Magnetic Studies of Persistent Photoconductivity in n-$Al_xGa_{1-x}As$

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Low-temperature magnetic-susceptibility measurements were made during illumination of n-$Al_xGa_{1-x}As$ with DX centers to investigate the microscopic origin of persistent photoconductivity. Experiments using a dc SQUID magneto-optic microsusceptometer revealed the change of electronic susceptibility as a function of illumination time and temperature. The results indicate that the DX center is a paramagnetic donor with one unpaired electron.

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There has been a considerable amount of experimental and theoretical attention directed towards the understanding of persistent photoconductivity in the n-type III-V semiconductor $Al_xGa_{1-x}As$ ($x > 0.23$). It has been well established that illuminating these systems at temperatures below $T \simeq 100$ K induces a conductivity which persists long after the illumination has ended. Previous investigations[1] on the metastable properties of Si, Se, Sn, and Te in $Al_xGa_{1-x}As$ concluded that the deep state is related to a defect with a large lattice relaxation which produces a thermal barrier preventing recapture at low temperatures. An optically induced transition to the unrelaxed metastable shallow state cannot be reversed at low temperatures. Early studies[1] ascribed this effect to a defect complex (donor "D" with an unknown partner "X"), and later demonstrated the excited state of the DX center to be a hydrogenic donor. Recently, theoretical efforts[2] to explain the metastable properties of the DX center have suggested a redistribution of electrons, $2D^0 \rightarrow D^+ + D^-$, where, rather than all donors being neutral, half the donors have two electrons and become negatively charged whereas the other half have none and are positively charged. According to the Pauli exclusion principle, if both electrons are in the singlet state of the same donor atom they must have opposite spins, this model thereby predicting all donors to be diamagnetic. However, the fundamental mechanism for transformation of a shallow hydrogenic donor into a deep relaxed DX state is still controversial[3] and poorly understood.

In this Letter we report direct magnetic-susceptibility measurements of the DX center in doped $Al_xGa_{1-x}As$ as a function of optical illumination time and temperature. Although there have been a large number of transport and deep-level transient spectroscopy studies on these systems, sensitive magnetic experiments bearing on the issue of spin dynamics have proven difficult to perform. A new magneto-optic microsusceptometer comprised of an integrated dc SQUID and a superconducting pair of miniature counterwound pickup coils has made such measurements possible. Contrary to theoretical expectations, we find that there are paramagnetic centers in n-$Al_xGa_{1-x}As$ epilayers and that their concentration is equal to the number of DX centers.

Three thick-film $Al_xGa_{1-x}As$ samples were fabricated for these studies, including two direct-gap and a third indirect-gap layer. A 14.3-μm $Al_{0.31}Ga_{0.69}As$:Si molecular-beam epitaxy (MBE) film doped with 3×10^{17} Si/cm^3, a 10-μm $Al_{0.43}Ga_{0.57}As$:Te metalorganic chemical-vapor deposition (MOCVD) epilayer doped with 3.6×10^{18} Te/cm^3, and a 12-μm indirect-gap $Al_{0.50}Ga_{0.50}As$:Si MBE film doped with 5.4×10^{17} Si/cm^3 were grown on semi-insulating GaAs substrates. Hall measurements on all three samples as a function of temperature yielded the thermal depth of the DX centers as 91.5, 114, and 133 meV, respectively. Persistent photoconductivity of the doped samples annealed away at 150, 90, and 100 K, respectively. The thickness of the epilayers was determined by scanning electron microscopy of a cleaved cross section, whereas the doping was measured by capacitance-voltage experiments. Finally, the depth of the metastable hydrogenic state in the $Al_{0.31}Ga_{0.69}As$:Si-doped sample was obtained at low temperatures (where electrons can freeze out only on metastable hydrogenic donors, but not on the ground state of the DX center[4,5]) and found to be 8.4 meV.

The experiment utilizes two separate superconducting integrated circuits which are interconnected to form a miniature magneto-optic susceptometer. A microfabricated pickup loop structure consists of two superconducting square counterwound Pb loops, 25 μm on a side, one of which is in close proximity to the sample. In addition, a center-tapped Nb field coil which takes a single square turn around each pickup loop is used to apply an ac magnetic field for susceptibility measurements as well as to apply static dc magnetic fields. This structure is built on a transparent quartz substrate allowing direct optical access to the sample. The gradiometer is connected with short superconducting lead-tin wire bonds to the ten-turn spiral input coil of an integrated planar dc SQUID

operating in a conventional flux-locked-loop circuit with room-temperature electronics.[6] Both circuits are mounted on a transparent sapphire carrier and placed on a brass heat sink surrounded by a superconducting, rf tight shield of copper-laminated fiberglass tubing with a plating of lead-tin solder. A small hole perforates both the heat sink and the shield with the carrier appropriately positioned to keep the sample directly in line with this access port. Finally, the entire assembly is placed into a variable-temperature optical Dewar and cooled to $T \sim 1.5$ K. A diode laser producing light below the band gap of the $Al_xGa_{1-x}As$ layers at $E = 1.6$ eV is used to illuminate the samples. This energy is above the band gap of GaAs and therefore the light cannot penetrate the GaAs substrate and interact with defects in the substrate. The total volume of the $Al_{0.31}Ga_{0.69}As$:Si, $Al_{0.43}Ga_{0.57}As$:Te, and $Al_{0.50}Ga_{0.50}As$:Si layers measured in our magnetic-susceptibility experiment is 9×10^{-9}, 6.3×10^{-9}, and 7.5×10^{-9} cm^3, respectively; the expected number of donor atoms contributing to the signal is therefore 2.7×10^9 Si, 2.3×10^{10} Te, and 4.0×10^9 Si.

Figure 1 shows the magnetic susceptibility $\chi(T)$ of the two direct-gap thick films as a function of inverse temperature before and after optical excitation. Curie-law analysis [Eq. (1) below] dictates the measured slope before illumination to be proportional to the number of paramagnetic impurities. The concentration of paramagnetic impurities may then be compared with the number of *DX* centers obtained from the capacitance-voltage measurements. For the $Al_{0.31}Ga_{0.69}As$:Si sample the slope of 1.67×10^{-15} emu K/G corresponds to 2.7×10^9 paramagnetic impurities, equal to the number of *DX* centers in the measured part of the epilayer. For the $Al_{0.43}Ga_{0.57}As$:Te sample the slope of 1.21×10^{-15} emu K/G corresponds to 1.94×10^{10} paramagnetic impurities, in very good agreement with the expected value of 2.3×10^{10}. The slope drastically decreases after illumination (Fig. 1), since most *DX* centers are then converted to shallow hydrogenic donors with strongly overlapping donor-electron wave functions. The magnetic susceptibility of the resulting metallic state is expected to be temperature independent.[7] The magnetic susceptibility of these two epilayers was also measured as a function of illumination time at $T = 2.85$ K and shown in Fig. 2. After an initial increase, the susceptibility saturates after $\sim$200 sec for the Si-doped layer and $\sim$100 sec for the Te-doped layer. The increase in magnetic susceptibility is persistent, and does not change when the illumination stops. However, the increase in magnetic susceptibility begins only after a certain time delay of approximately 8 and 15 sec for the cases of Si- and Te-doped epilayers, respectively. To demonstrate that these signals arise solely from the epilayer and not the GaAs substrate, the samples were flipped upside down in the susceptometer and the experiment repeated. No magnetic signal was observed.

Let us consider the temperature-dependent magnetic

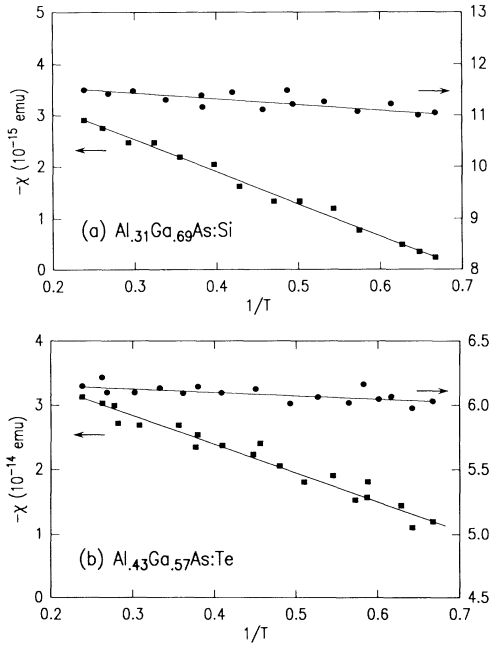

FIG. 1. Diamagnetic susceptibility of the epilayers vs inverse temperature before (squares) and after (circles) illumination in a field of 3.7 G. Illumination was made with 500 μW at $E = 1.6$ eV. The data offset is arbitrary but the same for the plots before and after illumination. (a) $Al_{0.31}Ga_{0.69}As$:(3×10^{17} Si). (b) $Al_{0.43}Ga_{0.57}As$:(3.6×10^{18} Te).

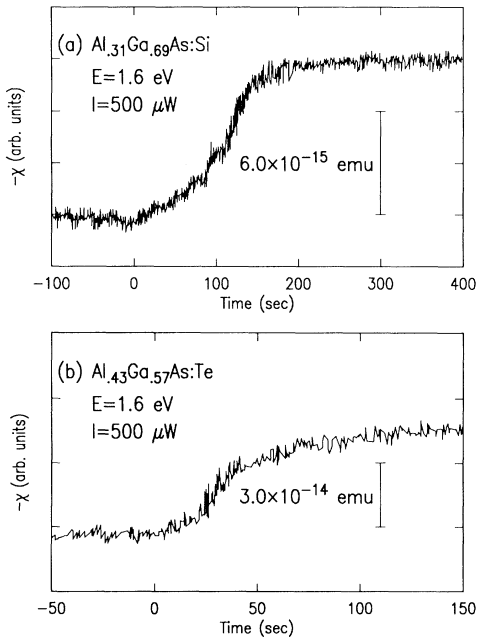

FIG. 2. Diamagnetic susceptibility of the epilayers vs illumination time at $T = 2.85$ K in a magnetic field of 3.7 G. Parts (a) and (b) are as in Fig. 1.

susceptibility of the n-$Al_xGa_{1-x}As$ epilayer both in the dark and after illumination given either a paramagnetic or a diamagnetic ground state of the DX center. In the case of a paramagnetic ground state, the magnetic susceptibility of the $Al_xGa_{1-x}As$ epilayer in the dark (at a temperature low enough for carrier freeze-out) with concentration of DX centers, N_{DX}, is given by

$$\chi(T) = -\chi_1 + N_{DX}\mu_B^2/k_BT, \quad (1)$$

where χ_1 is the temperature-independent diamagnetic susceptibility of the host lattice and the second term is the paramagnetic Curie susceptibility of deep donors (assuming noninteracting spins and $g \simeq 2$). However, in the case of diamagnetic DX centers the susceptibility should be temperature independent. It is clear from the data in Fig. 1 that there are paramagnetic centers in the $Al_xGa_{1-x}As$ epilayer and their concentration is equal to the concentration of the DX centers.

Paramagnetism of deep donors is well described by the Curie law (dashed line in Fig. 3), and the effect of illumination is to persistently convert the DX centers into hydrogenic donors[8] which are paramagnetic. However, the paramagnetism of hydrogenic donors obeys the Curie law only when the overlap between donor-atom-electron wave functions is negligible[9] (Fig. 3, region A). As the carrier concentration increases and the overlap between the donor wave functions increases, paramagnetism becomes smaller than predicted by the Curie law and is qualitatively described by the paramagnetism of donors

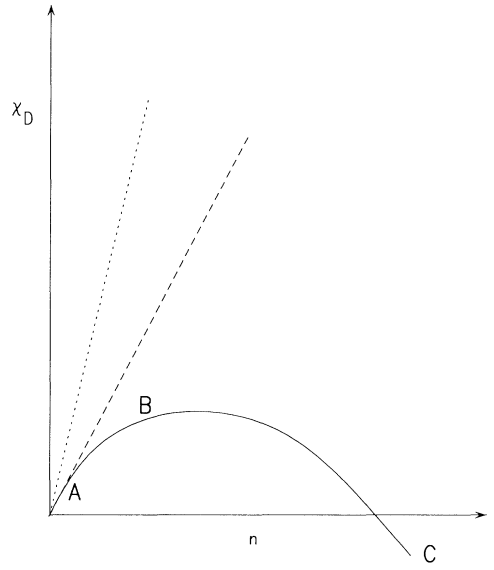

FIG. 3. Schematic representation for the paramagnetic susceptibility of deep paramagnetic donors with one electron (dashed line) and shallow paramagnetic donors (solid line) vs donor concentration [compare with data on P in Si (Refs. 10–13]. Dotted line represents a two electron ground-state model with $S = 1$.

associated in pairs of interacting atoms[9] (Fig. 3, region B). In the metallic conduction region (if the Fermi temperature is much greater than the measurement temperature), with even greater overlap between the hydrogenic donor wave functions, donor electrons become diamagnetic conduction electrons with a temperature-independent Landau-Peierls-Pauli (LPP) diamagnetic susceptibility[7] (Fig. 3, region C),

$$\chi_{LPP} = \mu_B^2 N(\epsilon_F)(1 - 1/3m^{*2}), \quad (2)$$

where $N(\epsilon_F)$ is density of states on the quasi-Fermi level and m^* is the ratio of effective mass of the electron in the conduction band to the free-electron mass.

If the DX center is a paramagnetic donor with one unpaired electron, the increase in the diamagnetic susceptibility $\chi(T)$ of the n-$Al_xGa_{1-x}As$ film upon illumination can be schematically represented by the difference between the dashed and solid curves in Fig. 3. In the case of a diamagnetic, two-electron ground state of the DX center, the change of $\chi(T)$ upon illumination should be described by the solid line alone, with a minus sign. However, the observed behavior (Fig. 2) is clearly consistent with the paramagnetic donor model. The total change in $\chi(T)$ seen at the end of the illumination period will then be a sum of two terms. The first term, $N_{DX}\mu_B^2/k_BT$, accounts for the disappearance of the DX center paramagnetism, whereas the second term χ_{LPP} [Eq. (2)] describes the appearance of LPP diamagnetism from the conduction electrons produced by the photoionization of the DX centers. The two terms can be separated from one another by extrapolation of $\chi(T)$ vs $1/T$ dependences in Fig. 1 to the high-temperature limit where the Curie paramagnetism vanishes. The χ_{LPP} term is then equal to the difference of the y intercepts of the curves before and after illumination, the values obtained for $Al_{0.31}Ga_{0.69}As$:Si- and $Al_{0.43}Ga_{0.57}As$:Te-doped samples being 2.0×10^{-15} and 6.0×10^{-15} emu/G, respectively.

Finally, if the ground state of a DX center were orbitally degenerate, one might consider the alternative of a two-electron ground state with parallel spins ($S = 1$). In this case the DX center paramagnetism may be given by

$$\chi(T) = \tfrac{1}{2} N_{DX} g^2 \mu_B^2 S(S+1)/3k_BT = \tfrac{4}{3} N_{DX}\mu_B^2/k_BT \quad (3)$$

and shown as a dotted line in Fig. 3. This assumes that only half the donors have two electrons and that the g factor for an electron on a deep donor is $\simeq 2$. The change of $\chi(T)$ upon illumination should then be described by the difference between the dotted and solid lines in Fig. 3, and seen immediately at $t = 0$. Both magnetic susceptibility and EPR studies were made on a third sample of $Al_{0.50}Ga_{0.50}As$:Si to distinguish between the possibilities of $S = \frac{1}{2}$ and 1. Unlike the first two samples, the metastable hydrogenic state of the DX

center in this indirect-gap material is a relatively deep X-like state with a large effective mass.[14] The effect of illumination is to convert one kind of deep paramagnetic donor into another kind of paramagnetic donor[8] deep enough to be localized. Magnetic experiments were unable to detect any change in the susceptibility upon illumination for over 5 min, indicating that the spin of the DX center ground state is identical to the $S=\frac{1}{2}$ spin of the metastable hydrogenic state. To confirm that illumination indeed converts the DX center into the X-like metastable hydrogenic donor, electron-paramagnetic-resonance studies were performed. An EPR signal with $g=1.93$ and a magnitude corresponding to 4.5×10^{17} spins/cm^3 at saturation appeared after illumination[15-17] and could be quenched by heating to $\simeq100$ K. In agreement with previous studies,[2,15,17] no EPR signal of the lattice relaxed ground state could be detected.

In conclusion, we have performed direct magnetic-susceptibility experiments on a variety of doped $Al_xGa_{1-x}As$ epitaxial layers with DX centers to investigate the microscopic origin of persistent photoconductivity. The measurements showed changes in the electronic susceptibility as a function of time and temperature demonstrating that the DX center is a paramagnetic donor. In contrast to theoretical expectations, the results are consistent with the donors having a single unpaired electron and $S=\frac{1}{2}$. The absence of an EPR signal from the paramagnetic donor remains to be explained.

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

[2]J. D. Chadi and K. Chang, Phys. Rev. Lett. **61**, 873 (1988); K. Khachaturyan, E. R. Weber, and M. Kaminska, in *Proceedings of the Fifteenth International Conference on Defects in Semiconductors, Budapest, Hungary, 1988,* edited by G. Ferenczi (Trans. Tech. Publications, Aedermannsdorf, Switzerland, 1989), p. 1067.

[3]D. K. Maude *et al.*, Phys. Rev. Lett. **62**, 1922 (1989); D. J. Chadi *et al.*, Phys. Rev. Lett. **62**, 1923 (1989).

[4]M. G. Craford, G. E. Stillman, J. A. Rossi, and N. Holonyak, Phys. Rev. **168**, 867 (1968).

[5]N. Chand, T. Henderson, J. Klem, D. Masselink, R. Fischer, and H. Morkoc, Phys. Rev. B **30**, 4481 (1984).

[6]D. D. Awschalom *et al.*, Appl. Phys. Lett. **53**, 2108 (1988).

[7]G. Busch and E. Mooser, Helv. Phys. Acta **26**, 611 (1953).

[8]T. N. Theis, T. F. Kuech, L. F. Palmateer, and P. M. Mooney, Inst. Phys. Conf. Ser. **74**, 241 (1985).

[9]E. Sonder and H. C. Schweinler, Phys. Rev. **117**, 1216 (1960).

[10]E. Sonder and D. K. Stevens, Phys. Rev. **110**, 1027 (1958).

[11]W. Sasaki and J. Kinoshita, J. Phys. Soc. Jpn. **25**, 1622 (1968).

[12]S. Ikehata, T. Ema, S. Kobayashi, and W. Sasaki, J. Phys. Soc. Jpn. **50**, 3655 (1981).

[13]A. Roy, M. Turner, and M. P. Sarachik, Phys. Rev. B **37**, 5522 (1988).

[14]J. E. Dmochowski, J. Langer, J. Raczynska, and W. Jantsch, Phys. Rev. B **38**, 3276 (1988); E. Glaser, T. A. Kennedy, R. S. Sillmon, and M. G. Spencer (to be published).

[15]P. M. Mooney, W. Wilkening, U. Kaufmann, and T. F. Kuech, Phys. Rev. B **39**, 5554 (1989).

[16]E. A. Montie and J. C. M. Henning, J. Phys. C **21**, L311 (1988).

[17]H. J. von Bardeleben, J. C. Bourgoin, P. Basmaji, and P. Gibart (to be published).