Formation of a *DX* Center in InP under Hydrostatic Pressure

J. A. Wolk,[1],[2] W. Walukiewicz,[2] M. L. W. Thewalt,[3] and E. E. Haller[2],[4]

[1]*Department of Physics, University of California, Berkeley, California 94720*

[2]*Lawrence Berkeley Laboratory, Berkeley, California 94720*

[3]*Department of Physics, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6*

[4]*Department of Material Science and Mineral Engineering, University of California, Berkeley, California 94720*

(Received 18 March 1992)

We have discovered a *DX* center in InP:S under hydrostatic pressure greater than 82 kbar. This defect exhibits the persistent photoconductivity typical of such centers. The optical ionization energy for this new *DX* center is between 0.86 and 1.02 eV, and we have measured the energy dependence of the optical absorption cross section. The thermal barrier for capture from the shallow donor state into the deep *DX* state is in the range 0.23–0.33 eV. We estimate that at zero pressure the energy of the *DX* center lies 0.51 ± 0.07 eV above the Γ conduction-band minimum.

PACS numbers: 71.55.Eq, 61.70.At, 78.50.Ge

We report the first observation of a *DX* center in InP. The new defect forms in InP:S under the application of hydrostatic pressure greater than 82 kbar. This finding provides further evidence that the metastability of donor dopants is a general phenomenon in III-V semiconductors [1].

DX centers are deep donor levels found in several *n*-type III-V semiconductor alloys [2]. These defects exhibit unusual characteristics including persistent photoconductivity below 110 K and a large difference between their thermal and optical ionization energy. These properties were explained by Lang and Logan [3] in terms of a large lattice relaxation of the defect. Recent theoretical [4,5] and experimental work [6–9] has also suggested that *DX* centers are examples of Anderson negative-*U* systems [10]. These centers were first discovered in GaAsP by Craford *et al.* [11] and were later found in $Al_xGa_{1-x}As$:Te for $x > 0.23$ by Nelson [12] and Lang, Logan, and Jaros [13]. *DX* centers have also been observed by Mizuta *et al.* [14] in unalloyed GaAs under hydrostatic pressure greater than 20 kbar.

At present it is clear that these defects are due to an isolated substitutional donor which undergoes a shallow-to-deep donor transition under the above-mentioned conditions of alloying or application of hydrostatic pressure. Alloying-induced conduction-band structure changes in GaAs are very similar to changes created by the application of hydrostatic pressure. The fact that *DX* centers form under these two circumstances therefore suggests that this defect becomes more stable than the shallow donor due to changes in the structure of the conduction band [4]. If this idea is correct, then it might be possible to use pressure to induce *DX* center formation in III-V compounds other than GaAs so long as they have a band structure and conduction-band minima pressure derivatives similar to those in GaAs. InP exhibits such characteristics, and we have in fact found that *DX* centers form in this compound under pressures greater than 82 kbar.

Figure 1 shows the configuration coordinate diagram for InP at 92 kbar. This type of diagram is a plot of the energy E of the defect (lattice plus electronic energy) versus the configuration coordinate Q, which is a measure of the lattice distortion around the defect. Looking at Fig. 1, it is clear that the *DX* center can be characterized by four energies: (1) E_0, the binding energy of the center relative to the shallow donor state; (2) E_e, the thermal energy required to emit an electron from the *DX* to the shallow state; (3) E_{opt}, the optical energy required to emit an electron from the deep to the shallow state; and (4) E_c, the capture barrier energy from the shallow into the deep *DX* state. Figure 1 illustrates the origin of the difference between the thermal and optical ionization energies of the *DX* center, as well as the origin of persistent photoconductivity. If the center is optically excited at low temperature, the electrons do not have sufficient energy to overcome the barrier and return to the deep *DX* state. The experimental work described in this Letter will focus on using optical techniques to determine (a) the pressure at which the shallow-to-deep donor transition occurs, (b) E_{opt} and the relative strength of the optical absorption cross section as a function of energy, and (c) E_c.

We now discuss our spectroscopic technique for finding

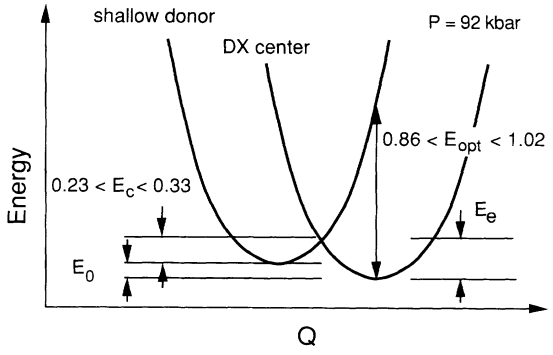

FIG. 1. Configuration coordinate diagram of InP:S at $P = 92$ kbar.

the shallow-to-deep donor transition pressure. The samples we used were InP:S with a free carrier concentration $n=2.1\times10^{18}$ cm^{-3}. Hydrostatic pressure was applied to the samples using a diamond anvil cell with liquid nitrogen as the pressure medium. Our technique for performing spectroscopy on a sample mounted in a diamond anvil cell has been described previously [15]. All spectra were taken at $T=5$ K. When the sample is at low pressure, the S donor electrons are all in the shallow state. At this high doping level, however, the shallow impurity band has broadened so much that it merges with the conduction band. This makes the sample opaque to far-infrared radiation because of free carrier absorption. When the sample is put under sufficient hydrostatic pressure, though, the electrons are trapped at the deep DX levels and the sample becomes transparent in the far infrared. Therefore, the transition pressure is the pressure at which the sample becomes transparent. We are able to obtain an infrared signal even below the transition pressure because of light leaking around the sample, but we of course see no InP-related features. Above the DX formation pressure we very clearly see the reststrahlen band of InP. By looking for the appearance of the reststrahlen band, we find that the pressure required for DX center formation in our samples is 82 kbar. This effect is clearly not due to a crossing of the Γ and X conduction bands, resulting in deeper X-band donors, since the new deep state exhibits persistent photoconductivity. The observed spectral behavior is reversible with pressure, so it also cannot be attributed to permanent structural defects created by the high pressure.

The transition pressure can be used to estimate the energy of the DX level at zero pressure relative to the shallow donor level. Chadi and Chang [4] proposed that, since the DX level is deep, its pressure derivative is the same as that of the conduction band averaged over all k space. This average pressure derivative of the conduction band can be estimated using the expression [4]

$$\frac{dE_{\mathrm{CB}}}{dP}=\frac{[dE(\Gamma)+3dE(X)+4dE(L)]/8}{dP}.$$

We use $dE(\Gamma)/dP=8.4\pm0.5$ meV/kbar, $dE(X)/dP=-2.0\pm1.0$ meV/kbar, and $dE(L)/dP=3.7\pm1.0$ meV/kbar with respect to the valence-band maximum [16–18]. This gives $dE_{\mathrm{CB}}/dP=2.2\pm0.6$ meV/kbar, which implies that the DX level approaches the conduction-band minimum at Γ at the rate $dE(\Gamma)/dP-dE_{\mathrm{CB}}/dP=6.2\pm0.8$ meV/kbar. We can observe the reststrahlen band when the free carrier absorption becomes sufficiently small. We have calculated [19] that the sample is 90% transparent by the time the DX level lies 25 meV below the shallow donor level, and therefore the DX level must lie within 25 meV of the conduction-band minimum at 82 kbar. Taking this 25 meV uncertainty into account, a transition pressure of 82 kbar implies that the DX level is 510 ± 70 meV above the conduction-band minimum at zero pressure. It is interesting to note that the difference between the energy at $P=0$ of the S DX center in InP (0.510 ± 0.07 eV) and GaAs [4] (0.150 eV) is equal to the band offset between InP and GaAs (≈0.4 eV) [20–22] within our experimental error. This is consistent with work showing that some deep levels may be used as absolute energy-level references in III-V semiconductors [23,24], suggesting that band offsets can be used to predict the energy of DX levels in other III-V semiconductors.

We next discuss our technique for determining the optical ionization energy of the InP DX center. In order to do this, the following modification was made to the basic experimental setup described above. A tungsten filament lamp with the glass case broken off was placed in front of the sample. Its output was blocked by a Ge filter, making the lamp a source of infrared radiation below the band gap of Ge. The whole apparatus (equipment described above plus the lamp assembly) was placed inside a Cary 2390 grating spectrometer. When the light from the grating spectrometer is of sufficient energy to optically ionize the DX centers, the sample becomes more opaque and the photocurrent through the photoconductor mounted behind the cell decreases. A black polyethylene filter was mounted in front of the photoconductor so it would not see any band-edge light from the monochromator. All data were taken at $T=9$ K. For increased sensitivity, we chopped the far-infrared lamp by pulsing the voltage supply to the lamp and locked in on the chopping frequency. The fraction of light going through the sample space and reaching the detector is $T=I(t)/I(0)=c_0(1-a)R^2\exp(-n\sigma_{\mathrm{free}}x)+a$, where $I(t)$=photocurrent through the photoconductor as a function of time t, a=fraction of the sample space area not covered by the sample, R=reflection coefficient for InP, n=free carrier concentration, σ_{free}=cross section for free carrier absorption, x=sample thickness, and c_0 is a constant taking into account all other absorption processes. We also have $n=N_D[1-\exp(-F\sigma_{\mathrm{opt}}t)]$, where F=light flux from the monochromator, σ_{opt}=defect optical absorption cross section, and N_D=donor concentration. Using these expressions and making the approximation that the optical cross section for free carrier absorption is independent of the ionized impurity concentration, we can fit the following function to our photoconductor response data:

$$\ln[I(t)/I(\infty)-a]=c_1-c_2(1-e^{-F\sigma_{\mathrm{opt}}t}),$$

where c_1 and c_2 are constants. Using the above expression to fit our data for various energies of light, correcting for the fact that F is a function of wavelength, we can make a plot of the relative optical cross section as a function of energy. This plot is shown in Fig. 2 for $P=92$ kbar.

The data can be fitted using the model for optical absorption by a deep level with large lattice relaxation

which was used by Lang, Logan, and Jaros [13] to fit the energy dependence of the optical ionization cross section of DX centers in $Al_xGa_{1-x}As$. The following equation gives the cross section:

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

where $\rho(E)$ is the density of free electron states, $E_F=11.2$ eV is the free-electron Fermi energy, $E_g=2.2$ eV is the forbidden band gap at $T=9$ K and $P=92$ kbar, $E_A=5$ eV is the Penn gap, $\eta=\exp(-2E/E_A)$, and $U=2S(h\nu)^2/\tanh(h\nu/kT)$, where $S=$Huang-Rhys factor and $h\nu=0.0085$ eV is the TA phonon energy, which is the appropriate phonon to use for DX centers [25]. This model has two parameters, which are (1) the Franck-Condon shift of the defect $=d_{\rm FC}=Sh\nu$, and (2) $E_{\rm opt}=E_0+Sh\nu$. Since we do not know the temperature dependence of the cross section (we can only observe a narrow temperature range with our apparatus), we are not able to find a unique fit to our data. However, we can roughly estimate E_0, and this allows us to narrow the acceptable range for $E_{\rm opt}$. Increasing the pressure from 82 to 92 kbar moves the DX level down in energy roughly 60 meV relative to the Γ conduction-band minimum. This implies by our previous arguments that E_0 should be in the range 60–85 meV. Using these constraints, we find good fits for our data for $E_{\rm opt}$ between 0.86 and 1.02 eV. We show in Fig. 2 our experimental data fitted by $E_{\rm opt}=d_{\rm FC}+E_0=0.87+0.07=0.94$ eV.

The technique used to find the thermal capture barrier from the shallow donor state into the DX state is essentially the same as that used to find the optical ionization energy. The only difference in the experimental setup is that a lamp capable of shining white light is now placed in front of the mirror and the entire apparatus is mounted in a Digilab 80-V Fourier transform spectrometer. This allows us to use the glowbar of the spectrometer as our source of far-infrared radiation. The sample is first cooled to 11 K and the donors are pumped into the metastable shallow state by shining white light on the sample. The white-light lamp is then turned off and the photoconductor signal at zero path in the interferogram is recorded. The signal at zero path is the sum of all the wavelengths reaching the detector, so this is exactly analogous to the chopped photoconductor signal discussed in the section on determining the optical ionization energy. The sample is then brought up to the annealing temperature for a predetermined time, recooled, and the photoconductor signal again recorded. As the annealing progresses, more shallow donors transform into DX centers and the photoconductor signal increases as the sample becomes more transparent. Starting from a similar expression for T as for the analysis of our optical ionization data, with the only difference being that $T=I(t)/I(\infty)$, the response of the photoconductor can be related to n, the concentration of free carriers in the sample, by

$$n(t)=-(1/\sigma_{\rm free}x)\{\ln[I(t)/I(\infty)-a]+c_3\},$$

where $c_3=$const. The parameters c_3 and $1/\sigma_{\rm free}x$ can be fit using $n(0)=2.1\times10^{18}$ cm^{-3} and $n(\infty)\ll n(0)$. We theoretically modeled our data using the following expression given by Theis and Mooney [7] for $n(t)$ for a negatively charged DX center:

$$dn/dt=-\sigma_\infty\langle v\rangle n(N_D+n)\exp[(-E_C-E_F)/kT],$$

where $\sigma_\infty=$electron capture cross section at $T=\infty$ and $\langle v\rangle=$average electron velocity. This model has E_c and σ_∞ as adjustable parameters. We performed isothermal anneals at 59, 63, and 70 K, and show our experimental

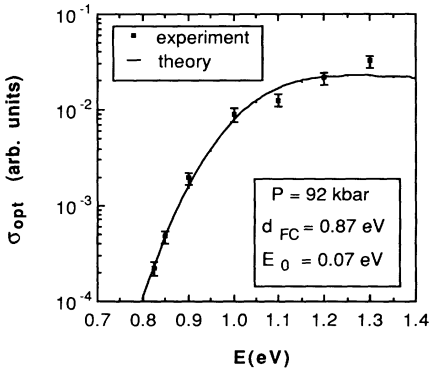

FIG. 2. Comparison of experimental data with theory for energy dependence of the DX center optical cross section at $P=92$ kbar. Parameters used in fit are $d_{\rm FC}=0.87$ eV and $E_0=0.07$ eV.

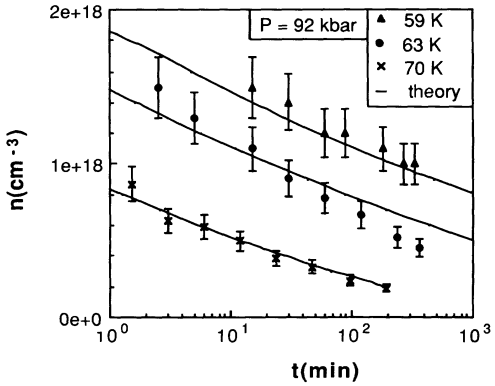

FIG. 3. Comparison of experimental data with theory for capture barrier from shallow donor state to DX state at $P=92$ kbar. Theoretical fit is for $E_c=0.275$ eV.

data along with the theoretical fits for $E_c = 0.275$ eV in Fig. 3. Reasonable fits to our data can be obtained with E_c in the range 0.23–0.33 eV, and this implies $\sigma_\infty(DX) \approx 10^{-31}$ cm^{-3}, which is comparable to results for DX centers in $AlGa_xAs$ [25].

In conclusion, we have discovered a pressure-induced deep donor level in InP which has the properties of a DX center. The pressure at which the new defect becomes more stable than the shallow donor is 82 kbar. The optical ionization energy of this defect is between 0.86 and 1.02 eV and the thermal ionization energy is in the range 0.23–0.33 eV. The fact that DX centers can be formed in InP by applying pressure suggests that the existence of DX states should be very common in n-type III-V semiconductors, though these levels may not be able to be brought into the forbidden gap.

The authors would like to gratefully acknowledge D. Hoffman for supplying our InP:S samples, M. Kruger for his continuous advice on high-pressure work, R. Jeanloz for the use of his high-pressure laboratory, and Jeff Beeman for the construction of our photoconductors. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Science Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098 and the NSF under Grant No. DMR91-15856.

[1] As suggested by K. Khachaturyan, E. R. Weber, and M. Kaminska, Mater. Sci. Forum, **38-41**, 1067 (1989).
[2] P. M. Mooney, J. Appl. Phys. **67**, R1 (1990).
[3] D. V. Lang and R. A. Logan, Phys. Rev. Lett. **39**, 635 (1977).
[4] D. J. Chadi and K. J. Chang, Phys. Rev. Lett. **61**, 873 (1988).
[5] J. Dabrowski, R. Strehlow, and M. Scheffler, in *Proceedings of the Twentieth International Conference on the Physics of Semiconductors*, edited by E. M. Anastassakis and J. D. Joannopolous (World Scientific, Singapore, 1990), p. 729.
[6] J. A. Wolk, M. B. Kruger, J. N. Heyman, W. Walukiewicz, R. Jeanloz, and E. E. Haller, Phys. Rev. Lett. **66**, 774 (1991).
[7] T. N. Theis and P. M. Mooney, in *Impurities, Defects, and Diffusion in Semiconductors: Bulk and Layered Structures*, edited by J. Bernholc, E. E. Haller, and D. J. Wolford, MRS Symposia Proceedings No. 163 (Materials Research Society, Pittsburgh, 1990), p. 729.
[8] T. Fujisawa, J. Yoshino, and H. Kukimoto, Jpn. J. Appl. Phys. **29**, L388 (1989).
[9] W. Jantsch, Z. Williamowski, and G. O. Ostermayer, Semicond. Sci. Technol. **6**, B47 (1991).
[10] P. W. Anderson, Phys. Rev. Lett. **34**, 953 (1975).
[11] M. G. Craford, G. E. Stillman, J. A. Rossi, and N. Holonyak, Jr., Phys. Rev. **168**, 867 (1968).
[12] R. J. Nelson, Appl. Phys. Lett. **31**, 351 (1977).
[13] D. V. Lang, R. A. Logan, and M. Jaros, Phys. Rev. B **19**, 1015 (1979).
[14] M. Mizuta, M. Tachikawa, H. Kukimoto, and S. Minomura, Jpn. J. Appl. Phys. **24**, L143 (1985).
[15] J. A. Wolk, M. B. Kruger, J. N. Heyman, W. Walukiewicz, R. Jeanloz, and E. E. Haller, Semicond. Sci. Technol. **6**, B78 (1991).
[16] S. W. Tozer, D. J. Wolford, J. A. Bradley, D. Bour, and G. B. Stringfellow, in *Proceedings of the Nineteenth International Conference on the Physics of Semiconductors*, edited by W. Zawadzki (Institute of Physics, Polish Academy of Sciences, Warsaw, 1988), p. 881.
[17] K. J. Chang, S. Froyen, and M. L. Cohen, Solid State Commun. **50**, 105 (1984).
[18] A. R. Goñi, K. Syassen, K. Strössner, and M. Cardona, Phys. Rev. B **39**, 3178 (1989).
[19] W. Walukiewicz, J. Lagowski, L. Jastrzebski, P. Rava, M. Lichtensteiger, C. H. Gatos, and H. C. Gatos, J. Appl. Phys. **51**, 2659 (1980).
[20] D. D. Nolte, Ph.D. thesis, University of California at Berkeley [Lawrence Berkeley Laboratory Report No. LBL-25242 (unpublished)].
[21] C. G. Van de Walle, Phys. Rev. B **39**, 1871 (1989).
[22] J. Tersoff, Phys. Rev. B **32**, 6968 (1985).
[23] D. D. Nolte, W. Walukiewicz, and E. E. Haller, Phys. Rev. Lett. **59**, 501 (1987).
[24] J. M. Langer and H. Heinrich, Phys. Rev. Lett. **55**, 1414 (1985).
[25] D. V. Lang, in *Deep Levels in Semiconductors*, edited by S. T. Pantelides (Gordon and Breach, New York, 1986), p. 489.