Photoionization cross section of the *DX* center in Si-doped $Al_xGa_{1-x}As$

R. Legros,* P. M. Mooney, and S. L. Wright
IBM Thomas J. Watson Research Center, P.O. Box 218, Yorktown Heights, New York 10598
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We report measurements of the photoionization cross section for the *DX* center in Si-doped $Al_xGa_{1-x}As$. The temperature dependence of the photoionization cross section for the Si *DX* center is reported for the first time. Data have been measured in both direct- and indirect-gap material and over a much wider temperature range than was possible for the Te *DX* center, thus providing a more stringent test of any model than the earlier data. The results agree well with the large-lattice-relaxation model proposed by Lang *et al.*

INTRODUCTION

The conductivity of *n*-type $Al_xGa_{1-x}As$ for $x > 0.20$ is controlled by a deep donor[1,2] which is called the *DX* center.[3] Trapping at this deep donor occurs by a thermally activated capture process and thus the *DX* center is the cause of persistent photoconductivity (PPC) in this material.[3-5] The *DX* center is present in all *n*-type $Al_xGa_{1-x}As$ whether the dopant is on a group-III site (Ge,Si,Sn) or on a group-V site (S,Se,Te) and its concentration is the order of the concentration of donor atoms, independent of the method or conditions of epitaxial crystal growth.[6-8] The activation energies for thermal emission and capture vary with the donor species.[9] The emission energy is independent of the alloy composition[10-12] but the capture energy is a strong function of the crystal band structure.[11-14] The optical ionization energy for the *DX* center is larger than the thermal ionization energy and depends strongly on the donor species.[15]

Lang *et al.*[3-5] proposed the large-lattice-relaxation (LLR) model to account for the properties of the *DX* center. In this model the ionized *DX* level lies well above the bottom of the conduction band. When an electron is captured, there is a rearrangement of the atoms resulting in a lower total energy when the electron is trapped at the *DX* center compared to when it is in the conduction band. The occupied (neutral) *DX* level lies below the bottom of the conduction band for $x > 0.22$, but remains above the bottom of the conduction band for $x < 0.22$ and thus is not observed by deep-level transient spectroscopy (DLTS). In order to account for the large relaxation of the lattice, Lang *et al.* suggested that the *DX* center was a complex consisting of the donor and an unknown native defect, perhaps an arsenic vacancy. Capture of an electron results in a change in the microscopic configuration of the defect.

Recently, other models have been proposed for the deep donor. A proposal which retains the notion of a large lattice relaxation but rejects the idea of a complex defect is that the donor atom is displaced from the substitutional site.[16-18] The *DX* center is a bound state of the donor atom associated with the *L* conduction-band minimum. It is argued that since the *DX* center concentration does not depend on the growth conditions, an arsenic vacancy or other native defect cannot be involved. In this model the large lattice relaxation results from the displacement of the donor when an electron is trapped.

Small-lattice-relaxation (SLR) models have also been proposed[19,20] in which the donor atom remains on or very close to the substitutional site. Again the *DX* center is proposed to be a bound state associated with the *L* minimum of the conduction band. In this model capture and emission occur via the *L* conduction-band minimum and are thermally activated processes in the temperature range where they are measured as they are for the LLR model. A key difference between these models is the predicted threshold energy for the optical ionization of the *DX* center. The small-lattice-relaxation (SLR) models require a photoionization threshold which is close to the donor binding energy. LLR was proposed to account for the large difference in the optical and thermal ionization energies for the *DX* center observed by Lang *et al.*[3,15] A model which attributes the observed properties of the *DX* center to fluctuations in the conduction-band structure due to the random distribution of atoms in the alloy has also been proposed.[21] This model, like the SLR models, predicts an optical ionization threshold nearly equal to the binding energy of the *DX* center.

The LLR model of Lang *et al.* is consistent with the observed properties of the *DX* center. They suggested that capture and emission of an electron at the *DX* center occur by multiphonon processes. The temperature dependence of the optical ionization cross section is predicted by this model. Lang *et al.* measured the temperature dependence of the optical ionization cross section of the *DX* center in Te-doped $Al_xGa_{1-x}As$.[3] However, because of the relatively small thermal emission energy for the *DX* center in Te-doped $Al_xGa_{1-x}As$, the temperature range of their experiment was limited to $40 < T < 78$ K, thus providing only a weak test of the model.

We report here new experimental results on the temperature and alloy composition dependence of the optical ionization cross section for the *DX* center in Si-doped $Al_xGa_{1-x}As$. The larger thermal emission energy for the *DX* center in Si-doped $Al_xGa_{1-x}As$ permits measurements of the optical ionization cross section over a much larger temperature range, up to $T=140$ K, providing a much better test of the model. Previously, the tempera-

ture dependence was investigated only in direct-gap samples. We report results for samples with direct and indirect band gaps. We discuss the implications of these results for the various models for the *DX* center.

SAMPLES AND EXPERIMENTAL METHOD

The samples used for these experiments were $Al_xGa_{1-x}As$ layers grown by molecular-beam epitaxy (MBE). One series of samples consisted of thick (1 μm) layers doped with 5×10^{16} to 2×10^{17} cm^{-3} Si. They were grown on *n*-type GaAs substrates and Mo was deposited in the MBE machine, while the sample remained under high vacuum, to form semitransparent Schottky-barrier diodes. A second series consisted of modulation-doped field-effect transistors (MODFET's). These were layers of $Al_xGa_{1-x}As$, approximately 500 Å thick, doped with 4×10^{17} to 1×10^{18} cm^{-3} Si, which were grown on undoped GaAs buffer layers on semi-insulating GaAs substrates. Schottky gates were made by depositing Ti/Pt/Au. The Ohmic contacts in both cases were standard AuGe/Ni/Au alloy contacts. The composition of the $Al_xGa_{1-x}As$ was measured by electron microprobe and ranged from $x=0.22$ to $x=0.74$. Thermal emission and capture energies were measured previously for both sets of samples.[11–14]

The optical emission transient was detected using a capacitance feedback circuit to maintain a constant capacitance and measuring the voltage applied to the diode as a function of time. The technique maintains a constant depletion depth, thus avoiding nonexponential transients due to the large trap concentrations in these samples.[3] The sample was cooled to the measurement temperature at forward bias to establish an initial condition with the *DX* centers in the neutral state. At the measurement temperature, the capacitance corresponding to the desired depletion width was selected and the sample was then exposed to monochromatic light. The voltage required to maintain this depletion width varies as the *DX* centers in the depletion region are photoionized and the carriers are swept away by the electric field. A temperature controller maintained the sample at constant temperature to within 1 K. The temperature range was from 21 to 140 K for these experiments. At $T>140$ K the time constant for thermal emission was sufficiently fast to interfere with the measurement of the slowest optical emission transients.

A quartz halogen lamp with narrow-band interference filters ($\Delta\lambda=10$ nm) was used as a monochromatic light source; a special housing arrangement was used to prevent any stray light from entering the cryostat. The light intensity at each wavelength was measured with a thermopile. The absolute intensity absorbed in the $Al_xGa_{1-x}As$ layer varied with the sample position and the type of sample, so comparisons of the absolute value of the cross section from sample to sample could not be made. For the series of samples with semitransparent Schottky contacts, measurements were made with photon energies up to the energy of the band gap of the $Al_xGa_{1-x}As$. For the MODFETS, however, this was not possible. Since the Schottky contacts were not transparent, multiple reflections of light from the back surface of the sample were required in order to provide sufficient light intensity to the *DX* centers. For energies greater than the band gap of GaAs, the light was absorbed in the underlying GaAs layers and was not reflected back into the $Al_xGa_{1-x}As$. For these samples the largest photon energy was 1.46 eV.

RESULTS AND DISCUSSION

Figure 1 shows optical emission transients for a sample with $x=0.33$. Data were taken at $T=84$ K with different photon energies. When the photon energy is reduced, the magnitude of the transient remains the same but the time constant of the transient increases. Except for one sample, the optical emission transients at all temperatures, for all photon energies, and for all samples, could be fit by a single exponential function. For the Schottky diode with $x=0.22$, the magnitude of the optical emission transients was very small and was not a single exponential. The data could be fit with two exponentials, suggesting that there is a second transient due to another deep level in this sample. The magnitude of the *DX* center emission transient is small because the DX level cannot be fully occupied in this sample. At room temperature the *DX* center is partially ionized since it is close to the bottom of the conduction band at this alloy composition.[2] The large capture barrier at this alloy composition prohibits capture as the sample is cooled to lower temperatures.[12,14] The sample characteristics are listed in Table I.

The optical ionization cross section is calculated from the emission transients using the equation $\sigma_n^0(h\nu)=(\phi\tau)^{-1}$, where ϕ is the photon flux and τ is the time constant of the emission transient. Figure 2 shows the optical ionization cross section $\sigma(h\nu)$, measured at $T=84$ K for samples with $x=0.33$ (direct gap), and $x=0.51$ and 0.74 (indirect gap). For the two MODFETs ($x=0.33$ and $x=0.51$) the highest photon energy used was 1.46 eV,

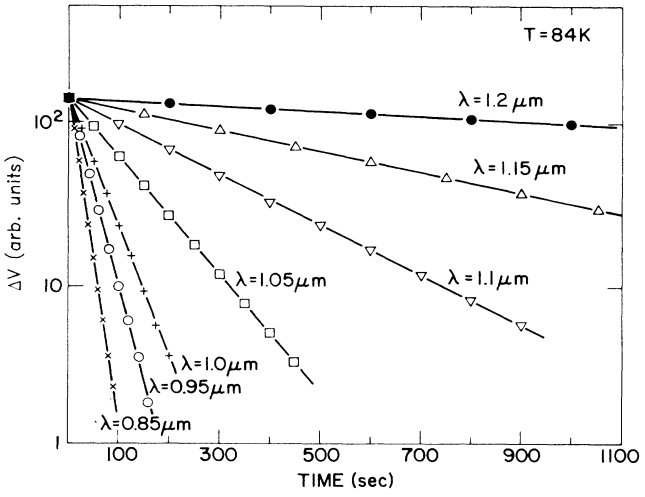

FIG. 1. Optical ionization transients at $T=84$ K for sample No. 2 ($x=0.33$) with light of different wavelengths. The capacitance was held constant and the change in applied voltage was measured.

TABLE I. Summary of sample characteristics and parameters from fits. (CB denotes conduction band.)

Sample No.	Al mole fraction x	N_D-N_A (cm^{-3})	Fit parameters (Bottom of CB) d_{FC}	E_0	E_n	Fit parameters (L minimum) d_{FC}	E_0	E_n
1 (Schottky)	0.22	1.2×10^{17}						
2 (MODFET)	0.33	8.7×10^{17}	1.20	0.083	1.283	1.12	0.160	1.280
3 (MODFET)	0.51	5.8×10^{17}	1.23	0.151	1.381	1.22	0.160	1.380
4 (Schottky)	0.74	7.0×10^{16}	1.24	0.087	1.327	1.16	0.160	1.320

whereas for the transparent Schottky diode it was 2.06 eV. Data for the $x=0.74$ sample were normalized to 1.0 at the maximum value of σ_n^0 and the data for the other two samples were normalized to that of the $x=0.74$ sample at a photon energy of 1.46 eV. The data sets were matched at a single point and the whole data set was multiplied by the same normalization factor. The data for the $x=0.33$ sample are in good agreement with those published for a Si-doped sample with $x=0.37$.[15] The data show little dependence on the alloy composition except at low photon energy as was found for the case of Te-doped $Al_xGa_{1-x}As$.[3]

A true optical threshold was not observed for these samples. A transient was observed for photon energies lower than 1.03 eV, the lowest energy for which data was plotted. However, the optical cross section becomes so small for lower photon energies that the transient could not be measured. For example, for a photon energy of 0.95 eV the ionization rate was so slow that a full day would have been necessary to record the complete transient. Therefore a much more intense light source is needed in order to get useful data for photon energies of 0.95 eV and lower.

The optical ionization cross section for the $x=0.74$ sample taken at two different temperatures is shown in Fig. 3. Note that the temperature dependence is small near the maximum; however, for smaller values of the photon energy, the optical ionization cross section is significantly smaller at lower temperature. Since only the temperature was changed here, the same normalization factor was applied to both data sets. The data taken at 84 K are those shown in Fig. 2. In Fig. 4, data for the optical ionization cross section at a photon energy of 1.305 eV are plotted as a function of temperature for the direct-gap sample ($x=0.33$). The data are normalized to those for this sample shown in Fig. 2 at a photon energy of 1.305 eV and at 84 K.

The solid lines in Figs. 3 and 4 are fits to the data using the LLR model of Lang *et al.*[3-5] The calculated values of the optical ionization cross section were normalized to the experimental data at a single point and the same normalization factor was applied to the whole curve. For the data in Fig. 3 the normalization was done near the maximum value of σ_n^0. In Fig. 4 the calculated curve was normalized to the experimental points at $T=120$ K.

In the LLR model thermal capture and emission occur

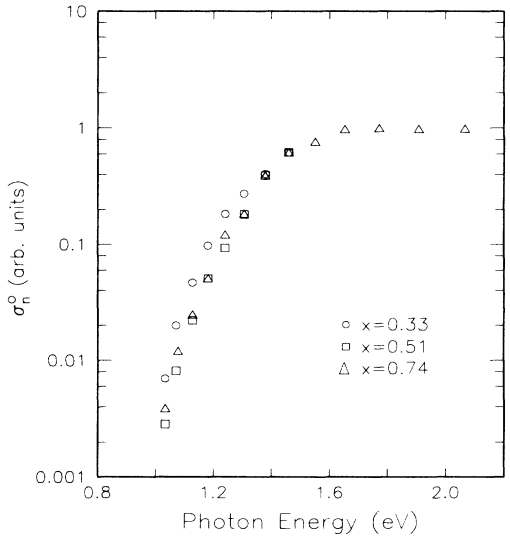

FIG. 2. Photoionization cross section as a function of the photon energy at $T=84$ K for three samples of different alloy composition. The uncertainty in the cross section is about 8%. Data for the $x=0.74$ sample are normalized to 1 at the maximum value. Data for the other samples are normalized to that of the $x=0.74$ sample at $h\nu=1.46$ eV.

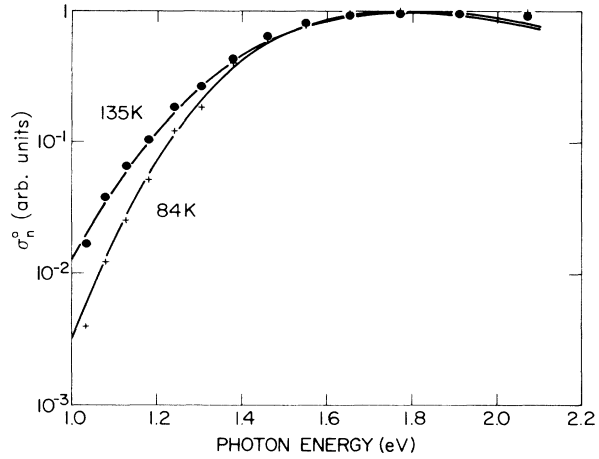

FIG. 3. Photoionization cross section as a function of the photon energy for sample No. 4 ($x=0.74$) at $T=84$ and 135 K. The points are experimental data and the solid lines are the values from Eq. (1).

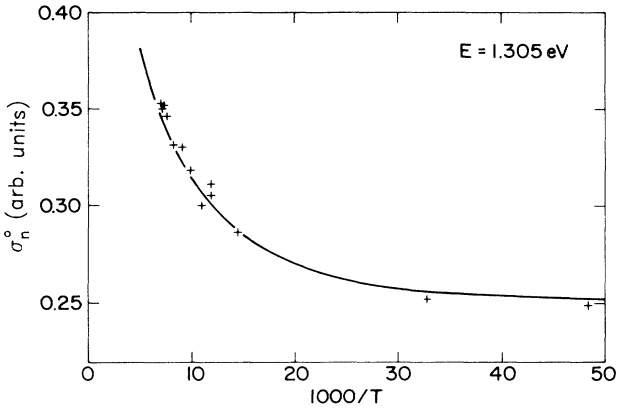

FIG. 4. Photoionization cross section as a function of temperature for sample No. 2 ($x=0.33$). The points are the data and the solid line gives the values from Eq. (1).

by multiphonon processes. The optical ionization cross section per photon, $\sigma(h\nu)$, is given by Eq. (11) of Ref. 3:

$$\sigma(h\nu)\sim\frac{1}{h\nu}\int_0^\infty dE\,\rho(E)\left[\frac{(1+\eta)E^{1/2}}{E_n+E}+\frac{(1-\eta)E_F^{1/2}}{E_n-E-(E_g+E_A)/2}\right]^2\times U^{-1/2}\exp\left[-\frac{[h\nu-(E_n+E)]^2}{U}\right], \quad (1)$$

where the density of electron states $\rho(E)$ was taken to be proportional to $E^{1/2}$, the function $\eta(E)=\exp(-2E/E_A)$, E_F is the free-electron Fermi energy, E_g is the band gap, E_A is the Penn gap, and E_n is the optical ionization energy. The function $U=2S(\hbar\omega)^2/\tanh(\hbar\omega/2kT)$, where ω is the phonon frequency, explicitly contains the temperature dependence. In this latter expression, S is the Huang-Rhys factor; it can be expressed by $S=d_{\rm FC}/\hbar\omega=(E_n-E_0)/\hbar\omega$, where $d_{\rm FC}$ is the Frank-Condon shift. A localized wave function and strong electron-phonon coupling are assumed. In the limit of a large Frank-Condon shift the lattice-relaxation Gaussian dominates the expression for $\sigma(h\nu)$. Figures 3 and 4 show clearly that the temperature dependence of the data for samples with both direct and indirect band gaps is in good agreement with the LLR model.

The fits have been made assuming that the optical transition is from the DX center to the lowest conduction-band minimum; Γ for the direct-gap sample and X for the indirect-gap samples. In the LRR model, the DX level is a highly localized state; it is extended in k space and, thus, momentum conservation is not violated by an optical transition to any of the conduction-band states. The values of the DX-center binding energy were taken from the Hall measurements of Chang *et al.*[2] The values for the other parameters are similar to those used by Lang *et al.*[3] and are as follows: free-electron Fermi energy $E_F=11.5$ eV and related phonon energy $\hbar\omega=0.010$ eV. Valence-band-like states were assumed. The Penn gap (average gap), $E_A=4.5$ eV, was taken as an adjustable parameter following Jaros.[22] As in Ref. 3, we have also assumed that the electron density of states and the optical ionization energy are independent of the temperature in the temperature range of the experiment. The fitting parameters are shown in Table I.

The value of the Frank-Condon shift $d_{\rm FC}$ obtained from the fits to the data is constant for the three samples. The value of the optical ionization energy is the sum of $d_{\rm FC}$ and the binding energy of the DX center. Thus the difference in the optical ionization energy among these samples is just the difference in the binding energy of the trap as the conduction-band structure varies with the alloy composition.

Other fits to these data were made assuming that the optical transition is from the DX center to the L conduction-band minimum. Since the density of states in the Γ band is low compared to that in the L band, this might be a reasonable assumption for direct-gap samples. This assumption would also be correct for the case where selection rules forbid transitions to the Γ or X minima. In this case the binding energy of the DX center was assumed to be constant and equal to 0.160 eV, since the DX level follows the L minimum.[2] The values of the optical ionization energy from these fits are nearly the same as in the previous case. The variation with the alloy composition shows up as a small variation in $d_{\rm FC}$ since the donor binding energy is constant with respect to the L conduction-band minimum. The fitting parameters are listed in Table I. The fits are about as good as in the first case so that we cannot rule out of the L conduction band as the final state for the optical transition on the basis of the fits. In the LLR model, however, the deep state is localized and selection rules forbidding a transition to a particular minimum are not operative. For the indirect-gap samples there is a large density of states in the lowest conduction band (X), and thus a transition to the X band seems more likely for such samples.

A Frank-Condon shift which is constant with alloy composition is consistent with DLTS measurements. The activation energy for thermal emission is also constant over this range of alloy compositions.[10,12,14] Both of these parameters are a measure of the lattice relaxation when the trap is ionized either optically or thermally. In both experiments the lattice relaxation does not vary with the alloy composition.

The group-VI donors (S, Se, and Te) all have about the same thermal emission energy and also the same optical ionization energy showing consistency between the two types of experiments as expected for the LLR model.[9,15] On the other hand, the thermal activation energy for the group-IV donors (Si, Ge, and Sn) decreases as the mass of the donor atom increases, and a similar trend was observed for the optical ionization energy.[9,15] The differences in the optical ionization energy have been related to differences in the force constant for atomic vibration in the LLR model.[15]

As discussed earlier, measurements of the optical ionization cross section at photon energies lower than 1.0 eV

were not possible by this method due to the steep decrease in the capture cross section. As the LLR model predicts, the optical ionization cross section gets smaller rapidly as the photon energy is decreased. Measurements of PPC, in modulation-doped samples (doped $Al_xGa_{1-x}As$ grown on undoped GaAs) show a threshold at about 0.85 eV and a rapid increase of the PPC with increasing photon energy which is consistent with the energy dependence of the optical ionization cross section reported here.[23,24] On the other hand, PPC has sometimes been observed for lower photon energies. Henning and Ansems report PPC for a photon energy of 0.3 eV in lightly doped samples; however, the magnitude of the effect is very small.[20] The small magnitude suggests either that there is only partial ionization of the *DX* center (the emission process is very slow and longer time is needed to complete the process) or that another process or trap gives rise to the PPC in this case. Further work would be needed to determine if this PPC is due to the *DX* center.

Subthreshold optical ionization has been reported for some point defects, e.g., the sulfur donor in silicon.[25,26] In that case the mechanism was a two-step photothermal process in which the photon excites the electron to an excited state of the donor from which it is thermally excited to the conduction band. It is possible that a similar mechanism may account for the reported PPC at low photon energy since it is known that other higher-energy states of the Si donor are present in $Al_xGa_{1-x}As$.[17,27] However, data taken at much lower photon energies are needed to determine if such a mechanism could apply to the *DX* center.

The threshold energy for optical ionization of the *DX* center is a key feature in distinguishing between the SLR or random-alloy models and the LLR models. Both the proposed SRL models and the random-alloy model require a threshold for the photoionization cross section of about 200–300 meV, much smaller than what our data suggests for the threshold energy. None of the SLR models nor the random-alloy model has predicted the dependence of the optical cross section on the photon energy in the range where we have data, or on the temperature or the alloy composition, so our data cannot yet be used to quantitatively test these models. However, our data seem to rule out these models since the very rapid decrease of the photoionization cross section near 1.0 eV implies a threshold energy near 0.9 eV.

Further evidence that the LLR models for the *DX* center are valid and that the *DX* center is a highly localized state is the strong dependence of the degree of nonexponentially of the thermal emission transient on the alloy composition. Calleja *et al.* have shown that the nonexponential behavior of the thermal emission transient is due to the random distribution of the Ga and Al atoms in the alloy.[28] The fact that the *DX* center is so sensitive to this variation of the second-nearest-neighbor atoms confirms that the wave function is highly localized.

CONCLUSIONS

In this paper we present measurements of the photoionization cross section for the *DX* center in Si-doped $Al_xGa_{1-x}As$. The temperature dependence of the photoionization cross section of the Si *DX* center is reported for the first time. Data are reported for both direct- and indirect-gap material. The data are taken over a much wider temperature range than was possible for the Te *DX* center and are thus a more stringent test of any model than the earlier data. The results agree well with the LLR model proposed by Lang *et al.*

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*Permanent address: Laboratoire de Physique des Solides, Centre National de la Recherche Scientifique 1, place A. Briand, F-92195 Meudon Cedex, France.

[1]A. K. Saxena, Phys. Status Solidi B **105**, 777 (1981).

[2]N. Chand, T. Henderson, J. Klem, T. Masselink, R. Fischer, Y. C. Chang, and H. Morkoç, Phys. Rev. B **30**, 4481 (1984).

[3]D. V. Lang, R. A. Logan, and M. Jaros, Phys. Rev. B **19**, 1015 (1979).

[4]D. V. Lang and R. A. Logan, Phys. Rev. Lett. **39**, 635 (1977).

[5]D. V. Lang, in *Deep Centers in Semiconductors,* edited by S. T. Pantelides (Gordon and Breach, New York, 1986), pp. 489–539.

[6]K. Yamanaka, S. Naritsuka, M. Mannoh, T. Yuasa, Y. Nomura, M. Mihara, and M. Ishii, J. Vac. Sci. Technol. B **2**, 229 (1984).

[7]P. M. Mooney, R. Fischer, and H. Morkoç, J. Appl. Phys. **57**, 1928 (1984).

[8]M. O. Watanabe, K. Morizuka, M. Mashita, Y. Ashizawa, and Y. Zohta, Jpn. J. Appl. Phys. **23**, L103 (1984).

[9]O. Kumagai, H. Kawai, Y. Mori, and K. Kaneko, Appl. Phys. Lett. **45**, 1322 (1984).

[10]M. Tachikawa, M. Mizuta, and H. Kukimoto, Jpn. J. Appl. Phys. **23**, 1594 (1984).

[11]P. M. Mooney, Mater. Res. Soc. Symp. Proc. **46**, 403 (1985).

[12]P. M. Mooney, N. S. Caswell, and S. L. Wright (unpublished).

[13]P. M. Mooney, *Semi-insulating III-V Materials,* edited by H. Kukimoto and S. Miyazawa (OHMSHA, Tokyo, 1986), p. 537.

[14]P. M. Mooney, E. Calleja, S. L. Wright, and M. Heiblum, *Proceedings of the 14th International Conference on Defects in Semiconductors, Materials Science Forum,* edited by H. J. von Bardeleben, (Trans. Tech. Publications, Switzerland, 1986), Vol. 10-12, Pt. 1, p. 417.

[15]D. V. Lang, *Proceedings of the 14th International Conference*

on the Physics of Semiconductors, Edinburgh, 1978, Inst. Phys. Conf. Proc. No. 43, edited by B. L. H. Wilson (IOP, Bristol, 1979), p. 433.
[16]K. L. Kobayashi, U. Uchida, and H. Nakashima, Jpn. J. Appl. Phys. **24**, L928 (1985).
[17]T. N. Morgan, Phys. Rev. B **34**, 2664 (1986).
[18]A. Oshiyama and S. Ohnishi, Phys. Rev. B **33**, 4320 (1986).
[19]H. P. Hjalmarson and T. J. Drummond, Appl. Phys. Lett. **48**, 656 (1986).
[20]J. C. M. Henning and J. P. M. Ansems, Semicond. Sci. Technol. **2**, 1 (1987).
[21]L.-Å. Ledebo, *Semi-insulating III-V Materials,* edited by H. Kikimoto and S. Miyazawa (OHMSHA, Tokyo, 1986), p. 543.
[22]M. Jaros, Phys. Rev. B **16**, 3694 (1978).
[23]M. I. Mathan, T. N. Jackson, P. D. Kirchner, E. E. Mendez, G. D. Pettit, and J. M. Woodall, J. Electron. Mater. **12**, 719 (1983).
[24]M. I. Nathan and M. Heiblum, J. Vac. Sci. Technol. B **2**, 167 (1984).
[25]L. L. Roiser and C. T. Sah, J. Appl. Phys. **42**, 4000 (1971).
[26]C. T. Sah, T. H. Ning, L. L. Rosier, and L. Forbes, Solid State Commun. **9**, 917 (1971).
[27]T. N. Theis, T. F. Kuech, L. F. Palmateer, and P. M. Mooney, in *Galluim Arsenide and Related Compounds 1984,* Inst. Phys. Conf. Ser. No. 74, edited by B. de Cremoux (IOP, London, 1985), p. 241.
[28]E. Calleja, P. M. Mooney, S. L. Wright, and M. Heiblum, Appl. Phys. Lett. **49**, 657 (1986).