there exists a stronger electron–lattice coupling, and therefore that the 0.96 eV emission band has a broad Gaussian line shape without any fine structure.[7–10] Thus, the FC shift $\Delta_{\rm FC}$ of the 0.96 eV emission band in GaAs/Si epilayers is given by

$$\Delta_{\rm FC}=S\hbar\omega=0.11\ \ \text{eV}. \tag{3}$$

Kim *et al.*[10] established a relation of the band-gap shift with temperature in GaAs. Liang *et al.*[11] indicated that taking into account FC and band-gap shifts, the energy relationship of DAP recombination luminescence could be reformulated as

$$h\nu=(E_g)_{\max}-\Delta E_g-(E_d+E_a-e^2/\epsilon r)-\Delta_{\rm FC}. \tag{4}$$

For the transition from donor to valence band or from conduction band to acceptor, Eq. (4) can be simplified as

$$h\nu=(E_g)_{\max}-\Delta E_g-E_d-\Delta_{\rm FC} \tag{5}$$

or

$$h\nu=(E_g)_{\max}-\Delta E_g-E_a-\Delta_{\rm FC}+E_k, \tag{6}$$

respectively, where $h\nu$ is an emission peak energy, E_d and E_a are the binding energies of the isolated donor and acceptor, respectively, $-e^2/\epsilon r$ is the Coulomb interaction energy of DAP, E_k the kinetic energy of the carrier at the conductor band, $(E_g)_{\max}$ the maximum of the band gap, and ΔE_g the band-gap shifts with temperature (ΔE_{g_1}) and with strain

(ΔE_{g_2}). GaAs/Si samples exhibit thermal tensile stress (~100 MPa) and it shifts the band gap of GaAs/Si to lower energies ($\Delta E_{g_2} \sim 10$ meV). Thus, for GaAs/Si,

$$\begin{aligned}&(E_g)_{\max}=1.517\ \text{eV},\\ &\Delta E_g=\Delta E_{g_1}+\Delta E_{g_2}=aT^2/(b+T)+10\ \text{meV},\end{aligned} \tag{7}$$

where T is the temperature of epilayers in K, $a=5.6\times10^{-4}$ eV/K, and $b=226$ K.[10]

Some published results indicated that in GaAs/Si exist Ga vacancies (electron trap), which are located at 0.29 eV above the top of the valence band.[12–14] Our experimental results demonstrate that with the increase of the [As]/[Ga] ratio, which reduces the concentration of V_{As} in GaAs, the PL intensity of the 0.96 eV emission rapidly decreases, as shown in Fig. 5. It means that the 0.96 eV emission possibly depends on V_{As}. Gutkin *et al.*[15] proposed that the 0.95 eV emission in GaAs doped with Te or Sn was caused by $V_{As}V_{Ga}Te_{As}$ or $V_{As}V_{Ga}Sn_{Ga}$ complexes. Wong *et al.*[16] suggested that the V_{Ga} complex in GaAs seems to be the defect responsible for a broad PL band at 0.95 eV. Using techniques based on positron annihilation, Ambigapathy *et al.*[17] have measured the ionization energies of the charged states of V_{As} in n-type Si-doped GaAs and one of those is located at 140 meV below the bottom of the conduction band. Xu *et al.*[18] performed the self-consistent tight-binding calculation of the energies and electronic structures on the neutral and charged states of V_{As}^n ($n=1+$, 0, $1-$, $2-$, $3-$, $4-$) and V_{Ga}^n ($n=1+$, 0, $1-$, $2-$, 3-) in GaAs with the Lanczos–Haydock recursion method. The deep-level energies of V_{Ga}^{1-} and V_{As}^{1-} are equal to 0.283 and 1.365 eV above the top of the valence band in GaAs with a band gap of 1.51 eV, respectively. Both theoretical and experimental values of the deep levels of the As and Ga vacancies in question are in good agreement. V_{As}^{1-} and V_{Ga}^{1-} compose the DAP in GaAs/Si. According to Eq. (4) and these experimental and theoretical data, the transition energy of the DAP, composed of V_{As}^{1-} donor and V_{Ga}^{1-} acceptor, is equal to 0.95–0.96 eV, which is in good agreement with our experiments, as shown in Fig. 1.

Harrison *et al.*[19] interpreted the 0.99 eV emission in Si-doped GaAs as a transition of the DAP, composed of Si_{Ga} and Si_{As}, Some experimental results[13,20,21] indicated that donor Si_{Ga} and acceptor Si_{As} are at 5 meV below the bottom of the conduction band and at 35 meV above the top of valence band in GaAs, respectively. Therefore, according to Eq. (4), the transition energy of the Si_{Ga}–Si_{As} pair should be equal to 1.33 eV instead of 0.99 or 0.96 eV. Thus the 0.96 eV emission in Fig. 1 originates from the transition of V_{As}^{1-}–V_{Ga}^{1-} pair instead of the Si_{Ga}–Si_{As} pair.

B. The 0.84 eV PL emission

As to the 0.84 eV PL emission in GaAs/Si, the variation of its PL intensity with temperature between 77 and 300 K was measured. Different from the 0.96 eV emission, the dependence of its PL intensity versus temperature could not be fitted with an Arrhenius plot. It appeared that the data could be fitted to a relation valid for amorphous semiconductors or localized states,[22,23]

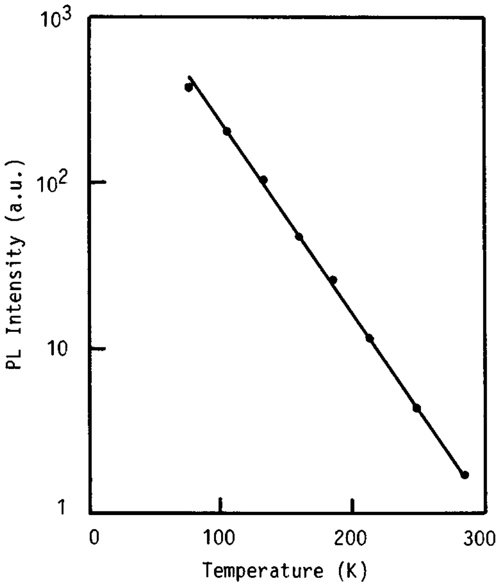


FIG. 4. Dependence of PL intensity vs temperature for the 0.84 eV emission. $T_0=37.4$ K.

$$I=I_0/[1+A\ \exp(T/T_0)] \tag{8}$$

which approached

$$I=I_0'\ \exp(-T/T_0) \tag{9}$$

when the measured temperature $T>677$ K, as shown in Fig. 4, where I_0' scales the PL intensity at the low-temperature limit and T_0 is a characteristic temperature corresponding to the energy depth of localized states. It means that the large misfit of lattice constants and the discrepancy of thermal expansion and coefficients between GaAs and Si lead to the creation of defects in the heteroepitaxial GaAs/Si layers and these defects cause the localized states with a characteristic temperature $T_0=37.4$ K, which reflects the degree of disorder in GaAs/Si epilayers.

Figures 5(a) and 5(b) show the NIPL spectra of the GaAs/Si grown with [As]/[Ga]=50 and 30, respectively, by MOCVD. With the increase of the [As]/[Ga] ratio, which leads to a decrease in As-vacancy concentration and to an increase in As-interstitial defects in GaAs/Si, the PL intensity of 0.96 eV emission rapidly decreases and 0.78, 0.84 eV emissions become stronger and stronger, as shown in Fig. 5.

Yu *et al.*[24,25] indicated that with the increase of the [As]/[Ga] ratio in the growth of GaAs samples by molecular beam epitaxy, the concentration of the As-interstitial related center increases. They attributed the 0.8 eV emission with $\Delta_{Fc}=0.34$ eV to the localized $EL6$ complex center, composed of an As interstitial and Ga vacancy, As_i–V_{Ga}, located at 0.36 eV below the bottom of conduction band. According to Eq. (5), $h\nu=0.78$ eV is obtained, by taking $E_d=0.36$ eV, $\Delta_{FC}=0.34$ eV, $(E_g)_{\max}=1.571$ eV, and $\Delta E_g=0.027$ eV ($T=100$ K). Thus, the 0.78 eV emission in Fig. 5 corresponds to the transition from As_i–V_{Ga} complex center to the valence band in GaAs/Si layers.

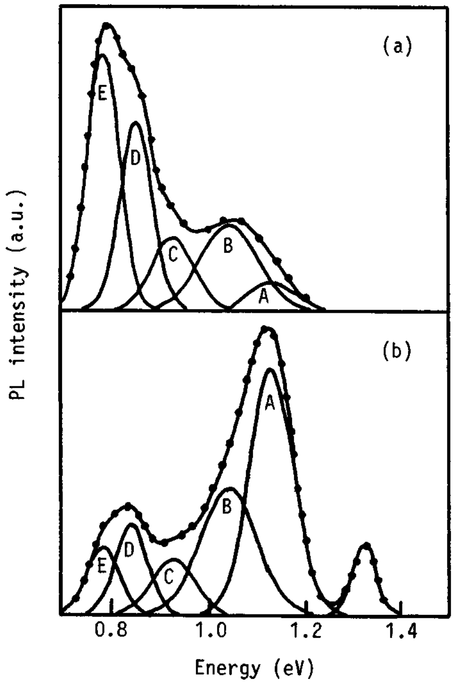


FIG. 5. NIPL spectra of the GaAs/Si epilayers grown with [As]/[Ga]=50 (a) and 30 (b), respectively, at 77 K and excitation intensity of 1.0 W/cm^2. (●)—experimental points. (-●-●-)—a sum of five Gauss-type curves.

According to the 0.84 eV emission characteristics and Eq. (4), where E_d and E_a are binding energies of As_i–V_{Ga} center and V_{Ga}^{1-}, which are equal to 0.36 eV below the bottom of conduction band and 0.283 eV above the top of the valence band,[18] respectively, $(E_g)_{\max}=1.517$ eV and $\Delta E_g=0.027$ eV ($T=100$ K), the 0.84 eV emission with no FC shift might originate from the transition between the localized As_i–V_{Ga} complex center and V_{Ga}^{1-}.

IV. CONCLUSION

We demonstrated that the deep-center PL at GaAs/Si layers strongly depends on their growth conditions, especially, on the [As]/[Ga] ratio. Taking FC and band-gap shifts into account, we revised the energy relations of the transitions from donor to acceptor, conduction band to acceptor, and donor to valence band. In terms of the transition-energy relations and emission characteristics, we explained the 0.96 eV emission as the recombination luminescence of the DAP, composed of an arsenic vacancy donor and a gallium vacancy acceptor. When the [As]/[Ga] ratio increased to 50 from 20 in the growth of GaAs/Si layers, the density of $EL6$ complex centers increased. And then, the 0.78 and 0.84 eV emissions became stronger and the 0.96 eV emission weaker. As to the 0.84 eV emission, the variation of its PL intensity with temperature obeys a relation valid for localized states because of the presence of defects ($EL6$ complex centers) in high density in the heteroepitaxial GaAs/Si layers studied. The 0.84 eV emission originates from the transition between $EL6$ complex center and V_{Ga} according to its emission characteristics and transition-energy relation in question.

ACKNOWLEDGMENT

We would like to thank the support of the Laboratory of Excited State Processes, Changchun Institute of Physics, Chinese Academy of Sciences.

[1] R. M. Lum, J. K. Klingert, B. A. Davidson, and M. G. Lamont, Appl. Phys. Lett. **51**, 36 (1987).
[2] Y. Huang, P. Y. Yu, M. N. Charasse, Y. Lo, and S. Wang, Appl. Phys. Lett. **51**, 192 (1987).
[3] J. E. Fouquet, R. R. Saxena, and G. A. Patterson, IEEE J. Quantum Electron **QE-25**, 1025 (1989).
[4] A. Mlayah, R. Carles, G. Landa, E. Bedel, C. Fontaine, and A. Munoz-Yague, J. Appl. Phys. **68**, 4777 (1990).
[5] C. P. Kuo, S. K. Vong, R. M. Cohen, and G. B. Stringfellow, J. Appl. Phys. **57**, 5428 (1985).
[6] J. Dabrowski and M. Scheffler, Phys. Rev. B **40**, 10391 (1989).
[7] J. Zhao, Y. Gao, J. Liang, and H. Gao, J. Mater. Sci. Lett. **13**, 1694 (1994).
[8] M. O. Manasreh and D. W. Fischer, Appl. Phys. Lett. **53**, 2429 (1988).
[9] P. W. Yu, Phys. Rev. B **42**, 11889 (1990).
[10] C. K. Kim, P. Lautenschager, and M. Cardona, Solid State Commun. **59**, 797 (1986).
[11] J. Liang, J. Zhao, and Y. Gao, J. Lumin. **63**, 41 (1995).
[12] Q. Dong, X. Zheng, P. Chen, and X. Fei, Chinese J. Semicond. **12**, 257 (1991).
[13] F. Bridges, G. Davies, J. Robertson, and A. M Stoneham, J. Phys. C **2**, 2875 (1990).
[14] I. Ohbu, M. Takahama, and K. Hiruma, Appl. Phys. Lett. **61**, 1679 (1992).
[15] A. A. Gutkin, M. A. Reshchikov, and V. R. Sosnovskii, Semicond. Sci. Technol. **9**, 2247 (1994).
[16] Z. G. Wong, C. J. Li, S. K. Wan, and L. Y. Lin, J. Cryst. Growth **103**, 38 (1990).
[17] R. Ambigapapthy, A. A. Manuel, P. Hautojarvi, K. Suarnen, and C. Corbel, Phys. Rev. B **50**, 2188 (1994).
[18] H. Xu and U. Lindefelt, Phys. Rev. B **41**, 5979 (1990).
[19] I. Harrison, L. Pavesi, M. Henini, and D. Johnston, J. Appl. Phys. **75**, 3151 (1994).
[20] S. A. McQuaid, R. C. Newman, M. Missous, and S. O'hagan, Appl. Phys. Lett. **61**, 3008 (1992).
[21] D. J. Ascen, P. J. Dean, D. T. J. Hurle, J. B. Mullin, and A. M. White, J. Phys. Chem. Solids **36**, 1041 (1975).
[22] R. A. Street, T. M. Searle, and I. G. Augustin, in *Amorphous and Liquid Semiconductors*, edited by J. Stuke and W. Brenig (Taylor and Francis, London, 1974), p. 953.
[23] T. Yamamoto, M. Kasu, S. Noda, and A. Sasaki, J. Appl. Phys. **68**, 5318 (1990).
[24] P. W. Yu, G. D. Robinson, J. R. Sizelove, and C. E. Stutz, Phys. Rev. B **49**, 4689 (1994).
[25] P. W. Yu and C. E. Stutz, J. Electron. Mater. **22**, 1441 (1993).