Identification of donor species in high-purity GaAs using optically pumped submillimeter lasers


Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, Massachusetts 02173

(Received 17 August 1972)

An optically pumped NH$_3$ laser has been used in conjunction with careful doping experiments in high-purity GaAs to determine the ionization energy of isolated tin donors. The energy obtained is 5.820 meV, which corresponds to a central-cell correction of 0.081 meV. This technique for impurity analysis is estimated to be sensitive to donor concentrations of less than $10^{11}$ cm$^{-3}$.

The recent development of optically pumped submillimeter lasers has greatly increased the number and power of available lines for spectroscopy. In particular, we have found that the 280.5-μ laser line from TEA CO$_2$ laser-pumped NH$_3$ is ideal for investigation of isolated shallow-donor impurities in GaAs. By Zeeman tuning the hydrogenic $1s-2p m = -1$ transition of residual and intentionally added donors through this laser line, we obtained the first accurate measurement of the isolated binding energy and a positive identification of a specific donor impurity, tin, in GaAs. This accurate determination for tin may make it possible to calculate other donor central-cell corrections, and the experimental technique should permit identification of the residual and other intentionally added donors in high-purity GaAs.

The laser configuration employed was similar to that used by Chang and Bridges, except that a TEA CO$_2$ laser was used instead of a cw source to generate the desired NH$_3$ line, whose wavelength was determined with a scanning Fabry-Perot interferometer. The unattenuated NH$_3$ radiation, with peak power of several watts, saturated the impurity transitions, and the unsaturated line shape was only observed after attenuating by nearly a factor of 100. Further reduction of intensity did not appear to affect the linewidth, and the measurements were made with an attenuation of approximately 125. For comparative purposes, spectra were also obtained with a conventional cw H$_2$O laser. The submillimeter radiation was directed via light pipes onto the GaAs sample, which was immersed in liquid helium and located within the bore of a superconducting solenoid. The sample photoconductivity was then monitored as the magnetic field was varied.

The samples were grown on seminsulating GaAs substrates with an AsCl$_3$–Ga–H$_2$ vapor-phase system. Before introducing tin into the growth system, the donor and acceptor concentrations ($N_D$ and $N_A$) for samples from a consecutive series of runs were obtained from Hall measurements and set of starting materials. When the residual $N_D$ and $N_A$ were found to be relatively constant, subsequent samples were doped by adding small measured amounts of tin to the gallium melt. The total $N_D$ and $N_A$ (both residual and tin donors and acceptors) were then determined from electrical measurements on the doped samples.

The number of tin donors was also estimated from the measured tin added to the gallium melt. In Table I we have summarized these results for the samples discussed in this letter. Sample No. 1 is the undoped control sample, grown just previous to the addition of tin, which had two different residual donor species (see Fig. 1) of total concentration $1.3 \times 10^{14}$ cm$^{-3}$. Since the residual impurity concentration in this sample was approximately the same as in the samples of the two preceding runs, tin was added to the growth system to produce sample No. 2. Sample No. 3 is a tin-doped sample with only one residual donor (see Fig. 2), grown in a different reactor with different starting materials than those used for samples No. 1 and No. 2.

The data obtained using optically pumped submillimeter lasers, shown in Fig. 1, give the strongest support to the identification of the tin donor. The peaks observed at 280.5 μ correspond to the $1s-2p m = -1$ hydrogenic impurity transition. The presence of residual donor species in undoped GaAs, whose ground-state energies are slightly different because of small central-cell corrections, has been reported recently. In the undoped sample studied here, transitions from two unidentified donor species are observed. The spectrum of the tin-doped sample shows an additional well-resolved transition corresponding to the tin donor. In both samples the peaks are narrow with the broadest having an energy half-width of approximately 0.10 cm$^{-1}$. Furthermore, no shift in position of the residual donor peaks is observed in the tin-doped sample. Therefore, we believe that these measurements provide the first observation of an isolated donor species in intentionally doped GaAs.

Previous work by Stillman et al. has determined that the effective hydrogenic Rydberg for GaAs donors, defined in the parabolic band approximation as

$$R_e = \frac{m_e e^4}{2\epsilon_0 h^2},$$

has the value $R_e = 46.10 \pm 0.15$ cm$^{-1}$ (5.715 meV). Furthermore, the ionization energies of the residual impurities responsible for the photoconductivity peaks at 60.51 and 67.95 kG in Fig. 1 were calculated to be 47.24 cm$^{-1}$ (5.856 meV) and 46.82 cm$^{-1}$ (5.804 meV), respectively. The ionization energy of the tin donor can be determined by a linear interpolation between these values, using the magnetic field measurements of the three $1s-2p m = -1$ donor transitions shown in Fig. 1. Using this method, we find that the tin donor in GaAs has an ionization energy of 46.95 ± 0.15 cm$^{-1}$ (5.820 meV) and an absolute central-cell correction of 0.65 ± 0.15 cm$^{-1}$ (0.081 meV), in good agreement with the values previously obtained from an unidentified donor.

Appl. Phys. Lett., Vol. 21, No. 9, 1 November 1972

Downloaded 17 May 2005 to 129.63.129.195. Redistribution subject to AIP license or copyright, see http://apl.aip.org/apl/copyright.jsp
DONOR SPECIES IN HIGH-PURITY GaAs

The magnetospectroscopy data for three samples taken at 78.45 μ with a cw H₂O laser are shown in Fig. 2 for comparative purposes. (Data were also taken at 79.09 μ.) The peaks in these spectra correspond to the 1s→2p m = +1 hydrogenic impurity transition. For the undoped sample No. 1, four peaks are observed which arise from the two residual donor impurities observed in the NH₃ spectra. We attribute the presence of two peaks for each of the central-cell−shifted species to a combination of spin-splitting and excited-state nonparabolicity. Although the different transition energies for spin-up and spin-down electrons are not in quantitative agreement with theories for nonparabolicity in the donor states, similar splitting is found in cyclotron resonance measurements. The tin-doped sample No. 2, with three donor species, exhibits five peaks (instead of six) because of overlap of the high-field tin peak with a residual donor transition. This donor is not present in the other tin-doped sample (No. 3) where we observe the spin-up and spin-down transitions corresponding to the tin donor.

Examination of the spectra taken with the NH₃ laser (Fig. 1) and the H₂O laser (Fig. 2) demonstrates the advantages of the former for the purpose of discrimination among different donor species in GaAs. The donor peaks for the 1s→2p m = −1 transition, when magnetically tuned for coincidence with the NH₃ laser, are found to be extremely narrow. For this case the major contribution to the breadth of the transitions is predicted to arise from the quadratic Stark effect—that is, from the interaction of the electric field of the charged donors and acceptors with the induced dipole moment of the donor wave function. Since this Stark perturbation always lowers the energy of the 2p m = −1 state, the resultant effect (due to the random distribution of charged sites) is an asymmetric line shape with a tail on the low-energy (high-magnetic-field) side. The 1s→2p m = −1 transition shown in Fig. 1 clearly exhibits such asymmetry.

For the case of the 1s→2p m = +1 transitions which can be reached with the H₂O laser line, other broadening effects dominate. In particular, since the 2p m = +1 transitions for the undoped sample No. 1 are well resolved, it is possible to determine the magnitude of the spin-splitting parameter δ, which is dominated by contributions from the electric fields of the charged donors and acceptors. The results of these measurements are given in Table 1. As expected, δ increases with increased concentration of charged donors and acceptors.

![Image](https://example.com/image1)

**Fig. 1.** Photoconductivity spectra for an undoped and tin-doped GaAs sample. The transition at 65.73 kG is attributed to the tin donor. Magnetic fields were determined by observing NMR in ⁷¹Al simultaneously with the photoconductivity peaks.

![Image](https://example.com/image2)

**Fig. 2.** Photoconductivity spectra for the samples in Table 1, measured using a cw H₂O laser. Two spin-split peaks corresponding to the tin donor are indicated by dashed lines at 66.83 and 66.94 kG.

---

**TABLE 1.** Donor concentrations (cm⁻³) for undoped (sample No. 1) and tin-doped (samples No. 2 and No. 3) GaAs.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Total</th>
<th>Residual</th>
<th>Tin</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.3×10¹⁴</td>
<td>1.3×10¹⁴</td>
<td>⋯</td>
</tr>
<tr>
<td>2</td>
<td>3.0×10¹⁴</td>
<td>1.3×10¹⁴</td>
<td>1.7×10¹⁴</td>
</tr>
<tr>
<td>3</td>
<td>2.7×10¹⁴</td>
<td>1.8×10¹⁴</td>
<td>9.2×10¹³</td>
</tr>
</tbody>
</table>

---

*Appl. Phys. Lett., Vol. 21, No. 9, 1 November 1972*
energy lies above the continuum at these magnetic fields, decay to lower energy states is possible, shortening the lifetime and broadening the line. As a consequence of the broadened linewidth and spin splitting, it is difficult to precisely determine the tin binding energy from the \( H_2O \) laser measurements. However, these measurements do reveal several interesting points: (a) The residual and tin donor peaks remain at the same energies in different samples grown in different reactors with different starting materials; (b) the tin donor peaks do not shift in energy in this donor concentration range (sample No. 2 has twice as many tin donors as sample No. 3); (c) the relative integrated spectral response from the residual and tin donors is in reasonable agreement with the relative donor concentration as determined from electrical measurements (see Table I).

Using \( NH_3 \) laser sources in conjunction with careful doping experiments, it should be possible to determine the ionization energies of a number of other shallow-donor species in GaAs and identify the residual donors in high-purity GaAs. This should lead to further purification of the material. The technique used here promises to be a powerful analytical tool for nondestructive trace impurity analysis. From the results obtained in the present experiments for tin donors, we conservatively estimate that it will be possible to detect shallow donors at concentrations of less than \( 10^{14} \text{ cm}^{-3} \) in high-purity \( n \)-type GaAs.

The authors thank Dr. D.M. Larsen for many helpful discussions, and W.E. Barch and L. Krohn, Jr. for expert technical assistance.

---

*Work sponsored by the Department of the Air Force.

†Also, Lowell Technological Institute, Lowell, Mass. 01854.

---

**Mass motion as observed by light-beating spectroscopy**

**N. Ben-Yosef, S. Zweigenbaum, and A. Weitz**

*School of Applied Science and Technology, The Hebrew University of Jerusalem, Jerusalem, Israel*

(Received 14 August 1972)

In the power spectra of the scattered light from silver chloride colloidal particles in water, a Lorentzian shifted from zero frequency has been observed in addition to the zero-centered one. The shifted peak is attributed to the mass motion due to liquid flow resulting from the heating of the illuminated part by the laser beam.

Light-beating spectroscopy is an accepted method of measuring narrow spectral lines, particularly those obtained by scattering laser light from various samples. In this letter we wish to report an observed interaction between the original laser beam and the scattering medium as observed in the power spectra of the scattered light.

The spectrometer used is similar to those already reported in the literature. The laser used was a Spectra Physics Model No. 124A He-Ne laser. The scattered light is accepted by the photomultiplier whose output is connected to a Tektronix 1155 spectrum analyzer. The spectrum analyzer output is averaged by an active integrating circuit. The time-averaged spectrum is then recorded and squared to obtain the power spectra of the scattered light.

The entire system has been checked by measuring the light scattered from a dilute suspension of polystyrene latex spheres and from carbon particles suspended in water containing a detergent additive. In both cases the power spectrum of the scattered light is a Lorentzian whose half-width corresponds to that predicted by theory and to the size of the scattering particles. In both cases the absorption of laser light by the solution was less...