Symmetry determination of the $EL2$ defect by numerical fitting of capacitance transients under uniaxial stress

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The symmetry of the $EL2$ center in n-type liquid-encapsulated Czochralski GaAs is investigated through numerical fitting of capacitance transients measured under uniaxial stress. From experimental data which superficially appears compatible with T_d symmetry, we extract reproducible defect energy-level splitting under uniaxial stress and conclude that $EL2$ has C_{3v} symmetry, supporting the As_{Ga}-As_i pair model with As_i weakly bound to As_{Ga}.

I. INTRODUCTION

Along with the controversy about its microscopic structure, the properties of the $EL2$ defect in GaAs have been under investigation for a long time. The consensus is that the $EL2$ defect involves an arsenic antisite, As_{Ga}, while the dispute is whether it is only an isolated arsenic antisite or a complex of an arsenic antisite and other constituents. A recent excellent review is given in Ref. 1. Two prominent models have emerged. One is the isolated arsenic antisite, As_{Ga}, with T_d symmetry, supported by the stress splitting of the zero-phonon line (ZPL) of the intracenter transition,[2] and by the lack of splitting of the photoluminescence (PL) transition under uniaxial stress.[3] This model is also favored by many theoretical studies,[4–8] particularly for characterizing the $EL2$ metastability. The interpretation of the ZPL splitting results was, however, questioned,[9] raising the possibility of C_{2v} symmetry as an alternative. The same ZPL experiment was then independently repeated,[10] confirming that the original interpretation was correct and the $EL2$ center possesses T_d symmetry. The discussion continued when it was suggested that the so-called ZPL and its replica are due to electronic excitation from the antisite to the conduction band (CB) at the L minimum.[11] T_d symmetry was, therefore, suggested as a mere reflection of the bulk symmetry. The identity of the ZPL was further questioned when the hydrostatic pressure dependence of the ZPL final state was found to reflect that of the L CB minimum;[12] when the basically same ZPL and its replica have been observed on another As_{Ga}-related defect;[13] and when the ZPL and its related broad band move in opposite directions and overlap under hydrostatic pressure, questioning whether they are related to optical transition to the same final electronic state.[14] These experimental findings left the results from the PL uniaxial stress experiment[3] as the only solid experimental evidence supporting the isolated As_{Ga} model with T_d symmetry. It found no splitting of the photoluminescence transition under uniaxial stress, i.e., no orientational degeneracy. The main competing model is an arsenic antisite and arsenic interstitial pair, As_{Ga}-As_i, with C_{3v} symmetry, supported initially by electron paramagnetic resonance (EPR) and deep-level transient spectroscopy (DLTS),[15] later by optically detected electron-nuclear double resonance (ODENDOR),[16] and most recently by optically detected magnetic resonance (ODMR) and magnetic-circular dichroism of the absorption.[17] These microstructure-sensitive experiments indicate that As_i is located at a [111] tetrahedral site and is weakly bound to the antisite at about two As-Ga bond lengths away. C_{3v} symmetry is also shown by photocapacitance quenching behavior under uniaxial stress[18] and anisotropic electron-emission-rate enhancement induced by an electric field under various directions.[19] Theoretical works[20,21] examining the As_{Ga}-As_i pair model showed that, for both constituents to be in a singly positive-charge state in order to explain the EPR and ODENDOR results, the complex is not stable due to Coulombic repulsion. Recently, Chadi[22] proposed a modified model as As_{Ga}^{+}-As_i^{-} with improved stability. The overall symmetry of this model, however, has to be C_2 or C_{2v}.

We report in this paper improved analysis of the $EL2$ symmetry using DLTS with uniaxial stress. The standard rate-window DLTS analysis[23] is replaced by a more sophisticated analysis using full transient. Both our earlier experiments[24] and others[25] had difficulty accurately detecting the small stress-induced shifts of the DLTS peak using standard method. The low resolution is mainly due to two factors: (1) defect density comparable to donor density, and (2) difficulty in applying high stress to relatively soft GaAs crystals. Our previous work[26] has shown that the rate-window analysis, based on the approximation that the defect density N_T is much less than the donor doping density N_D, is substantially improved by numerically fitting the transients in the case of the $EL2$ defect center. We found for our sample ($N_T \approx 2\times10^{15}$ cm^{-3}, $N_D \approx 4\times10^{15}$ cm^{-3}) the $EL2$ thermal activation energy, $E_a \approx 756$ meV, as compared to 820 meV (Refs. 27 and 28) from the standard method. Second, unlike silicon where high enough uniaxial stress (e.g., >0.5 GPa) is rather easily achieved producing an appreciable DLTS peak shift and splitting for the A center,[29] for GaAs, high stress is difficult to achieve without damaging the sample. Particularly, considering that the $EL2$ defect may be a complex with As_i loosely

bound to As_{Ga}, any possible splitting would be small, and perhaps not visible via the rate-window DLTS peak with low stress. Therefore, we chose the improved numerical fitting method with higher resolution to analyze the capacitance transients measured under uniaxial stress. We concentrate the discussion on analysis assuming T_d and C_{3v} models, while briefly discussing the C_2 or C_{2v} alternative.

II. EXPERIMENTS AND DATA ANALYSIS

The uniaxial stress apparatus consists of a compound lever, capable of applying up to 5 GPa pressure from room temperature to 450 K.[30] The n-type liquid-encapsulated Czochralski GaAs sample is cut to approximately 1.5 mm×2.2 mm×3.5 mm with the long axes, determined from x-ray diffraction, parallel to [100], [110], and [111], respectively. A Schottky diode and an Ohmic contact are made by evaporating gold and tin, respectively, on two polished and etched surfaces. Negatively biased pulses (bias voltage −4.5 V, pulse height 4.3 V, pulse width 0.1 s, pulse period 1 s) are applied to the diode. The digitized capacitance transients[26] are recorded every 1.5 K from 340 to 410 K and under stresses ranging from zero up to 0.35 GPa on the three principal axes. High-quality diodes and clean transients are essential to successful numerical fitting. High signal-to-noise ratio is achieved by averaging over 50 separate transients while keeping the temperature variation within ±0.2 K.

The model for fitting the transients was fully explained previously.[26] Prior to the approximation resulting in the rate-window analysis, the capacitance transient is

$$C(t)=C(\infty)[1-Re^{-t/\tau}]^{1/2}, \quad (1)$$

where $R=N_T/(N_D+N_T)$, N_T (N_D) is the $EL2$ defect (donor doping) density, and τ is the electron-emission time constant from the defect. Any visible rate-window DLTS peak shift or splitting can be measured with higher accuracy by fitting the full transient to this model.

Because of the existence of both experimental and theoretical evidences supporting strongly either the isolated antisite model or the complex model, there are speculations that the $EL2$ defect may be a complex with an As interstitial weakly bound to an As antisite; that C_{3v} symmetry results from slightly disturbing T_d symmetry of As_{Ga}; and that some experiments may not detect the symmetry lowering due to small deviations from the isolated antisite behavior. If these are true, it is quite conceivable that any energy-level splitting could be too small to be measured by the standard DLTS method or even by fitting full transient to a single exponential model of Eq. (1). Attempting to resolve any possible hidden energy-level changes, we thus also fit the full transient to a double exponential model,

$$C(t)=C(\infty)[1-R_1e^{-t/\tau_1}-R_2e^{-t/\tau_2}]^{1/2}, \quad (2)$$

where $R_1+R_2=R$. R_1, τ_1, R_2, and τ_2 appear because under stress the centers form two groups with densities N_{T1} and N_{T2} and emission time constants τ_1 and τ_2. This model is based on Kaplyanskii's[31] analysis. For an anisotropic center of C_{3v} symmetry, the number of splitting components under uniaxial stress is 2, the orientational degeneracy is 4, and under [100], [110], and [111] stresses, the ratios between the densities of the splitting components are, respectively, 4:0, 2:2, and 1:3, and the splitting magnitudes are, respectively, A_1:0, A_1+A_2:A_1-A_2, and A_1+2A_2:$A_1-\frac{2}{3}A_2$. Here A_1 and A_2 are piezospectroscopic tensor components (meV/GPa) linking the energy shift to the applied stress, and are characteristic of each anisotropic center. The hydrostatic pressure coefficient of the defect energy is $3A_1$ since hydrostatic pressure is equivalent to applying three [100] stresses simultaneously in cubic crystals, and A_2 is a measure of the anisotropy of the defect center. For C_2 symmetry, the orientational degeneracy is 6, the number of splitting components under uniaxial stress could be 3, and a third exponential component is, therefore, necessary in Eq. (2) for certain stress directions. In addition, there are three independent piezospectroscopic tensor components instead of two, see Ref. 31.

The nonlinear least-squares Marquardt method[32,33] is used to fit the experimental data. Transients taken under various temperatures and stresses are fit to both Eqs. (1) and (2). While fitting to Eq. (2), assuming the defect center has C_{3v} symmetry, we restricted the densities of two splitting groups such that they can only be varied under the conditions satisfying R_2:$R_1\approx 2$:2 under [100] stress, R_2:$R_1\approx 2$:2 under [110] stress, and R_2:$R_1\approx 3$:1 under [111] stress. Though the overall trend does not differ fundamentally without the restrictions, the fitting does not consistently converge for every transient and R_2/R_1 occasionally varies drastically. For [100] stress, if the center has C_{3v} symmetry, we will obtain two identical groups with $\tau_1=\tau_2$ under the above condition, i.e., no splitting should appear. We also attempted to fit the experimental data to a multiple exponential model for C_{2v} or C_2 symmetry with inconsistent results. The fitted emission time constant (τ,τ_1,τ_2) from each transient with its temperature can then be used to calculate the apparent defect thermal activation energy E_a through the Arrhenius equation $\tau_n^{-1}=K_nT^2\sigma_n\exp(-E_a/kT)$, with K_n being constant and σ_n being the capture cross section for electrons.

III. RESULTS AND DISCUSSIONS

Figure 1 shows the defect activation energy plotted versus the applied uniaxial stress in the three principal directions as obtained by fitting the transients to Eq. (1). No energy splitting is observable in this case. The pressure derivatives dE_a/dP under the three stress directions are listed in Table I, in comparison with the data from other experiments. Measurements using uniaxial stress with the standard rate-window DLTS (Ref. 25) showed no splitting of the DLTS peaks. Only minute peak shifts for the three orientations were detected. Similar peak shifts are also observed with low accuracy in our experiment when using the rate-window method to analyze the same data, see Ref. 35. PL uniaxial stress[3] also did not see any splitting of the $EL2$ PL transition peak and obtained roughly the same pressure derivative for the $EL2$

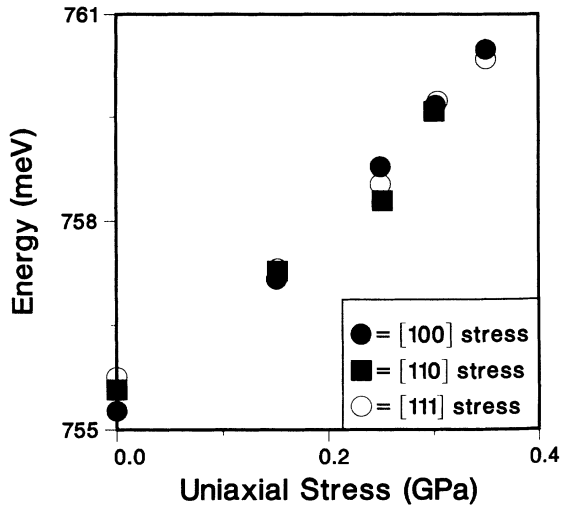


FIG. 1. $EL2$ thermal activation energy E_a as a function of uniaxial stress. Results are obtained by fitting the experimental data to Eq. (1).

ground energy level, dE_T/dP, under each stress direction. The corresponding dE_a/dP from PL uniaxial stress experiment is estimated by adding one-third of the hydrostatic pressure derivative of the capture barrier energy, $dE_b/dP=-41$ meV/GPa,[36] to dE_T/dP measured under each stress direction, since $E_a=E_T+E_b$. Our results from fitting to the single exponential model appear to be within the range of the results from Refs. 25 and 34, and agree particularly well with the PL uniaxial stress results,[3] all easily leading to a conclusion that the $EL2$ defect seems to possess T_d symmetry.

Fitting to a multiple exponential model results in small energy-level splitting. Figure 2 shows the results obtained by fitting the data to Eq. (2) with the R_2:R_1 restrictions stated above. In Fig. 2(a), under [100] stress we see two components of almost identical energy shift, indicating there is indeed no splitting under [100] stress. In Figs. 2(b) and 2(c), we clearly see two components of different rates of energy shift with stress, showing there is a splitting of the thermal activation energy, and, therefore, a break of orientational degeneracy of the $EL2$ center under [110] and [111] stresses. The pressure derivative of each branch in the figure, dE_a/dP, is listed in the bottom half of Table I. The 1:2:2 splitting pattern in Fig. 2, with the corresponding defect density distributions proportional to R_2:R_1, clearly indicates that the $EL2$ defect possesses C_{3v} symmetry. For the C_{2v} or C_2 model with the corresponding splitting density ratios restrictions,[31] except for the [100] direction in orthorhombic I center (i.e., R_2:$R_1\approx 4$:2) where two components with the same energy shift are again observed, the fittings do not converge consistently, implying that C_{2v} or C_2 is not correct. Actually, the lack of [100] splitting already denies C_{2v} or C_2 symmetry.

The theoretical splitting magnitude under the three directions is also listed in Table I. We use the pressure derivative under [100] stress in Fig. 1 as A_1, since only a single component should exist under [100] stress. We then use the obtained A_1 and the corresponding theoretical expressions for the splitting magnitude under [110] and [111] stresses to calculate A_2 for all four branches. As can be seen, within fitting errors all four A_2 values are essentially the same, with the average $A_2=2.2\pm0.5$ meV/GPa. Compared with $A_1=14.9\pm0.5$ meV/GPa, A_2 is almost an order of magnitude smaller, an indication of weak anisotropic character of the $EL2$ center. We can also compute the hydrostatic component of dE_a/dP, which is equal to $3A_1$. Table II lists our result and the results from other hydrostatic pressure experiments[37–40] and PL uniaxial stress experiment.[3] Our result agrees reasonably well with these earlier values.

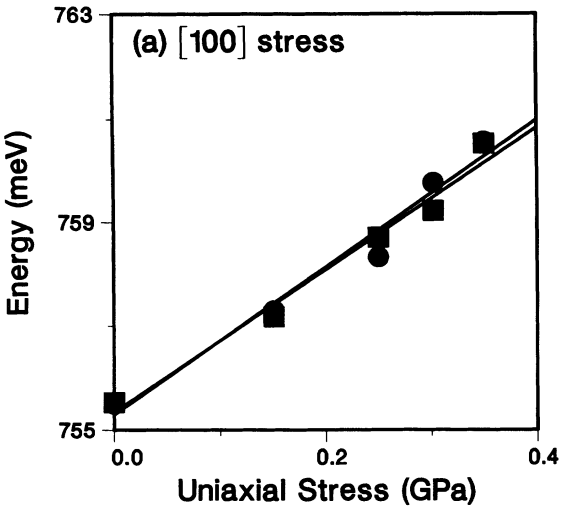
The above findings of weak anisotropy and C_{3v} symmetry support the proposed As_{Ga}-As_i model with As_i weakly bound to As_{Ga}. It may be argued that if one looks for two or more components when fitting experimental data one will see them. However, the fact that the energy-splitting pattern obtained matches only a trigonal center's behavior and not other symmetry types (i.e., no

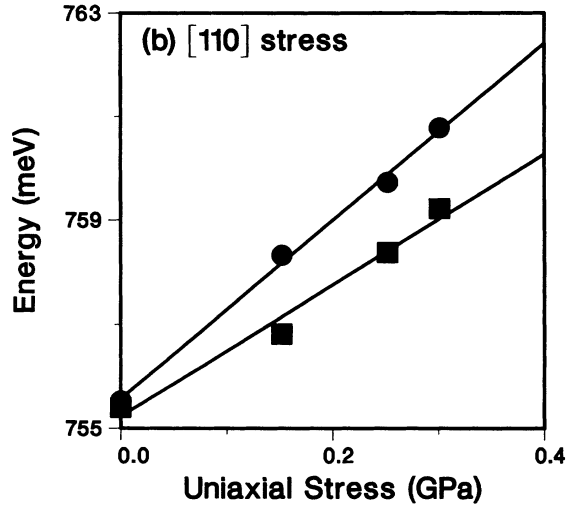
TABLE I. Pressure derivative of the $EL2$ thermal activation energy under the three uniaxial stress directions, dE_a/dP (±0.5 meV/GPa), obtained from fitting the experimental data to the single exponential model and the double exponential model, respectively. Listed also are the results from other uniaxial stress experiments.

Stress	[100]		[110]		[111]	
Fig. 1 [Eq. (1)]	14.9		12.5		13.2	
Splitting magnitude[a]	A_1					
Ref. 25	5		10		9	
Ref. 34	12		N/A		8	
Ref. 3[b]	13.2		13.6		13.9	
Fig. 2 [Eq. (2)]	14.2	13.7	16.8	12.6	18.8	13.4
Splitting magnitude[a]			A_1+A_2	A_1-A_2	A_1+2A_2	$A_1-\frac{2}{3}A_2$
Piezospectroscopic tensor		$A_1=14.9$	$A_2=2.2$	$A_2=2.3$	$A_2=1.9$	$A_2=2.3$

[a]See Ref. 31.

[b]Estimated by adding one-third of dE_b/dP from Ref. 36 to each dE_T/dP measured under stress by these authors.





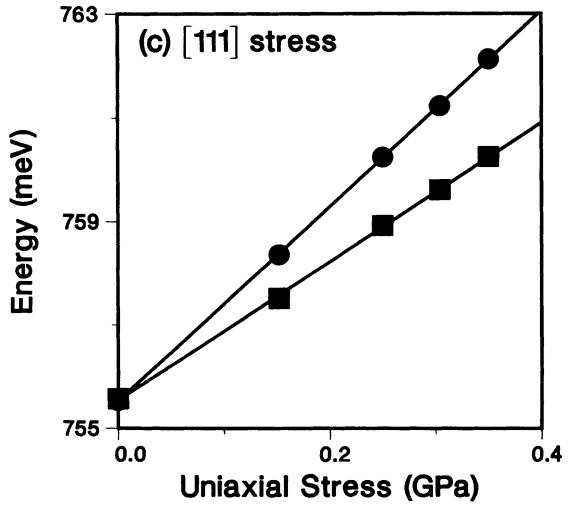


FIG. 2. *EL*2 thermal activation energy E_a as a function of uniaxial stress. Results are obtained by fitting the experimental data to Eq. (2). The solid line is the fit of the data points shown, with (a) for [100] stress, (b) for [110] stress, and (c) for [111] stress.

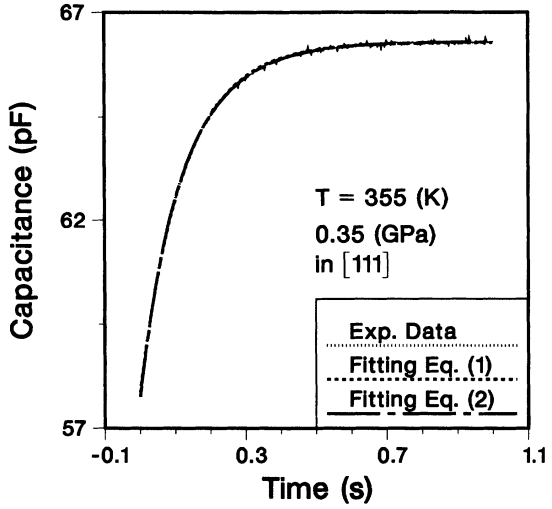


FIG. 3. Examples of experimental transient and its fittings to Eqs. (1) and (2), with the experimental data taken under 0.35 GPa in the [111] direction. The difference among the three transients is very small as they are shown on top of each other. Note, there is 1000 data points per transient with 1 ms time interval between two points.

splitting under [100] stress and two splitting components under [110] and [111] stresses) and the computed values of piezospectroscopic tensor components, A_1 and A_2, are reasonable should eliminate the possibility that the obtained double exponential transient and the energy-level splitting are coincidental and without physical meaning. Taking the data taken under 0.35 GPa in the [111] direction as an example, Fig. 3 shows a typical experimental transient and its fittings to Eqs. (1) and (2). The difference between fitting Eq. (1) and fitting Eq. (2) can hardly be seen as all three transients are on top of each other, illustrating that both fit very well to the experimental data. However, Fig. 4 shows the corresponding

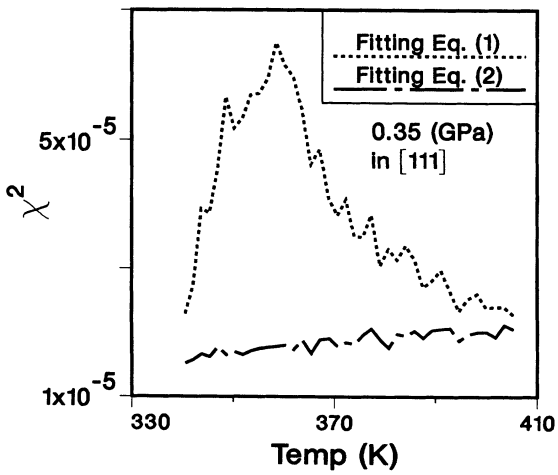


FIG. 4. Examples of χ^2 from fitting Eqs. (1) and (2) for data taken under 0.35 GPa in the [111] direction.

TABLE II. Hydrostatic pressure derivative of the $EL2$ thermal activation energy, dE_a/dP (meV/GPa), from current work and other experiments.

	Current work	Ref. 37	Ref. 38	Ref. 39	Ref. 40[a]	Ref. 3[a]
Hydrostatic $\frac{dE_a}{dP}$	$44\pm1.5(3A_1)$	41	44	38	42	40.6

[a]Calculated by adding the hydrostatic dE_b/dP from Ref. 36 to the hydrostatic dE_T/dP measured and calculated by these authors.

χ^2 obtained from fitting Eqs. (1) and (2). It shows χ^2 from fitting Eq. (2) is smaller than that from fitting Eq. (1), indicating that Eq. (2) represents the experimental data better than Eq. (1) and there is indeed an energy-level splitting. Note also, though, when fitting the full transient to the double exponential model, the restrictions of the splitting defect density ratios of a trigonal center are imposed, they do not guarantee to produce the energy-splitting pattern matching that of a trigonal center if the defect center does not actually possess trigonal symmetry. The same procedure is also applied when fitting the C_{2v} or C_2 model without obtaining consistent results. Therefore, the consistency of the energy-splitting pattern with the corresponding defect density populations and the weak anisotropic character of the center put the earlier results showing T_d symmetry and agreeing with the isolated As_{Ga} model in serious doubt. This conclusion is in conflict with other results, particularly that of PL uniaxial stress experiment which showed the $EL2$ defect has T_d symmetry. While we do not intend to assess the validity of other results, the behavior of our data does raise the possibility that a more careful data analysis or an experimental technique with finer resolution may reveal different results.

IV. CONCLUSIONS

We have used the numerical fitting of capacitance transients, instead of the standard rate-window DLTS, to investigate the symmetry of the $EL2$ center under uniaxial stress. Our results indicate that the $EL2$ defect has C_{3v} symmetry supporting the As_{Ga}-As_i model for the $EL2$ defect. The bonding between the arsenic antisite and arsenic interstitial is probably very weak; and thus, as shown here, it would be very easy to conclude that the $EL2$ defect is the isolated arsenic antisite. The lack of fine resolution of experimental data analyses and, possibly, of experimental techniques may have to be considered more seriously. In light of the difficulty of successfully applying high uniaxial stress to GaAs due to the nature of the crystal, experiments capable of providing the microstructural information directly, such as ODENDOR, ODMR, etc., may give more reliable information about this defect. Our results bring the DLTS data into agreement with these experiments.

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[1]G. A. Baraff, Acta Phys. Pol. A **82**, 599 (1992).
[2]M. Kaminska, M. Skowronski, and W. Kuszko, Phys. Rev. Lett. **55**, 2204 (1985).
[3]M. K. Nissen, A. Villemaire, and M. L. W. Thewalt, Phys. Rev. Lett. **67**, 112 (1991).
[4]J. Dabrowski and M. Scheffler, Phys. Rev. B **40**, 10 391 (1989).
[5]G. A. Baraff, Phys. Rev. Lett. **62**, 2156 (1989).
[6]D. J. Chadi and K. J. Chang, Phys. Rev. Lett. **60**, 2187 (1988).
[7]Q.-M. Zhang and J. Bernholc, Phys. Rev. B **47**, 1667 (1993).
[8]C. Ziegler, U. Scherz, and M. Scheffler, Phys. Rev. B **47**, 16 624 (1993).
[9]T. Figielski and T. Wosinski, Phys. Rev. B **36**, 1269 (1987).
[10]P. Trautman, J. P. Walczak, and J. M. Baranowski, Phys. Rev. B **41**, 3074 (1990).
[11]M. Skowronski, in *Defects in Electronic Materials,* edited by M. Stavola, S. J. Pearton, and G. Davis, MRS Symposia Proceedings No. 104 (Material Research Society, Pittsburgh, 1988), p. 405.
[12]H. J. von Bardeleben, Phys. Rev. B **40**, 12 546 (1989).
[13]J.-M. Spaeth, K. Krambrock, and D. M. Hofmann, in *Proceedings of the 20th International Conference on the Physics of Semiconductors,* edited by E. M. Anastassakis and J. D. Joannopoulos (World Scientific, Singapore, 1990), p. 441.
[14]P. Dreszer, M. Baj, and K. Korzeniewski, in *Proceedings of the 16th International Conference on Defects in Semiconductors,* Materials Science Forum, edited by G. Davis, G. G. DeLeo, and M. Stavola (Trans Tech, Zurich, 1992), Vol. 83-87, p. 875.
[15]H. J. von Bardeleben, D. Stievenard, D. Deresmes, A. Huber, and J. C. Bourgoin, Phys. Rev. D **34**, 7192 (1986).
[16]B. K. Meyer, D. M. Hofmann, J. R. Niklas, and J.-M. Spaeth, Phys. Rev. B **36**, 1332 (1987).
[17]K. Krambrock, J.-M. Spaeth, C. Delerue, G. Allan, and M. Lannoo, Phys. Rev. B **45**, 1481 (1992).
[18]M. Levinson and J. A. Kafalas, Phys. Rev. B **35**, 9383 (1987).
[19]L. Dobaczewski, in *Proceedings of the 15th International Conference on Defects in Semiconductors,* Materials Science Forum, edited by G. Ferenczi (Trans Tech, Switzerland, 1989), Vol. 38-41, p. 113.
[20]G. A. Baraff, M. Lannoo, and M. Schluter, Phys. Rev. B **38**, 6003 (1988).
[21]G. A. Baraff, M. Schluter, and M. Lanoo, in *Proceedings of the 15th International Conference on Defects in Semiconductors* (Ref. 19), p. 91.
[22]D. J. Chadi, Phys. Rev. B **46**, 15 053 (1992).
[23]D. V. Lang, J. Appl. Phys. **45**, 3023 (1974).
[24]C. D. Lamp, S. Yang, and S. Gangopadhyay, J. Appl. Phys. **73**, 2854 (1993).
[25]D. D. Nolte, W. Walukiewicz, and E. E. Haller, Phys. Rev. B **36**, 9374 (1987).

[26]S. Yang and C. D. Lamp, J. Appl. Phys. (to be published).
[27]J. C. Bourgoin, H. J. von Bardeleben, and D. Stievenard, J. Appl. Phys. **64**, R65 (1988), and references therein.
[28]G. M. Martin and S. Makram-Ebeid, in *Deep Centers in Semiconductors,* edited by S. T. Pantelides (Gordon and Breach, New York, 1986), p. 399, and references therein.
[29]J. M. Meese, J. W. Farmer, and C. D. Lamp, Phys. Rev. Lett. **51**, 1286 (1983).
[30]S. Yang and C. D. Lamp, Rev. Sci. Instrum. **64**, 221 (1993).
[31]A. A. Kaplyanskii, Opt. Spektrosk. **16**, 602 (1964) [Opt. Spectrosc. **16**, 329 (1964)].
[32]W. H. Press, B. P. Flannery, S. T. Teukolsky, and W. T. Vetterling, *Numerical Recipes* (Cambridge University Press, Cambridge, England, 1986), Chap. 14.
[33]D. W. Marquardt, J. Soc. Ind. Appl. Math. **11**, 431 (1963).
[34]G. Bastide, G. Sagnes, and C. Merlet, Rev. Phys. Appl. **15**, 1517 (1980).
[35]The apparent peak splitting reported earlier in Refs. 24 and 30 was very likely due to the sample's partial fracture. Similar phenomena are observed in the current experiment when the stress is applied with insufficient care. The results presented in this paper are fully reproducible as long as high-quality diodes and clean transients are obtained.
[36]P. Dreszer and M. Baj, Acta Phys. Pol. **73**, 219 (1988).
[37]G. A. Samara, D. W. Vook, and J. F. Gibbons, Phys. Rev. Lett. **68**, 1582 (1991).
[38]L. Dobaczewski and A. Sienkiewicz, Acta Phys. Pol. A **71**, 341 (1987).
[39]A. Zylbersztein, R. H. Wallis, and J. M. Besson, Appl. Phys. Lett. **32**, 764 (1978).
[40]O. Kumagai, K. Wunstel, and W. Jantsch, Solid State Commun. **41**, 89 (1982).