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Photocapacitance Study of Pressure Induced Deep Donors in GaAs:Si

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ABSTRACT

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 have also been measured and the results indicated 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 GaAlAs alloys in their optical properties.

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The DX centers in GaAlAs 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 et al.[1] of deep donors in GaAs doped with Si or Sn under pressure with many properties very similar to the DX centers in GaAlAs.[2,3] Based on their Deep Level Transient Spectroscopy (DTLS) measurements Mizuta et al.[1] concluded that these pressure induced deep donors (to be abbreviated as PIDD in this article) in GaAs are identical to the DX centers in GaAlAs. To substantiate this conclusion it is necessary to compare all the known properties of the DX centers with that of the PIDD in GaAs. The DX centers in GaAlAs alloys have many characteristic properties. One of these characteristics is the large difference between its 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 in GaAs under pressure because their high pressure cell has no optical access. Although Tachikawa et al.[4] demonstrated PPC due to the PIDD 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 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 in GaAs. We showed that our optical results for the PIDD in GaAs:Si are very similar to those of the DX centers in GaAlAs alloys.

The samples used in our photocapacitance measurements were Schottky

diodes fabricated from either GaAs doped with $2x10^{17}$ cm^{-3} of Si or $Ga_{0.65}Al_{0.35}As$ doped with $5x10^{16}$ 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 ^{0}C for one minute. Schottky barriers were formed by evaporating Al onto the other side. Chips of typically 200 x 200 $(micron)^2$ 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 has been determined by Erskine et al.[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 in GaAs. In the first experiment the dependence of the electron photoionization cross section (σ_n^o) 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 PPC can be calculated.

In the first experiment light from a tungsten halogen lamp is focussed 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 powder surrounding the sample. Since the diode is covered by metal electrodes on both the top and the 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^o 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^o of GaAlAs:Te at atmospheric pressure and compared our results with those reported by Lang et al.[3]

We have used the method of Chantre et al.[6] to measure σ_n^o. The sample, whether GaAlAs 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 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, σ_n^c and σ_p^c 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]

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

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 so $n_T=N_T$ and Eq.(1)

reduced to:

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

Using Eq.(2) and the measured dn_T/dt as a function of the incident photon energy $h\nu$ we have deduced the normalized $\sigma_n^o(h\nu)$ spectra shown in Fig.1. The open circles are results obtained from our GaAlAs: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^c of samples inside the diamond anvil cell. The solid circles and crosses in Fig. 1 represent the σ_n^c of PIDD 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:[8]

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

In Eq.(3) E_p is the average optical (Penn) gap[9], E_g is the band gap, E_F is the Fermi energy of the valence electrons, E_n is 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 the Boltzmann 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 wavefunction. The upper and lower signs correspond to deep centers with valence-band-like and conduction-band-like wave functions respectively.[7] 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.[7] 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^o is not very sensitive to the above energies anyway. The dispersion in σ_n^o is mainly determined by E_n and $\hbar\omega$ at a given T. Lang[11] has argued that the DX center coupled predominately to the transverse acoustic phonon (TA). We have considered both the longitudinal optical (LO) phonon and the zone-edge TA phonon of GaAs in fitting the results for the PIDD in GaAs. The phonon energies of GaAs under pressures of 33-38 kbar were 37 meV 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 wavefunction 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 and 1.48 and 1.4 eV respectively. Since both curves fit the experimental results equally well we conclude that $E_n=1.44\pm0.04$ eV. We note that the corresponding value for the DX center in GaAlAs: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

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 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 et al.[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 $t_1, t_2, .. t_n$ sec as shown schematically in the inset of Fig.2. In between these filling pulses reverse bias voltages of relatively short durations (~1 sec) was applied to measure the diode capacitance. Since at low temperatures the thermal emission rate of the PIDD in GaAs under pressure was rather small [13] the change in capacitance during the negative bias pulses were 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 ($t_1+t_2+..+t_n$) 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 of above 30 kbar trapping of free carriers in GaAs:Si is entirely dominated by the PIDD. 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 to be about 1 minute at 91 K and over 1 hour at 77 K. To compare these results with our DLTS measurements at higher temperatures,[13] we plotted the capture rate (τ_e^{-1}) versus 1/T in Fig.3 for the PIDD 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 from 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 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 in GaAs:Si. We found that the photocapacitance results of the PIDD in GaAs under pressure were very similar to the DX centers in GaAlAs alloys. However, there are significant quantitative differences between the two centers. We determined the optical ionization energy of PIDD 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 in GaAs was 0.2 eV lower than that of the DX center. Although the PIDD in GaAs:Si under pressure is

very similar in all respects to the DX center in GaAlAs alloys, these rather large differences in their energies should not be neglected.

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REFERENCES

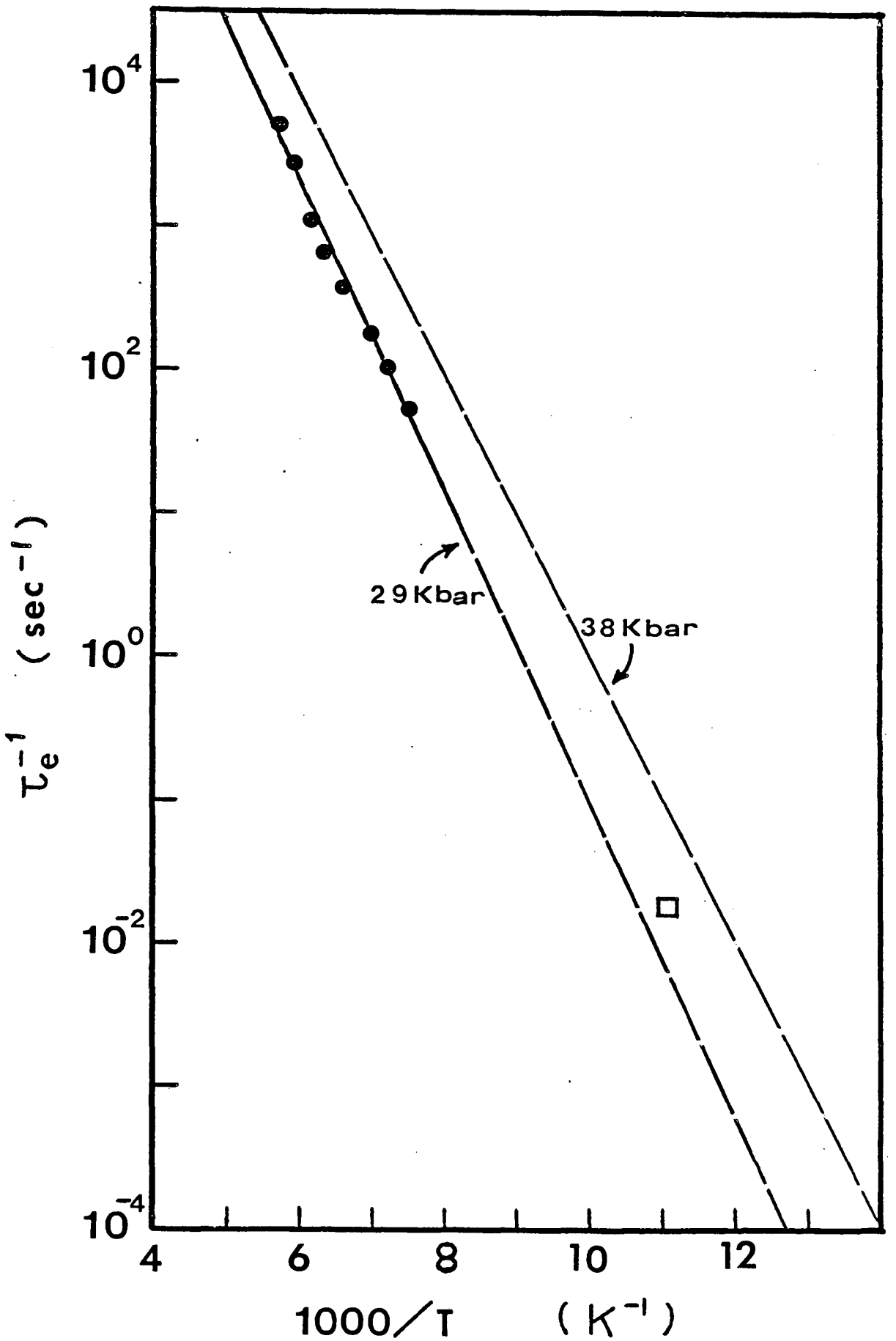
1. M. Mizuta, M. Tachikawa, H. Kikumot and S. Minomura, Jap. J. Appl. Phys. 24, L143 (1985).
2. D. V. Lang and R.A. Logan, Phys. Rev. Lett. 39, 635 (1977).
3. D.V. Lang, R.A. Logan and M. Jaros, Phys. Rev. B19, 1015 (1979).
4. M. Tachikawa, T. Fujisawa, H. Kukimoto, A. Shibata, G. Oomi and S. Minomura, Jap. J. Appl. Phys. 24, L893 (1985).
5. D. Erskine, P.Y. Yu and G. Martinez, Rev. Sci. Inst. 58, 406 (1987).
6. A. Chantre, G. Vincent and D. Bais, Phys. Rev. B23, 5335 (1981).
7. M. Jaros, Phys. Rev. B16, 3694 (1977).
8. K. Huang and R. Rhys, Proc. Roy. Soc. A204, 406 (1950).
9. D. R. Penn, Phys. Rev. 128, 2093 (1962).
10. P.Y. Yu and B. Welber, Solid State Comm. 25, 209 (1978).
11. D.V. Lang, in **Deep Centers in Semiconductors**, ed by S.T. Pantelides (Gordon and Beach, New York, 1985)p.489.
12. R. Tommer, E. Anastassakis and M. Cardona, in **Light Scattering in Solids**, ed. by M. Balkanski, R.C.C. Leite and S.P.S. Porto (Flamarion, Paris, 1976)p.396.
13. M.F. Li, P.Y. Yu, E.R. Weber and W. Hansen, Appl. Phys. Lett. (in press).
14. B.L. Zhou, K. Ploog and E. Gmelin, Appl. Phys. Phys. A28, 233 (1982).

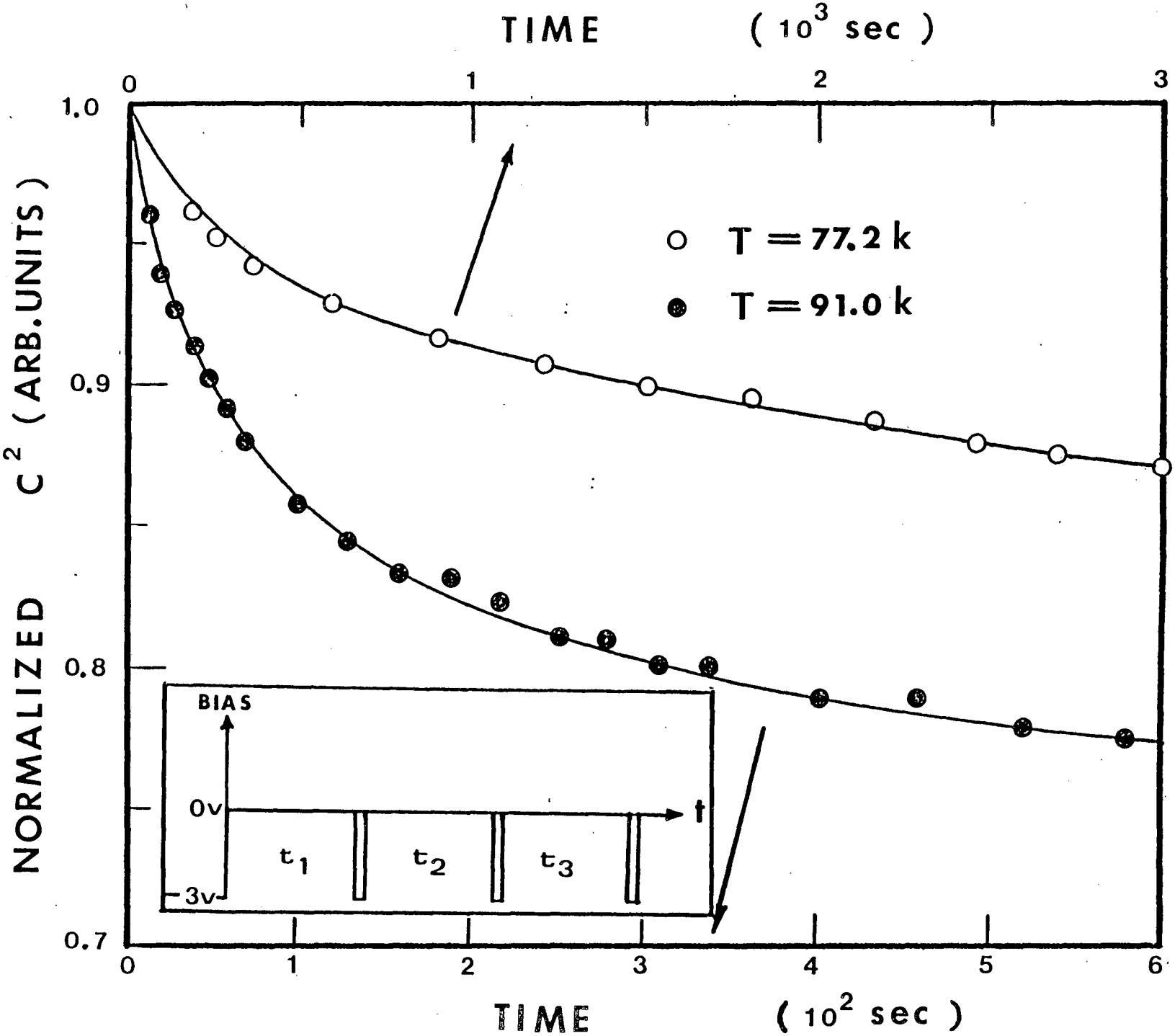
FIGURE CAPTIONS

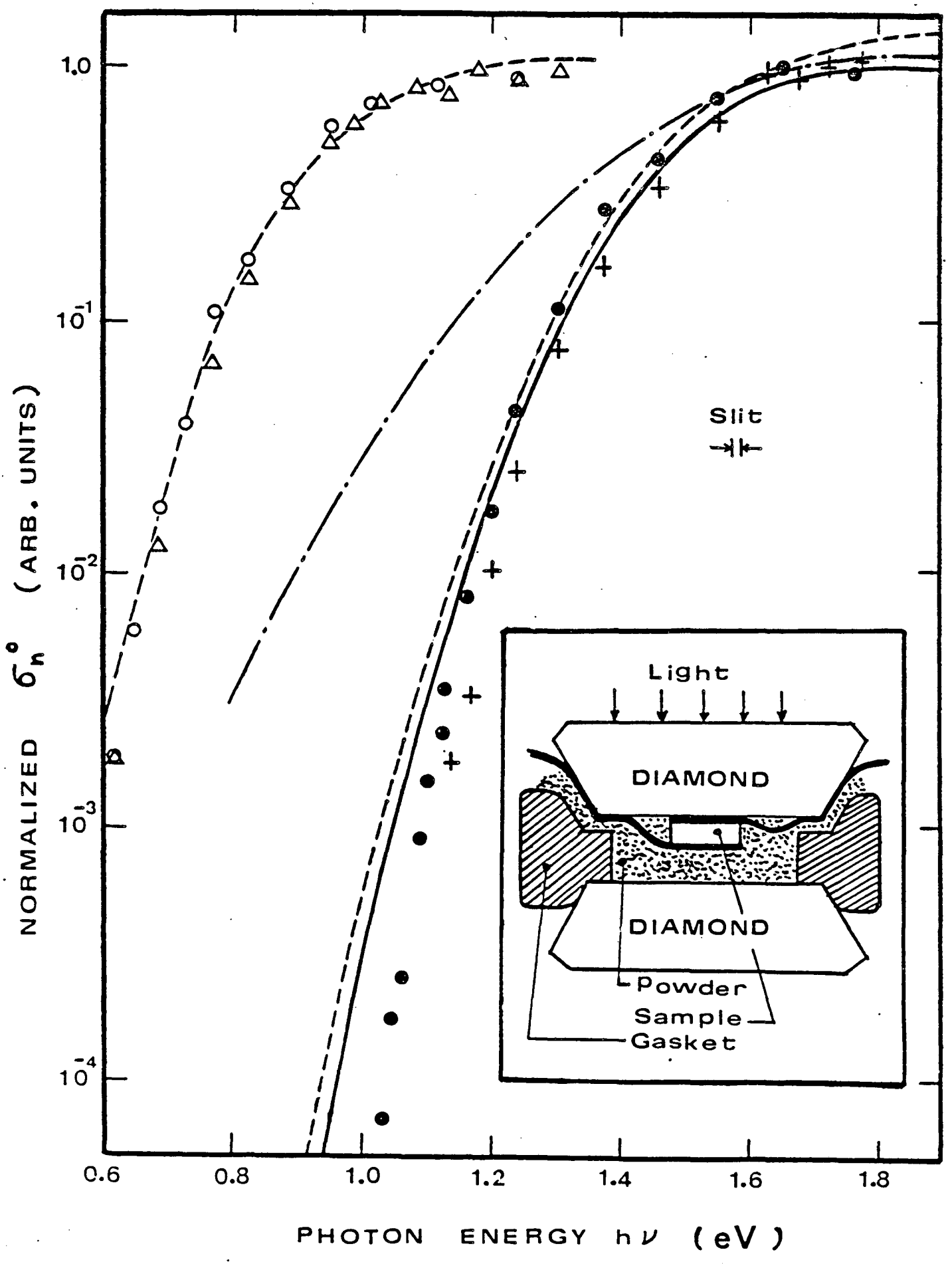
Fig. 1 The normalized photoionization cross section spectra of the DX center in GaAlAs (open circles and open triangles) and of the PIDD in GaAs under pressures of 33 (solid circles) and 38 kbars (crosses). The open triangles are the data of Lang et al. reproduced from Ref. 3 while the open circles represent 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.

Fig. 2 Shows 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 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.


10^4
10^2
10^0
10^{-2}
10^{-4}
τ_e^{-1} (sec^{-1})
29 Kbar
38 Kbar
4
6
8
10
12
1000/T (K^{-1})


TIME (10^3 sec)
0
1
2
3
1.0
0.9
0.8
0.7
NORMALIZED C^2 (ARB.UNITS)
T = 77.2 k
T = 91.0 k
BIAS
0v
-3v
t
t_1
t_2
t_3
0
1
2
3
4
5
6
TIME (10^2 sec)


1.0
10^{-1}
10^{-2}
10^{-3}
10^{-4}
NORMALIZED σ_n° (ARB. UNITS)
Slit
Light
DIAMOND
DIAMOND
Powder
Sample
Gasket
0.6
0.8
1.0
1.2
1.4
1.6
1.8
PHOTON ENERGY $h\nu$ (eV)

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