Shallow donors in semi-insulating GaAs and their role in the excitation of the 0.64-eV photoluminescence

D. Paget
Laboratoire de Physique de la Matière Condensée, Ecole Polytechnique, 91128 Palaiseau Cédex, France

P. B. Klein
Naval Research Laboratory, Washington, D.C. 20375-5000
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Detailed studies of the shallow donor levels in semi-insulating (si) GaAs have been carried out with use of photoluminescence excitation (PLE) spectroscopy of the donor-acceptor pair (DAP) band as well as far-infrared magnetoabsorption. These studies show that in si GaAs there exist shallow donors with anomalously large binding energies in a continuous distribution between the effective-mass value (5.8 meV) and ≈ 12 meV. This effect most probably results from the Coulomb interaction between the electron bound to the donor and charged impurities which arise naturally as a result of the compensation process in si GaAs. In addition, PLE spectroscopy has been carried out for the deep 0.64-eV photoluminescence band, which has been associated with the presence of midgap centers. The similarity of the PLE spectra for the deep band and the DAP band is interpreted as evidence that the 0.64-eV band is excited by populating shallow donors. By combining these data with measurements of the PL time decay for this band, we conclude that the excitation mechanism for the 0.64-eV PL is the nonradiative capture by a deep center of an electron bound to a neutral donor, and that the most probable recombination mechanism is the radiative capture by the deep center of a hole trapped at a shallow acceptor.

I. INTRODUCTION

Because of the great technological interest in semi-insulating (si) GaAs as a substrate material for a whole range of electronic devices and for multiple-quantum-well structures, the basic properties of this material have been studied rather extensively by various resonance, transient capacitance, transport, and optical techniques.[1] Of all of the optical techniques, the results of photoluminescence (PL) measurements are probably the least well understood. Several broad PL bands have been observed near midgap at energies of 0.64, 0.68,[2-7] and 0.8 eV.[8,9] An unambiguous assignment of the center involved or of the excitation mechanism has yet to be reported for any of these bands. The 0.64-eV band has probably been the most extensively studied of these features, and has been associated with recombination at the EL2 center by several authors.[2,3,5,7] The most convincing evidence for this was the observed quenching of the 0.64-eV PL intensity under 1.17-eV excitation,[3] which was shown to be analogous to the quenching of the EL2 photocapacitance signal.[10] However, recent photoluminescence excitation spectroscopy[11] (PLE) and time-resolved PL measurements[12] show that this is not the case, and that the 0.64-eV PL band is due to recombination at a midgap level other than EL2. The transition of EL2 to its metastable state, by, e.g., 1.17 eV illumination, may indirectly affect the properties of other deep levels as well by inducing a shift in the Fermi level or by quenching the below-gap optical absorption.

Although the precise chemical origin for the 0.64-eV PL feature is still undetermined, some aspects of the excitation and recombination mechanisms associated with this feature have been reported. PLE measurements by Shanabrook *et al.*[5] revealed a threshold near the shallow acceptor—to—conduction-band transition energy and a sharp excitation feature peaking near 1.50 eV which was associated with a thermal activation energy of 30 ± 10 meV. This was interpreted as evidence that the PL transition was from the midgap level believed to be EL2 to a neutral acceptor. In addition, oscillations in the PLE spectrum observed above the band gap were interpreted as clear indications of resonant cooling of carriers in the conduction band, and suggested that shallow levels were participating as intermediate states in the excitation process for the 0.64-eV PL. Martin and Makram-Ebeid have suggested an alternative interpretation in which the 0.64-eV PL is due to the internal transition from an electron in a shallow donor excited state of the midgap level to the ground state of that center.

In the present work we have addressed the question of the excitation and recombination mechanisms associated with the 0.64-eV band by applying dye-laser-excited PLE measurements as well as several other experimental techniques, including far-infrared (FIR) magnetoabsorption, selective pair luminescence (SPL), and time-resolved PL. The results of these measurements have allowed us to make the following conclusions. In si GaAs there exists a continuous distribution of shallow donor binding energies between the effective-mass value of 5.8 meV and ≈ 12 meV. These abnormally large donor binding energies, which we shall refer to as "deeper shallow donors," result from the Coulomb interaction between the donor electron and charged defects (ionized shallow levels as well as charged deep levels) that arise naturally from the compen-

sation process that gives rise to the si material. Also, the 0.64-eV PL feature is excited by populating shallow donors (effective-mass donors as well as the deeper shallow donors), followed by the nonradiative capture of the donor electron by the deep center involved. The PL transition is most probably the radiative capture of a hole which is bound to a shallow acceptor.

Following a brief discussion of the experimental details in the next section, the notion of deeper shallow donors is presented in Sec. III as a consequence of the results of experiments involving PLE spectroscopy of the donor-acceptor pair (DAP) band, selective pair luminescence, and magnetoabsorption. In Sec. IV the excitation mechanism associated with the 0.64-eV PL band and the role of shallow donors in this process is discussed in light of PLE and time-dependent PL measurements on this band.

II. EXPERIMENTAL

The PLE measurements were carried out at 4.2 K using as a tunable excitation source an argon-ion laser-pumped cw dye laser operating with Styryl 9 dye. The 0.64-eV emission was detected using a PbS detector and a low resolution Jobin-Yvon monochromator. For the DAP PLE and the DAP and near-band-gap PL measurements a 0.75-m Jarrell-Ash double monochromator and a GaAs photomultiplier were employed. Most of the results in this work have been obtained using a liquid-encapsulated Czochralski-grown (LEC) si GaAs sample (No. CZ28) which was grown at Laboratoires d' Etudes et de Physique Appliquées. Similar results were also obtained in other bulk samples as well—in particular, sample RT715, which was grown at La Radiotechnique Compelec. For the samples studied it was determined that the dominant acceptor was carbon. This was achieved by using the technique of selective pair luminescence (SPL), which will be discussed in a later section. For comparison purposes, several high-purity samples grown by vapor-phase epitaxy (VPE) were also studied. Also, care was taken to avoid inadvertent irradiation of the sample by light near 1.17 eV, which is known to transfer the dominant EL2 center into its metastable state. This is important because this transition is known to affect the optical properties of other deep levels, and in particular the deep level associated with the 0.64-eV PL.[12]

Far-infrared magnetoabsorption experiments were carried out at 5 K using a far-infrared molecular gas laser cavity pumped by a CO_2 laser. The experimental apparatus was described in detail previously,[13,14] and only a brief description will be given here. The sample was placed in a cryostat which was in turn placed inside a Bitter solenoid which delivered a maximum field of ≈ 13 T. The far-infrared radiation was directed into the cryostat via a light pipe, and the incident radiation was split so that half was incident on the sample, which was in front of a Ge:Ga detector, and the other half was incident on a second identical detector. Both channels were fed into identical amplifiers and boxcar amplifiers, and the sample channel was then normalized to the reference channel by an analog ratiometer. This output was therefore proportional to the transmission of the far-infrared laser light through the sample, and this was monitored as the magnetic field was swept. A red-light-emitting diode was placed inside the light pipe in order to create a steady-state neutral donor concentration.

The time-resolved PL was obtained using a N_2 laser-pumped dye laser operating at 840 nm. Experiments were carried out at 4.2 K, and again care was taken to avoid inadvertent irradiation of the sample with light near 1.17 eV. The PL light was analyzed with a low resolution Bausch and Lomb monochromator and was detected with a fast (≈ 30 nsec) InSb detector. The PL waveforms were captured, stored, and averaged in a Tektronix 7912AD transient digitizer, which was controlled by a microcomputer.

III. DEEPER SHALLOW DONORS

In this section we present experimental evidence for the existence of shallow donors with binding energies that are larger than the effective-mass value of 5.8 meV found in high-purity GaAs. This evidence is derived from the results of PLE spectroscopy of the DAP band, selective pair luminescence of shallow donors, and ground—to—excited-state magnetoabsorption measurements of shallow donors.

A. Results

1. Donor-acceptor pair PLE spectra

The DAP PL spectrum for si sample CZ28 is shown at the bottom of Fig. 1 for above-gap excitation. The PL in this region was dominated by the DAP band, and no evidence of band-to-acceptor (e-A^0) emission was observed. The latter was found to be stronger in other samples, such as RT715, with different shallow impurity concentrations. The dominance of the DAP band in this sample allows for a more straightforward analysis of the data. The DAP band is quite featureless, as expected. However, it is noteworthy that the low-energy edge of the spectrum is expected to occur at $h\nu = E_G - E_A - E_D$ (where E_G, E_A, and E_D refer to the band gap and the binding energies of acceptors and donors, respectively), corresponding to the recombination of distant donor-acceptor pairs. Noting again that carbon is the dominant acceptor, this is expected to occur near 1.4875 eV for donor-carbon acceptor recombination. It is clear from Fig. 1 that there is significant DAP intensity well below this energy, and that the extrapolated low-energy cutoff is near 1.480 eV. The fact that the DAP PL extends to lower energies than normally expected may be viewed as a first indication of the existence of donors with binding energies substantially larger than the effective-mass value of 5.8 meV. Of course this is not the only possible interpretation of this phenomenon, since deeper DAP PL has been observed before, and has been interpreted in terms of the spatial variation of the band gap in heavily doped, highly compensated[15] and ion-implanted[16] samples. In the present case, however, an interpretation must await the presentation of all of the experimental data.

The central portion of Fig. 1 contains the PLE spectra of the DAP band. The experiment is carried out by set-

ting the spectrometer at one of several discrete positions on the DAP band (as indicated by the arrows), each of which corresponds to a specific donor-acceptor pair separation. The PL intensity at that setting is then recorded as a function of excitation wavelength, which is varied by scanning the dye laser. This results in a PLE spectrum, which represents the efficiency of various excitation wavelengths in exciting the chosen emission wavelength. By repeating this experiment for each spectral position along the DAP band, a family of PLE spectra is generated, such as that shown in Fig. 1. The wavelength of the detected PL emission is indicated to the left of each PLE spectrum and by the arrows on the DAP spectrum.

The general shape of the entire PLE spectrum can be seen most easily for spectral positions near the low-energy edge of the DAP spectrum, e.g., at 840 nm, where the passband of the spectrometer does not overlap substantially with the PLE spectrum itself. Two contributions to the PLE spectrum are observed: the first exhibits a threshold near 1.48 eV, and the second exhibits a peak at 1.507 eV. The 1.48-eV threshold corresponds well with the low-energy edge of the PL spectrum, and is clearly associated with acceptor-to-donor absorption. The peak at 1.507 eV is observed to shift continuously to higher energy as the spectrometer is shifted to shorter wavelengths along the DAP band, and reaches a maximum energy near 1.513 eV at a spectrometer setting of 828 nm, near the high-energy edge of the DAP spectrum. This energy corresponds well with that expected for valence-band—to—donor (VB-D) absorption (1.5137 eV). A similar PLE spectrum is measured in high-purity VPE material, and is shown in the top portion of Fig. 1. It is clear that the position of the VB-D feature in the high-purity material only corresponds well with the same feature in the LEC material *at the high-energy edge of the DAP band.*

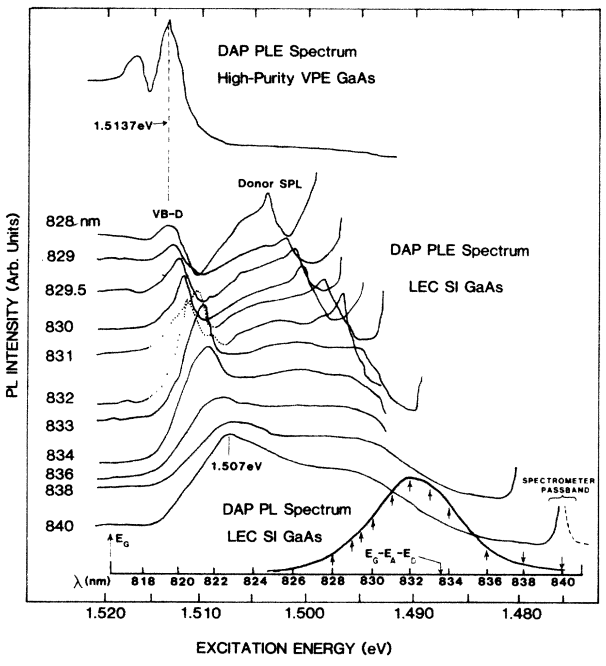

FIG. 1. Photoluminescence excitation spectra of the donor-acceptor pair band for LEC si GaAs measured at different spectral positions along the DAP PL band. The DAP PL spectrum is shown at the bottom, and the wavelengths along that spectrum at which the PLE measurements are carried out are indicated by arrows, and are also indicated to the left of the appropriate PLE spectra. At the top is the analogous PLE spectrum for high-purity VPE material, where the same PLE spectrum is obtained for all PL wavelengths. The dotted portions of the curves represent PLE data that has been distorted by acceptor SPL, as discussed in the text.

A continuous $\approx$6-meV shift of the VB-D transition from its usual value to near 1.507 eV is highly suggestive of a continuous distribution of donor binding energies between the effective-mass value of 5.8 meV and $\approx$12 meV. At the low-energy edge of the DAP PL spectrum only the deepest donors would be expected to contribute to DAP recombination, and the VB-D transition energy required to populate these donors would be at a minimum. Conversely, at the high-energy edge of the DAP band only the highest-energy donors (i.e., the 5.8-meV donors) would be expected to contribute, and the VB-D contribution to the PLE spectrum should occur at the usual position. For intermediate values of the DAP recombination energy the PLE spectrum is composed of overlapping contributions from donors with different binding energies, and would be expected to exhibit a continuous shift in the VB-D contribution to the DAP PLE spectrum. This behavior is just what is observed in the PLE spectra of Fig. 1.

It is important to note that the DAP PLE spectrum shown at the top of Fig. 1 for high-purity VPE material was found to be *independent* of the detected energy position along the DAP band. The VB-D feature did not shift with spectrometer position. This is consistent with a single donor binding energy, as expected for these samples. The width of this feature is essentially the same as that observed for the si GaAs sample detected at a wavelength of 828 nm. In contrast to this, the PL spectrum of the high-purity sample in the same spectral region exhibits extremely sharp structure associated with bound exciton recombination. In fact, this is expected because the PLE spectrum of the DAP band should not depend on excitonic features. The width and lack of structure in this PLE feature in the high-purity material confirm the interpretation that it results from VB-D absorption.

DAP PLE measurements were also carried out on si LEC samples that exhibited significant e-A^0 contributions to the PL spectrum near 1.493 eV, corresponding to transitions between the conduction band and neutral carbon acceptors. The DAP PLE results for these samples were similar to those reported above for sample CZ28, with the addition of a broad PLE feature at 1.493 eV. This feature is attributed to the photoneutralization of an ionized acceptor followed by the trapping of the conduction-band electron by a donor.

2. *Selective pair luminescence*

It should be noted that there are regions of the DAP PLE spectra near the VB-D transitions in Fig. 1 that are distorted by resonant contributions to the PLE spectrum resulting from selective pair luminescence (SPL), corre-

sponding to particular DAP separations.[17–19] SPL is often observed *in the PL spectrum*, and occurs when the energy of the spectrometer setting along the DAP band differs from the (fixed) energy of the excitation source by exactly the $1S$-$2S$ energy splitting of the acceptor. A resonant peak is superimposed on the DAP PL spectrum at that position, which corresponds to a specific DAP separation. In the *PLE spectrum*, acceptor SPL occurs [see Fig. 2(a)] when the energy of the excitation source is tuned to be exactly one acceptor $1S$-$2S$ energy above the (fixed) DAP recombination energy, as set by the spectrometer. A resonant peak appears in the PLE spectrum at that excitation energy. Other excited-state transitions may also be observed, but the $1S$-$2S$ is usually by far the strongest. SPL-related distortions of the VB-D portions of the DAP PLE spectra in Fig. 1 were found significant for the data taken at 831 and 832 nm, and that portion of the spectrum is indicated by a dotted line, since it has nothing to do with the VB-D contribution to the DAP PLE.

Acceptor SPL was also observed in PL measurements. In all of the bulk samples studied in this work, the SPL was dominated by carbon-related features associated with transitions between the carbon $1S$ state and several excited states. As we mentioned previously, this demonstrates that carbon is the dominant acceptor in these samples.

The PLE spectra in Fig. 1 also exhibit a series of peaks in the range 1.495 to 1.504 eV for DAP wavelengths between 828 and 833 nm. These peaks are all shifted from the corresponding spectrometer settings by a constant amount, 6.2 ± 0.2 meV. This is a clear indication of SPL, but the magnitude of the energy shift is too small to associate with acceptor SPL [e.g., $E(1S\text{-}2S)\approx 18.5$ meV].[19] The only reasonable assignment is SPL from donors. The process resulting in SPL from donors in a PLE measurement is shown schematically in Fig. 2(b). However, the $1S$-$2S$ separation for effective-mass donors is ≈ 4.35 meV. The observed SPL would have to be from *deeper donors*. In fact, a $1S$-$2S$ splitting of 6.2 meV would correspond to a binding energy of 8 meV, which is in the middle of the (6—12)-meV range determined from the PLE measurements. It should also be noted that the width of the donor SPL line is expected to be comparable to the spread in donor binding energies, ≈ 6 meV. The donor SPL features in Fig. 1 are dominated by a much sharper peak, although there appears to be some contributions to either side of the main peak. The details that determine the SPL line shape in this case are not known, but could involve, for example, the density of donor states at various donor binding energies.

To date there have been no reports of donor SPL observed in GaAs, presumably because of the small binding energy of the donor excited states, which allows significant spectral broadening from, e.g., donor-donor interactions.[17] It is not clear why this effect is observed in the present samples, but no other reasonable explanation for the observed peaks is apparent.

3. *Far-infrared magnetoabsorption*

These observations of donor SPL and of the VB-D contribution to the DAP PLE both suggest the existence in si GaAs of deeper shallow donors that are continuously distributed in binding energy over a range of ≈ 6 to 12 meV. In order to test this hypothesis more directly, we carried out internal donor ground—to—excited-state absorption measurements using the far-infrared magnetoabsorption technique. In these experiments the transmission of a fixed FIR laser wavelength is measured in a magnetic field. As the magnetic field is increased, the $1S$-$2P_{+1}$ energy splitting increases rapidly. At the magnetic field at which this splitting coincides with the photon energy of the FIR source, a strong absorption is observed. By scanning the magnetic field, an absorption spectrum may be mapped out. These measurements were carried out at 5 K with several different FIR laser wavelengths, and a typical example of the results is shown in Fig. 3 for 70.6-μm ra-

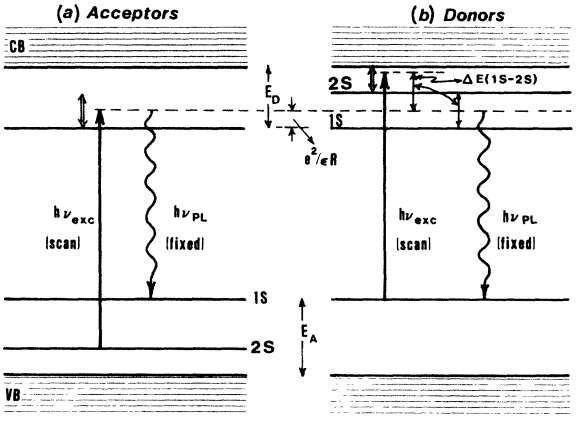

FIG. 2. Schematic level scheme illustrating the origin of selective pair luminescence in PLE measurements for (a) acceptors and (b) donors. SPL occurs in the PLE spectrum when the photon energy of the exciting light is tuned to exceed the photon energy being detected by just the separation (e.g., $1S$-$2S$) of the internal energy states of the impurity.

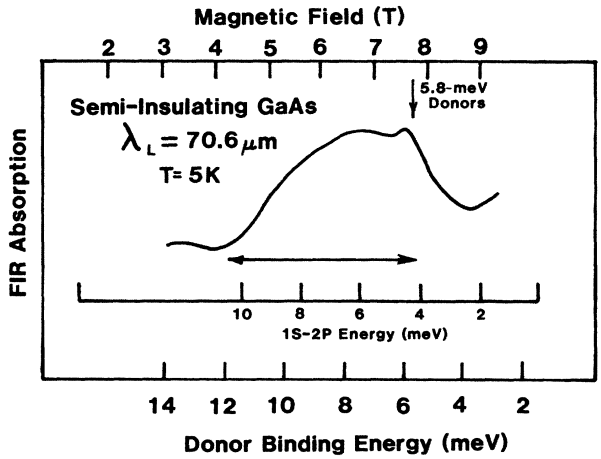

FIG. 3. FIR magnetoabsorption spectrum of si GaAs taken at 5 K with 70.6-μm radiation. In addition to absorption due to the $1S$-$2P$ transition associated with 5.8-meV effective-mass donors, a broad absorption band corresponding to deeper donors is also observed.

diation. An absorption peak corresponding to 5.8-meV donors is observed near 7.7 T. In addition, a broad absorption band is observed at lower fields, corresponding to $1S$-$2P$ splittings of $\approx 4-10$ meV, and donor binding energies in the range $\approx 6-12$ meV. Thus, direct shallow donor internal absorption measurements lead to precisely the same conclusions as the optical measurements described earlier, and give rather direct confirmation for the existence of anomalously deep shallow donors. It should be noted that in plotting the resonant absorption energy for the main absorption features versus magnetic field for each of the three FIR laser photon energies employed, we found that the resultant slope (a measure of the effective mass of the appropriate carrier) is similar to that of cyclotron resonance. This confirms that the carriers involved have an effective mass close to that of free electrons, as expected in the present case.

B. Discussion

In the preceding section we presented evidence for the existence of deeper shallow donors from the results of various experimental techniques. In this section we discuss the source of these increased shallow donor binding energies. There is one clear piece of evidence that suggests an origin for this phenomenon: there is no evidence of any kind for the existence of deeper shallow donors in high-purity VPE material. This suggests that the impurities inherent in LEC si GaAs are involved in this process. Under these circumstances, the most obvious explanation must be that the charged impurities (D^+, A^-, and charged deep centers) that result from the compensation process in this material produce a net Coulomb field that tends to bind the donor electron more tightly. Since the sample is electrically neutral there are equal numbers of positive and negative centers, so the contribution from centers outside of the Bohr orbit of the donor electron must cancel. Consequently, the effect must be the result of the Coulomb interaction between the donor electron and relatively nearby (≈ 100 Å) charged impurities. Ideally, one would like to calculate the expected shift in the donor binding energy due to a distribution of charged impurities in order to compare with the observed distribution of energy shift of $\approx 0-6$ meV. Although calculations of the Stark shift for donors in the presence of *very low* concentrations of charged impurities have been carried out some time ago,[20] these do not apply to impurity concentrations in the range $\geq 10^{16}$ cm^{-3}, which is typical of "undoped" si LEC GaAs. Calculations of this type are quite complicated, and are clearly beyond the scope of this paper.

There are two alternative explanations of the data presented in the preceding section that might be advanced in place of the notion of deeper shallow donors. First, as discussed briefly in the last section, a shift of the DAP PL band to anomalously low energies has been observed previously,[15,16] and has been associated with strong spatial variations of the valence- and conduction-band edges. Although this mechanism might be applied to account for the DAP PL spectrum on the bottom of Fig. 1, it fails to account for any of the other manifestations of deeper shallow donors discussed so far. The magnetoabsorption results and the large $1S$-$2S$ energy of the donor SPL both involve internal transitions that are unrelated to the band edges. The shift of the VB-D contribution to the DAP PLE would be expected to extend both above and below the usual energy of this transition if the aforementioned spatial variations were at the origin of the shift. Clearly, the evidence suggesting the existence of deeper shallow donors cannot be accounted for simply as a result of spatial variations of the band edges.

A second alternative mechanism might be that the observed effects are not related to shallow donors at all, but are associated with a shallow excited state of a deep donor. However, we have already observed that the VB-D transition (Fig. 1), which efficiently excites DAP emission, shifts continuously from the *normal* position associated with shallow donors to lower energy. Similarly, the FIR magnetoabsorption exhibited a broad band which stretched from the $1S$-$2P$ absorption associated with *normal* shallow donors down to lower fields. For these effects to be associated with a shallow excited state of a deep level, there would have to be a fortuitous coincidence between the energy of this state and that of normal shallow donors in GaAs.

In summary, the most reasonable explanation for the experimental results presented above is that, due to the presence of charged impurities, the binding energies associated with shallow donors in si GaAs are modified and do not correspond to the effective-mass value of 5.8 meV. In fact, there is a distribution of donor binding energies which extends from the effective-mass value down to ≈ 12 meV.

IV. THE EXCITATION MECHANISM FOR THE 0.64-eV PL BAND

In this section the results of the preceding section are applied to the PLE measurements for the deep 0.64-eV PL band. This allows us to determine the specific roles of donors and acceptors in the excitation of the 0.64-eV band. The addition of time-resolved studies of the same luminescence band leads to a consistent picture for the excitation and recombination mechanisms associated with this band.

The results presented in this section are also consistent with the conclusions arrived at by Shanabrook *et al.*[5] We recall that these workers have suggested the involvement of shallow donors in the excitation of the 0.64-eV PL as a result of the observation of oscillations in the PLE spectrum of the 0.64-eV band for above-band-gap excitation. The additional involvement of the shallow *acceptors* is a consequence of the details and of the specific shape of the PLE spectrum of this band and of the observation of an activation energy for PL quenching equal to the binding energy of shallow acceptors.

A. The role of shallow donors and acceptors

The involvement of shallow donors in the excitation of the deep 0.64-eV PL was investigated through a study of the PLE spectrum of that band. In Fig. 4(a) is shown the

PLE spectrum of the deep 0.64-eV PL band for the same range of dye-laser excitation energies as shown in Fig. 1 for the DAP PLE. A threshold near 1.48 eV and a peak near 1.50 eV is observed, as in previous PLE measurements.[5,7] In addition, a second peak is observed near 1.51 eV, near the region of the VB-D energy. Although observed previously,[21] this feature has not been reported in the literature. The 0.64-eV PLE spectrum is compared in Fig. 4 with the DAP PLE spectrum for 840 nm that appeared in Fig. 1. It is clear that both spectra have the same threshold and the same general shape. In addition, the VB-D peak of the DAP PLE occurs at the low-energy edge of the new peak in the 0.64-eV PLE. From the data in Fig. 1 it was shown that the VB-D peak *shifted* as a function of the DAP PL energy. The range over which the VB-D transition occurs for various DAP energies is indicated by the double-headed arrow in Fig. 4. The correspondence between this range and the new 0.64-eV PLE peak is excellent. Thus, the new peak near 1.51 eV reflects the entire distribution of VB-D transition energies, and suggests that both effective-mass donors and the deeper shallow donors are involved in the excitation of the 0.64-eV PL. We see, therefore, that the 0.64-eV PLE spectrum has all of the features of the DAP PLE spectrum. Furthermore, it is striking to observe that no structure is present at the position of the fundamental band gap. This suggests that free carriers play no special role in the excitation of the 0.64-eV luminescence. From the above considerations we can conclude that the PLE spectrum for the deep 0.64-eV PL is comprised of two contributions in this region: acceptor-to-donor and valence-band—to—donor transitions. In other words, it is necessary to populate neutral donors and acceptors (a rapid capture of free holes by ionized acceptors presumably follows the VB-D transition) in order to excite 0.64-eV PL in this region.

For samples where a significant e-A^0 contribution is observed in the DAP PLE spectrum, the PLE spectrum of the 0.64-eV luminescence has essentially the same shape as shown in Fig. 4. However, there is an additional contribution at the energy of the e-A^0 transition, 1.493 eV.

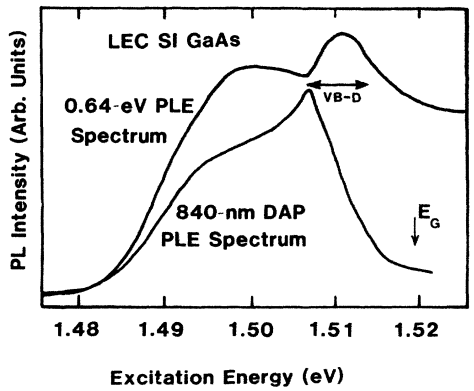

FIG. 4. PLE spectrum of the deep 0.64-eV PL band compared to the PLE spectrum of the DAP band at 840 nm, as in Fig. 1. The double-headed arrow indicates the range of observed VB-D transition energies, as in Fig. 1.

This contribution appears as a shoulder on the spectrum of Fig. 4. The fact that in these samples photoexcitation of free carriers from shallow acceptor levels produces an increase of the 0.64-eV luminescence is not in contradiction with the view that this luminescence is excited via the populating of shallow levels. Indeed, the same samples were studied by Shanabrook *et al.*,[5] who observed the oscillating behavior of the PLE of the 0.64-eV band for above-band-gap excitation energies. This indicates that, similar to the conclusions for sample CZ28, free carriers do not recombine at the midgap level directly, but do so via the shallow donor level.

It should also be noted that the peak of the VB-D contribution to the 0.64-eV PLE (Fig. 4) occurs at an energy of ≈ 1.511 eV, at least 2 meV below the value associated with transitions to effective-mass donors. Thus, the deep PL is more efficiently excited by creating neutral *deeper* shallow donors. This suggests the possibility of a special relationship between the deep levels associated with this PL band and the deeper shallow donors. Presumably, this would imply that the charged species of this center are in part responsible for the increase in the shallow donor binding energy. Alternatively, this behavior may simply be related to a density-of-states effect, where there is a larger number of donors with a binding energy ≈ 2 meV below the effective-mass value. At present, we cannot distinguish between these two possibilities.

Finally, the PLE spectrum of the 0.64-eV band was also obtained after irradiation of the sample with 1.17-eV light in order to determine the effect on the spectrum due to the transition of EL2 into its metastable state. All of the main features of the PLE spectrum were observed to remain. However, for excitation below the threshold for acceptor-to-donor transitions a factor of 4 decrease in intensity was observed, while only a factor of 40% decrease was observed within the main excitation band above ≈ 1.48 eV. This is not unreasonable, as the absorption processes below 1.48 eV are dominated by EL2—to—conduction-band transitions. The fact that all of the main features remain in the PLE spectrum after irradiation again indicates that EL2, and particularly an excited state of EL2, is not involved in the excitation process of the 0.64-eV PL.

B. Identification of the excitation and recombination mechanism responsible for the 0.64-eV luminescence

The observation of identical features in the PLE spectra of the DAP band and the 0.64-eV band suggests that the neutral shallow donors and acceptors are intimately involved in the excitation of the deep PL. There are really only two possibilities for the involvement of the donors in this process: Either the capture of the donor electron by the deep center is the radiative transition, or this capture process is nonradiative and results in the creation of the initial (luminescent) state of the radiative transition.

To investigate the associated kinetics more directly, time-dependent PL measurements of the 0.64-eV band were carried out at an excitation wavelength of 840 nm, which was shown to excite acceptor-to-donor transitions

(e.g., Fig. 1). The PL response following an $\approx$8-nsec exciting pulse is shown in Fig. 5. It is clear from the figure that the intensity of the 0.64-eV PL is still increasing up to 50—75 nsec after the exciting pulse has ended, and that the decay at later times is much slower and nonexponential. The observed PL growth, which corresponds to an exponential time constant of $\approx$25 nsec, strongly suggests that the radiative transition is *preceded* by the capture of a carrier by the deep level.

Thus, the PL process involves *two* transitions, a fast nonradiative transition that creates the luminescent state, followed by the radiative transition itself. From the appearance of VB-*D* and *A*-*D* features in the PLE spectrum of the 0.64-eV band, it is clear that the deep PL is excited by creating electrons bound on shallow donors and holes that are either free or bound on shallow acceptors. The (30$\pm$10)-meV activation energy for thermal quenching of the PLE spectrum of this band observed by Shanabrook *et al.*[5] would suggest that the hole is, in fact, bound to a shallow acceptor.

The simplest mechanism for the deep PL that is consistent with the data as described above is, therefore, the recombination of a donor-acceptor pair via the consecutive trapping of the two bound carriers by the deep center. In fact, this process is in direct competition with the usual DAP recombination, as it involves the recombination of a bound electron and a bound hole. This competition is seen to be very effective, as we have observed that the spectrally integrated PL intensity for the 0.64-eV band is $\geq$10 times larger than that of the DAP band. For this to be the case, the trapping time for one of the carriers by the deep center must be much shorter than the DAP recombination time. The $\approx$25 nsec rise in the PL intensity shown in Fig. 5, which we associated with the (nonradiative) capture process that created the luminescent state, is clearly consistent with this picture, as this time is considerably shorter than most DAP recombination times in GaAs.

Of course there also exists the alternative possibility that an excited state of the deep center plays the role as an intermediate state in the recombination of the bound carriers. In this case the radiative transition might also be due to an internal transition from an excited state to the ground state of the deep center. Thus far there has been no evidence brought forth to suggest the existence of such an excited state for this center. In particular, there have been no features observed in the below-gap PLE spectrum of this band that could be associated with such an excited state. Given the lack of any direct evidence for the involvement of such a state in the recombination mechanism for the 0.64-eV band, we will confine our interpretation of the data to the simplest model that makes good physical sense, that of simple carrier capture.

We are, therefore, left with two possible mechanisms for the excitation-recombination process: The 0.64-eV PL is excited by the nonradiative capture of a donor electron (acceptor hole) by the deep level, which is manifested as an initial $\approx$25-nsec growth in the PL time dependence. The recombination process is the radiative capture by the deep level of a hole (electron) bound on an acceptor (donor). The radiative recombination results in a nonexponential decay ($\approx$microseconds, see Fig. 5) in the PL time dependence. The two possibilities are illustrated in Fig. 6, and can be distinguished by the magnitudes of the characteristic times involved: We consider capture by a localized deep level of an electron bound to a neutral donor and a hole bound to a neutral acceptor. Since the Bohr orbit of the electron is considerably larger than that of the hole, the probability for capture of the electron by the deep level is expected to be much larger than that of the hole. Consequently, the characteristic time for the

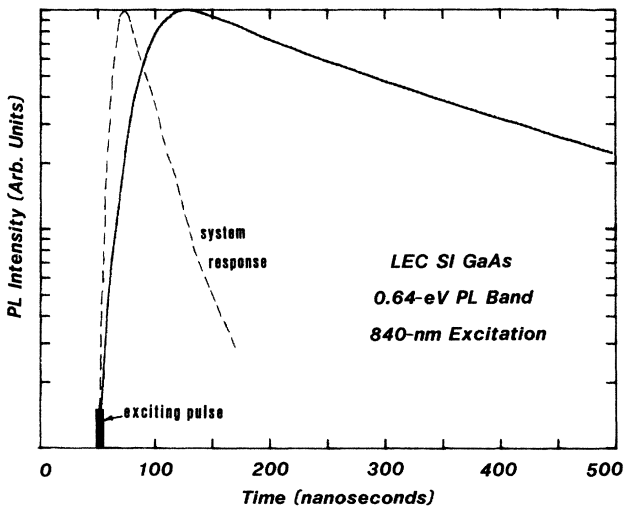

FIG. 5. Time dependence of the PL intensity of the 0.64-eV PL band. The time response of the detection system to the $\approx$8-nsec, 840-nm exciting pulse is also shown. As shown in relation to Fig. 1, excitation in this region gives rise to acceptor-to-donor transitions. The deep PL time response is shown to initially *increase* with time. This suggests that the PL mechanism involves *two* transitions, a fast nonradiative transition that creates the luminescent state followed by a slower radiative transition.

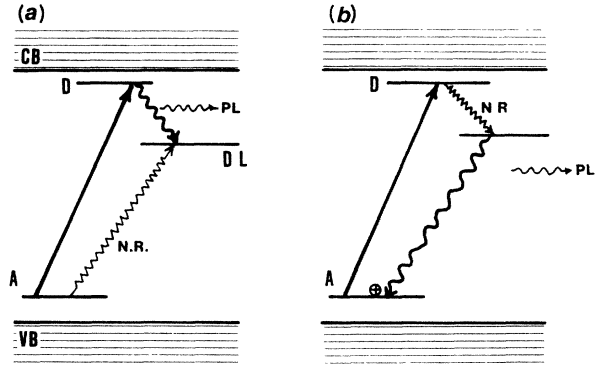

FIG. 6. Schematic representation of the possible excitation-recombination mechanisms for 840-nm excitation, where neutral donor-acceptor pairs are created. In (a) the electron on the neutral donor is captured radiatively after the deep level (DL) captures a hole. In (b) the electron capture is nonradiative and the PL transition is the radiative capture of the hole. The mechanism in (b) is consistent with the present data, as discussed in the text.

electron capture is expected to be much shorter than that for the hole capture. We therefore associate the ≈25-nsec PL growth with nonradiative electron capture, and the ≈microsecond nonexponential decay with radiative hole capture.

V. CONCLUSIONS

In conclusion, we show evidence for the existence of a distribution of shallow donor binding energies between the effective-mass value of 5.8 meV and ≈12 meV in LEC si GaAs. The anomalously large donor binding energies are consistent with the results of photoluminescence, photoluminescence excitation spectroscopy, selective pair luminescence, and FIR magnetoabsorption experiments. Since no evidence of this phenomenon is observed in high-purity VPE material, it is concluded that this effect is the result of the Coulomb interaction between the donor electron and charged defects in the material. These defects are a natural by-product of the compensation process inherent to si GaAs.

The dye-laser-excited PLE spectrum of the 0.64-eV band is closely analogous to that of the DAP luminescence. This provides further verification for the involvement of shallow donors (effective-mass donors as well as deeper shallow donors) and of shallow acceptors in the excitation of the 0.64-eV luminescence. Using the results of time-dependent PL measurements, we propose that the excitation-recombination process consists of (1) the fast, nonradiative capture by the deep center of the electron trapped on the shallow donor (in a time of typically 25 nsec), followed by (2) the slow (≈microseconds) radiative trapping by the same center of the hole bound to the shallow acceptor.

Thus, our experimental results involving time-resolved and steady-state PL and FIR magnetoabsorption allow us to obtain a relatively complete and simple picture for the excitation and recombination kinetics associated with the 0.64-eV deep PL band. It is important to note that these results have been obtained from a limited number of samples, and it is not clear to what extent this picture would change in samples of different impurity concentrations. Nevertheless, we emphasize that in this system, by using several complementary experimental techniques, we have been able to disentangle a complicated situation and to extract a relatively simple physical picture. Since our knowledge of this complicated system is still incomplete, the picture presented here may not be the only possible one. However, it is the simplest and most reasonable picture that explains the present results as well as the results obtained by other workers.

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