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Photocapacitance study of pressure-induced deep donors in GaAs:Si

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Photocapacitance transient measurements in GaAs:Si under pressures of 33 and 38 kbar are reported for the first time. The optical ionization energy of pressure-induced deep donors in GaAs was determined to be 1.44 ± 0.04 eV. The low-temperature capture times of photoexcited carriers were also measured and the results indicate that persistent photoconductivity would occur in GaAs under pressures in excess of 30 kbar. These results show that qualitatively the pressure-induced deep donors in GaAs are very similar to the *DX* centers in $Ga_{1-x}Al_xAs$ alloys in terms of their optical properties.

The *DX* centers in $Ga_{1-x}Al_xAs$ alloys have recently received much attention because of their influence on the performance of modulation-doped field-effect transistors and also because of their metastability. One significant development has been the discovery by Mizuta, Tachikawa, Kikumot, and Minomura[1] of deep donors in GaAs doped with Si or Sn under pressure with many properties very similar to the *DX* centers in $Ga_{1-x}Al_xAs$.[2,3] Based on their deep-level transient spectroscopy (DLTS) measurements Mizuta *et al.*[1] concluded that these pressure-induced deep donors (PIDD's) in GaAs are identical to the *DX* centers in $Ga_{1-x}Al_xAs$. To substantiate this conclusion it is necessary to compare all the known properties of the *DX* centers with those of the PIDD's in GaAs. The *DX* centers in GaAlAs alloys have many characteristic properties. One of these characteristics is the large difference between the optical ionization energy (E_n) and thermal ionization energy (E_t). Another characteristic, which is very important from the point of view of device performance, is that the *DX* centers produce persistent photoconductivity (PPC). Mizuta *et al.*[1] were unable to determine the optical ionization threshold of the PIDD's in GaAs under pressure because their high-pressure cell has no optical access. Although Tachikawa *et al.*[4] demonstrated PPC due to the PIDD's in GaAs by illuminating their sample with a light-emitting diode inside the high-pressure cell, no quantitative measurements were reported. We have used a diamond-anvil cell to study the PIDD's in GaAs:Si. Because of the transparency of the diamond anvils we were able to use photocapacitance transient techniques to study PPC quantitatively and to determine E_n for the PIDD's in GaAs. We showed that our optical results for the PIDD's in GaAs:Si are very similar to those of the *DX* centers in $Ga_{1-x}Al_xAs$ alloys.

The samples used in our photocapacitance measurements were Schottky diodes fabricated from either GaAs doped with 2×10^{17} cm^{-3} of Si or $Ga_{0.65}Al_{0.35}As$ doped with 5×10^{16} cm^{-3} of Te. Ohmic contacts to the samples were made by evaporating Au-Ge alloy on one side of a wafer followed by annealing at 450 °C for one minute. Schottky barriers were formed by evaporating Al onto the other side. Chips of typically 200×200 μm^2 in size were cut from the wafer. The cut sides of the chips were etched to reduce the reverse-bias leakage current. The chips were then mounted into a diamond-anvil cell with a soft powder ($CaSO_4$) as the pressure-transmitting medium. The details of loading the sample with leads into the diamond-anvil cell have been determined by Erskine, Yu, and Martinez.[5] A schematical diagram showing the sample and the wires inside the cell is shown in the inset of Fig. 1. The diode was always placed with the Al side facing the incoming light. The cell was pressurized with a hydraulic press at room temperature. The pressure was determined by the standard ruby-fluorescence technique.[5]

Two optical measurements have been performed to study the properties of the PIDD's in GaAs. In the first experiment the dependence of the electron photoionization cross section (σ_n^0) of deep centers on incident photon energy was measured. In the second experiment the thermal capture rates of optically excited carriers were determined at low temperatures. From these capture rates the decay times of free carriers in PPB can be calculated.

In the first experiment light from a tungsten halogen lamp is focused into a monochromator with a spectral width of 7 nm. The radiation from the monochromator is directed into the diamond-anvil cell and scattered by the

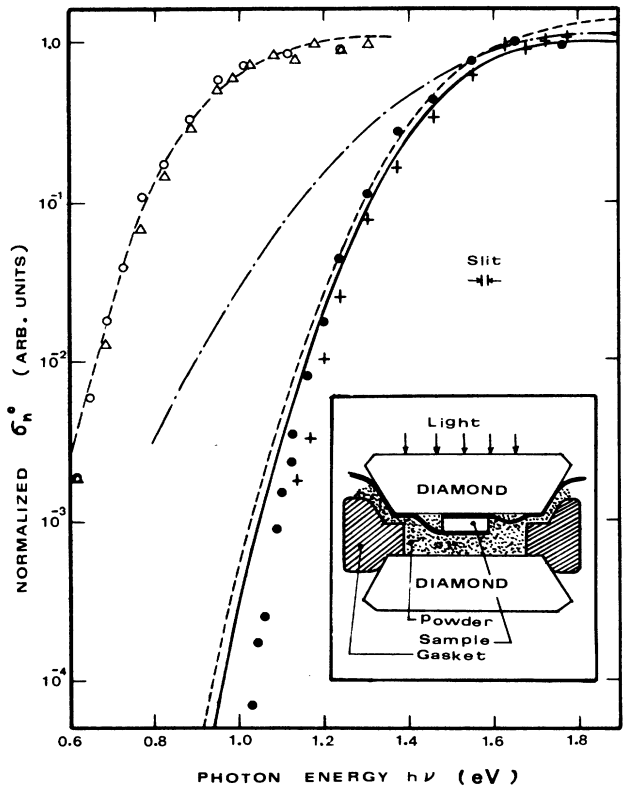

FIG. 1. The normalized photoionization cross-section spectra of the *DX* center in $Ga_{1-x}Al_xAs$ (open circles and open triangles) and of the PIDD's in GaAs under pressures of 33 kbar (solid circles) and 38 kbar (crosses). The open triangles are the data of Lang *et al.* reproduced from Ref. 3, while the open circles represent data obtained with the sample inside the diamond-anvil cell. The curves represent theoretical fits to the experimental points using Eq. (3) discussed in the text. The inset shows schematically the sample inside the diamond-anvil cell.

powder surrounding the sample. Since the diode is covered by metal electrodes on both the top and bottom, only the scattered light can enter the sample from the sides. As a result it is not possible to determine exactly the amount of light absorbed by the sample; however, it is still possible to measure the *relative* σ_n^0, provided we assume that the light scattering efficiency is constant over the range of photon energies in this study. Except for this assumption we have corrected for the dispersion in the diamond absorption and in the lamp emission. As a test of the reliability of our measurement we have used the same setup to measure the dispersion of the σ_n^0 of $Ga_{1-x}Al_x$-As:Te at atmospheric pressure and compared our results with those reported by Lang, Logan, and Jaros.[3]

We have used the method of Chantre, Vincent, and Bais[6] to measure σ_n^0. The sample, whether $Ga_{1-x}Al_xAs$ at atmospheric pressure or GaAs under pressure, was first maintained at zero bias at room temperature in order to fill the traps and then cooled to 77 K in the dark. A reverse bias of 3 V was then applied to the diode. As the thermal emission rates of the *DX* center and the PIDD's in GaAs at 77 K were both negligible, the traps in the depletion layer remained occupied. Next the sample was illuminated with radiation from the monochromator and the rate of change in the diode capacitance was measured. Since the change in capacitance was proportional to the change in the electron concentration in the deep centers (n_T) within the depletion layer, we obtained in this way dn_T/dt. If Φ is the incident photon flux density, and σ_n^0 and σ_p^0 are, respectively, the electron and hole photoionization cross sections for the deep center, then it has been shown that dn_T/dt is given by[6]

$$dn_T/dt = \Phi(h\nu)[\sigma_p^0(h\nu)(N_T - n_T) - \sigma_n^0(h\nu)n_T] \ , \qquad (1)$$

where N_T is the concentration of deep centers and $h\nu$ is the photon energy. At the point where the light was first turned on, most of the deep centers in the depletion layer were occupied and so $n_T = N_T$ and Eq. (1) reduced to

$$dn_T/dt = \sigma_n^0(h\nu)\Phi(h\nu)N_T \ . \qquad (2)$$

Using Eq. (2) and the measured dn_T/dt as a function of the incident photon energy $h\nu$ we have deduced the normalized $\sigma_n^0(h\nu)$ spectra shown in Fig. 1. The open circles are results obtained from our $Ga_{1-x}Al_xAs$:Te sample located inside our diamond-anvil cell but with no pressure applied. The open triangles are the data of Lang *et al.*[3] on the *DX* centers in $Ga_{0.63}Al_{0.37}As$:Te. The excellent agreement between the two sets of results justifies our method of measuring the σ_n^0 of samples inside the diamond-anvil cell. The solid circles and crosses in Fig. 1 represent the σ_n^0 of PIDD's in GaAs:Si measured with the same procedure under pressures of 33 and 38 kbar, respectively.

To analyze the experimental results in Fig. 1 we have used the following expression obtained by Jaros[3] using the strong coupling model of Huang and Rhys[7]

$$\sigma_n^0(h\nu) \sim \frac{1}{h\nu}\int_0^\infty dE\,(E)^{1/2}\left[\frac{(1 \pm e^{-2E/E_p})E^{1/2}}{|E_n| + E} + \frac{(1 \mp e^{-2E/E_p})E_F^{1/2}}{|E_n| - E - (E_g + E_p)/2}\right]^2 \exp\left[\frac{h\nu - (|E_n| + E)^2}{-U}\right] U^{-1/2} \ . \qquad (3)$$

In Eq. (3) E_p is the average optical (Penn) gap,[8] E_g is the band gap, E_F is the Fermi energy of the valance electrons, E_n is the optical ionization energy of the deep level measured from conduction band, and U is a function defined by

$$U = 2S(\hbar\omega)^2/\tanh(\hbar\omega/2k_BT) \ . \qquad (4)$$

In Eq. (4) k_B is Boltzmann's constant, T is the temperature, and S is the Huang-Rhys factor defined by $E_S = S\hbar\omega$, where E_S is the lattice relaxation energy and $\hbar\omega$ is the phonon energy. The thermal ionization energy E_T of the deep center is related to its optical ionization energy by $E_n = E_T + E_S$. The choice of the $\pm$ and $\mp$ signs in Eq. (3) depends on the nodal character of the electron

wave function. The upper and lower signs correspond to deep centers with valence-band-like and conduction-band-like wave functions, respectively.[9] The curves in Fig. 1 represent fits to the experimental points using Eq. (3). In fitting the data points for GaAs we have used the same values of $E_F = 11.5$ eV and $E_p = 5.2$ eV as Jaros.[9] For the band gap of GaAs at a pressure of 33–38 kbar we have used the approximate value of $E_g = 1.8$ eV.[10] It turns out that the shape of σ_n^0 is not very sensitive to the above energies anyway. The dispersion in σ_n^0 is mainly determined by E_n and $\hbar\omega$ at a given T. Lang[11] has argued that the DX center is coupled predominately to the transverse-acoustic (TA) phonon. We have considered both the longitudinal-optical (LO) phonon and the zone-edge TA phonon of GaAs in fitting the results for the PIDD's in GaAs. The phonon energies of GaAs under pressures of 33–38 kbar were 37 and 8 meV for the LO and TA phonons, respectively.[10,12] The remaining unknown parameters in Eq. (3) are E_S and E_n. Using the value of $E_T = 0.08$ eV obtained from DLTS measurements performed on the same samples[13] and the relation $E_n = E_S + E_T$ we reduce the adjustable parameters in fitting the data points for GaAs to E_n only. The resultant curves obtained by assuming that TA phonons are involved are shown as solid and broken lines in Fig. 1. The difference between the two curves is that the deep-center wave function was assumed to be conduction-band-like for the solid curve and valence-band-like for the broken curve. The values of E_n obtained are 1.48 and 1.4 eV, respectively. Since both curves fit the experimental results equally well we conclude that $E_n = 1.44 \pm 0.04$ eV. We note that the corresponding value for the DX center in $Ga_{1-x}Al_xAs$:Si obtained by Lang and Logan was 1.25 eV.[11] On the other hand, we could not obtain any reasonable fit to our results by assuming that the PIDD's couple to LO phonons. As an example, the dot-dashed line in Fig. 1 shows a plot of Eq. (3) using the LO-phonon energy and the value of $E_n = 1.40$ eV.

In the second experiment we have measured the thermal capture times of photoexcited free carriers by the PIDD's in GaAs:Si at a pressure of 38 kbar. The capture times are related to free-carrier lifetimes in PPC. The method we used to measure the capture times is very similar to those employed by Zhou, Ploog, and Gmelin.[14] Initially the sample inside the high-pressure cell was kept around liquid-nitrogen temperature under a reverse bias of 3 V. The sample was then illuminated with strong light to photoexcite electrons from the deep centers to the conduction band while the capacitance was monitored. This was carried out until the capacitance change became saturated. At this point we assumed that most of the deep centers in the depletion layer have been emptied. The light was then turned off and the carriers were allowed to be captured thermally by a sequence of filling pulses of zero bias and of durations $t_1, t_2, \ldots, t_n$ sec as shown schematically in the inset of Fig. 2. In between these filling pulses reverse-bias voltages of relatively short durations (~ 1 sec) were applied to measure the diode capacitance. Since, at low temperatures, the thermal emission rate of the PIDD's in GaAs under pressure was rather small[13] the change in capacitance during the negative-bias

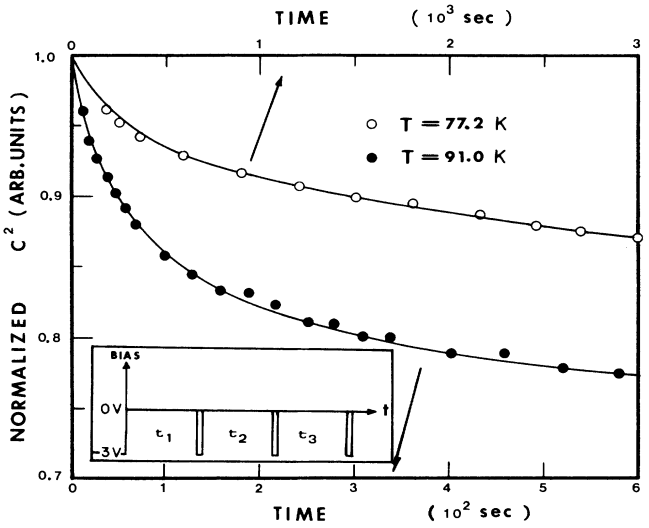

FIG. 2. The recovery in the capacitance after photoexcitation of GaAs:Si under 38 kbar of pressure at two different temperatures. Note the different time scales for the two temperatures. The solid curves have been drawn through the data points by hand. The inset shows the bias voltage sequence used in obtaining the time dependence of the capacitance recovery.

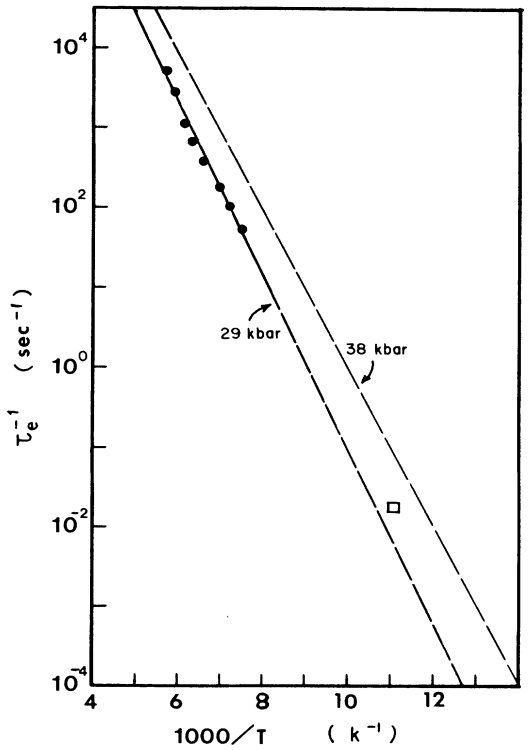

FIG. 3. The capture rate of carriers by the PIDD's in GaAs:Si plotted against $1/T$ for two different pressures. The solid circles are data points at 29 kbar reproduced from Ref. 13, while the open square is the result of photocapacitance measurement at 38 kbar. The broken lines represent results extrapolated from the 29-kbar experimental data.

pulses was negligible. The square of the capacitance (C^2) measured after the nth filling pulse was plotted as a function of the total time of the filling pulses ($t_1+t_2+\cdots+t_n$) in Fig. 2 for two different temperatures. Note the difference in the time scales for the two temperatures. From our DLTS measurements[13] and those reported by Mizuta *et al.*[1] we know that at pressures above 30 kbar trapping of free carriers in GaAs:Si is entirely dominated by the PIDD's. Thus the observed time dependence of C^2 is proportional to the time dependence of the bulk carrier concentration, and the trapping time of the free carriers can be determined from the plots in Fig. 2. Since the decay curves in Fig. 2 are not single exponentials we have used Lang's half-signal point method[11] to estimate the capture time of free carriers in GaAs in the presence of the PIDD's to be about 1 min at 91 K and over 1 h at 77 K. To compare these results with our DLTS measurements at higher temperatures,[13] we plotted the capture rate (τ_e^{-1}) vs $1/T$ in Fig. 3 for the PIDD's in GaAs at two different pressures. The solid circles represent the experimental data obtained by DLTS in Ref. 13. The broken lines are extrapolations of those experimental points to either lower temperatures or to higher pressures using the pressure coefficients reported in Ref. 13. The open square represents the result obtained in Fig. 2. Thus we see that the capture rates we obtained at low temperatures are quite consistent with the higher-temperature DLTS results.

In conclusion, we have performed photocapacitance measurements of the PIDD's in GaAs:Si under pressures of over 30 kbar. From these measurements we determined the photoionization thresholds and thermal capture times of carriers by the PIDD's in GaAs:Si. We found that the photocapacitance results of the PIDD's in GaAs under pressure were very similar to the *DX* centers in $Ga_{1-x}Al_xAs$ alloys. However, there are significant quantitative differences between the two centers. We determined the optical ionization energy of PIDD's in GaAs:Si to be 1.44 eV which is almost 0.2 eV higher than the corresponding value for the *DX* center in GaAlAs:Si. On the other hand, Mizuta *et al.*[1] have found that the DLTS activation energy of the PIDD's in GaAs was 0.2 eV lower than that of the *DX* center. Although the PIDD's in GaAs:Si under pressure is very similar in all respects to the *DX* center in $Ga_{1-x}Al_xAs$ alloys, these rather large differences in their energies should not be neglected.

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[1] M. Mizuta, M. Tachikawa, H. Kikumot, and S. Minomura, Jpn. J. Appl. Phys. **24**, L143 (1985).

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

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

[4] M. Tachikawa, T. Fujisawa, H. Kukimoto, A. Shibata, G. Oomi, and S. Minomura, Jpn. J. Appl. Phys. **24**, L893 (1985).

[5] D. Erskine, P. Y. Yu, and G. Martinez, Rev. Sci. Instrum. **58**, 406 (1987).

[6] A. Chantre, G. Vincent, and D. Bais, Phys. Rev. B **23**, 5335 (1981).

[7] K. Huang and R. Rhys, Proc. R. Soc. London, Ser. A **204**, 406 (1950).

[8] D. R. Penn, Phys. Rev. **128**, 2093 (1962).

[9] M. Jaros, Phys. Rev. B **16**, 3694 (1977).

[10] P. Y. Yu and B. Welber, Solid State Commun. **25**, 209 (1978).

[11] D. V. Lang, in *Deep Centers in Semiconductors,* edited by S. T. Pantelides (Gordon and Breach, New York, 1985), p. 489.

[12] R. Tommer, E. Anastassakis, and M. Cardona, in *Light Scattering in Solids,* edited by M. Balkanski, R. C. C. Leite, and S. P. S. Porto (Flammarion, Paris, 1976), p. 396.

[13] M. F. Li, P. Y. Yu, E. R. Weber, and W. Hansen, Appl. Phys. Lett. **51**, 349 (1987).

[14] B. L. Zhou, K. Ploog, and E. Gmelin, Appl. Phys. A **28**, 233 (1982).