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# ON THE CHARACTERIZATION OF SEMI-INSULATING GaAs BY HALL, PHOTO-HALL, PHOTOCONDUCTIVITY, AND PHOTOMAGNETOELECTRIC MEASUREMENTS*

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The electrical properties of semi-insulating Cr-doped GaAs are quite sensitive to monochromatic light irradiation, and thus photoelectronic data are of great value in elucidating the nature of this material. In this paper we present a theoretical basis for the determination of the photoconductivity, photo-Hall, and photomagnetoelectric effects, measure these effects in typical GaAs:Cr crystals, and show how the results lead to useful information about substrate quality.

Key words: semi-insulating GaAs, photo-Hall, photoconductivity, photomagnetoelectric.

## Introduction

The measurement of the electrical properties of semi-insulating GaAs is somewhat difficult for two reasons, (1) the high resistivities involved, and (2) the mixed nature of the conductivity. The first problem necessitates a carefully constructed apparatus, with leakage resistances not less than $10^{12}\Omega$. The second problem requires "extra" information, such as the magnetic field dependences of the Hall coefficient and resistivity, and this is best carried



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out with a magnet capable of producing 15 kG or more. On the other hand, these two "problems" of semi-insulating GaAs lead to easily measurable, and often highly spectral dependent, photoelectronic properties, such as the photoconductivity (PC), photo-Hall (PH), and photomagnetoelectric (PME) effects. In this paper we discuss the measurement and interpretation of each of these effects and how well some of them correlate with such things as the Cr content and the "layer conversion" propensity.

## Experimental Techniques and Relevant Formulae

The basic dc Hall-effect apparatus has been described earlier (1,2). The samples, mainly Cr-doped GaAs wafers, with typical dimensions of about 10mm x 5mm x 0.4mm, were carefully cleaned to avoid surface conduction. Soldered indium contacts proved to be sufficiently ohmic. Monochromatic light was provided by a high-intensity grating monochromator, with undesirable diffraction orders filtered out. The intensity was held constant at about 5 x $10^{14}$ photons/$cm^2$sec, from 0.56 to 1.8 eV.

We will illustrate the various techniques described in this paper by means of two representative samples, sample A, one of the most "n-type" of the GaAs:Cr samples that we have examined, and sample B, one of the more "p-type". Their respective "dark" characteristics are presented in Table I.

The conductivity, σ, and "apparent" Hall mobility, Rσ, are given, at B = 0, by the following well-known expressions, where all symbols have their usual meanings:

$$\sigma = e(p\mu_p + n\mu_n) \tag{1}$$

$$R\sigma = \frac{p\mu_p^2 - n\mu_n^2}{(p\mu_p + n\mu_n)} . \tag{2}$$

Table I. Dark electrical parameters of GaAs:Cr samples A and B.

| Sample | $\rho$ ($10^9 \Omega$-cm) | $-R_0\sigma_0$ ($10^3 cm^2$/Vsec) | $\mu_n$ ($10^3 cm^2$/Vsec) | n ($10^6 cm^{-3}$) | ($\epsilon_C - \epsilon_F$)(eV) |
|---|---|---|---|---|---|
| A | 0.355 | 2.58 | 3.28 | 4.44 | 0.645 |
| B | 1.18 | 1.84 | 4.65 | 0.549 | 0.699 |

It is clear that as $p\mu_p^2$ approaches $n\mu_n^2$, the "apparent" mobility approaches zero, and can even change sign. Such a phenomenon commonly occurs in the presence of monochromatic light of about 1.0 eV, especially at low temperatures. Whenever a sample is not strongly n-type or p-type, Eqs. 1 and 2 are insufficient to determine any of the relevant electrical parameters. It can be shown (1), however, that these parameters can be determined, in many cases, by a measurement of the magnetic field dependences of R and $\sigma$. Unfortunately, to get reasonable precision for typical GaAs:Cr samples it is necessary to have a range in B of 0 - 15 kG, or greater. This precludes the possibility of doing such measurements in many laboratories.

Irradiation with light can change the equilibrium values of n, p, $\mu_n$, and, to lesser extent, $\mu_p$. The "excess" conductivity, $\hat{\sigma} = \sigma - \sigma_o$, where $\sigma_o$ is the dark value, can be given for $\alpha d \gg 1$ (above-bandgap, or intrinsic irradiations), and $d/L \gg 1$, by (3,4)

$$\hat{\sigma} = \frac{eI_o\eta(\mu_n\tau_n + \mu_p\tau_p)}{d} \; \frac{1 + \alpha L_o}{1 + \alpha L} \tag{3}$$

where $I_o$ is the light intensity, $\eta$ the efficiency for the excitation of electron-hole pairs, $\tau_n$ ($\tau_p$) the electron (hole) lifetime, d the sample thickness in the direction of the light, and $\alpha$ the absorption constant. Also, $L = \sqrt{D_n^*\tau_n} = \sqrt{D_p^*\tau_p}$, where $D_n^* = (\sigma_p D_n + \sigma_n D_p \tau_p/\tau_n)/(\sigma_n + \sigma_p)$, $D_p^* = D_n^*\tau_n/\tau_p$, and $L_o = L/(1 + S_{on}\tau_n/L) = L/(1 + S_{op}\tau_p/L)$, where $S_{on}$ and $S_{op}$ are the front-surface recombination velocities for electrons and holes, respectively. If $\tau_n = \tau_p$, then the $D^*$'s are just the familiar ambipolar diffusion constants. The equations for the photoexcited carrier concentrations, $\hat{n}$ and $\hat{p}$, can be determined by comparing Eqs. 1 and 3. The theoretical photo-Hall mobility, in the light, will then be given by substituting $n = \hat{n} + n_o$, and $p = \hat{p} + p_o$, into Eq. 2.

Another useful quantity, which is easily measured with a standard Hall-effect apparatus, is the short-circuit photomagnetoelectric current, $I_{PME}$. Suppose the light propagation vector is in the y-direction, as shown in Fig. 1, and the magnetic field in the z-direction. The absorption of the light will set up carrier concentration gradients which will cause diffusion currents in the y-direction. (Note, however

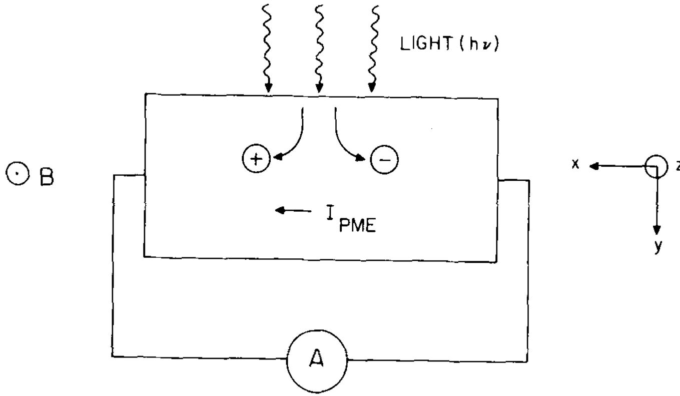


Fig. 1. The sample configuration for the measurement of the short-circuit PME current.

that the total current in this direction is zero.) The Lorentz force will then bend these diffusion currents in opposite directions, setting up a PME current in the x-direction. Again, for the intrinsic excitation case, with $\alpha d >> 1$, we can show that (3,4)

$$I_{PME} = eI_o wB\eta(\mu_n + \mu_p) \frac{\alpha L L_o}{1 + L} \qquad (4)$$

where w is the sample width, in the z-direction. Note that plots of $(I_{PME})^{-1}$ vs $\alpha^{-1}$ and $\delta/I_{PME}$ vs $\alpha^{-1}$, have x-axis intercepts of $-L$ and $-L_o$, respectively. Furthermore, a convenient means of measuring lifetime is given by the ratio $\delta/I_{PME}$:

$$\tau = \frac{(wd)^2 B^2 D^*}{[1 + (\alpha L_o)^{-1}]^2} \left(\frac{\delta}{I_{PME}}\right)^2 \qquad (5)$$

where we have assumed that $\tau_n = \tau_p \equiv \tau$ (i.e. no trapping), thus making $D_n^* = D_p^* \equiv D^* = (\sigma_p D_n + \sigma_n D_p)/(\sigma_n + \sigma_p) = 2D_n D_p/(D_n + D_p)$, since $n = p$, in this case. The individual diffusion coefficients, $D_n$ and $D_p$, can be related to the mobilities, in the Boltzman approximation, by the Einstein relationships: $D_n = kT\mu_n/e$, $D_p = kT\,\mu_p/e$. For well-above-bandgap light, often $\alpha L_o >> 1$, simplifying the determination of $\tau$. The correctness of the assumption $\tau_n \simeq \tau_p$, can be

ascertained if $\eta I_o$ is approximately known, by calculating $\tau$ from the individual equations, 3 and 4. We have generally found that $\tau_n \simeq \tau_p$ in the more "p-type" semi-insulating GaAs samples, but that this equality is sometimes violated in the more "n-type" samples. In principle, both $\tau_n$ and $\tau_p$ can be determined from Eqs. 3 and 4, if $\eta I_o$ is known.

We now consider extrinsic, or below-bandgap photoexcitation, for which, usually $\alpha L \ll 1$. The photoconductivity and PME current now become (3), for $d/L \gg 1$,

$$\hat{\sigma} = \frac{eI_o}{d} (1 - e^{-\alpha d})(\eta_n \mu_n \tau_n + \eta_p \mu_p \tau_p) \qquad (6)$$

$$I_{PME} = \frac{ewI_o B(\mu_n + \mu_p)\alpha(1-e^{-\alpha d})}{2} \times \left(\frac{\eta_n}{1 + S_n\tau_n/L} + \frac{\eta_p}{1 + S_p\tau_p/L}\right)\left(\frac{p\tau_n + n\tau_p}{n/D_p + p/D_n}\right) \qquad (7)$$

where $\eta_n$ and $\eta_p$ are the excitation efficiencies for electrons and holes, respectively, and where we have assumed the front- and back-surface recombination velocities are equal. The interesting thing to note here is that, for $\alpha d \ll 1$, $\hat{\sigma} \propto \alpha$, $I_{PME} \propto \alpha^2$. The stronger dependence of $I_{PME}$ upon $\alpha$ is due to the fact that $I_{PME}$ depends upon the gradients of n and p, which, in turn, depend upon the strength of the absorption, while the photoconductivity, on the other hand, depends only upon the totals of n and p.

## Data and Analysis

As mentioned earlier, the dark electrical characteristics of GaAs:Cr samples A and B are given in Table 1. Of the approximately 25 Cr-doped crystals that we have examined these two are fairly near the opposite ends of the ranges of $\rho$, n, and $\varepsilon_F$. Even so, both are within an order of magnitude of the theoretical maximum resistivity of GaAs ( $2.0 \times 10^9 \Omega$-cm for $\mu_n = 3000$, $\mu_p = 300$ cm$^2$/Vsec), and this is what makes Cr such a valuable dopant for substrate materials. Two other observations may be made from the data of Table I: (1) the "apparent" electron mobility, $-R_o\sigma_o$, is much different than the true electron mobility, $\mu_n$, especially for sample B; and (2) the Fermi levels cover a rather narrow range. (The quantities n, $\mu_n$, and $\varepsilon_F$ may be

determined from a mixed-conductivity analysis.) A rather simple model for the energy distribution of the Fermi levels, in the 25 samples, suggests a room temperature value for the Cr acceptor of 0.69 eV from the valence band (3). Other Cr levels may also, of course, exist.

The PC and PME data are presented in Fig. 2. A PC threshold appears at about 0.52 eV, a peak at 0.87 eV, and

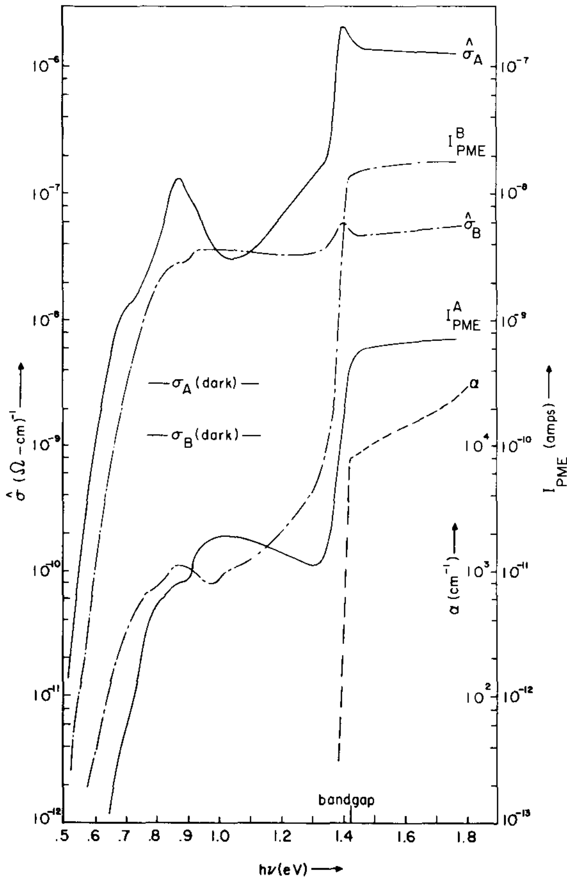


Fig. 2. The spectral dependences of the PC ($\hat{\sigma}$) and PME current ($I_{PME}$) for GaAs:Cr samples A and B. The light intensity was held constant. Also shown is the absorption constant (α) for "pure" GaAs, as taken from Ref. 5.

another threshold at 0.90 eV. A mixed-conductivity analysis shows that the peak at 0.87 eV is due to electron excitation, and the threshold at 0.90 eV is due to hole excitation. We attribute these phenomena to Cr because, as far as we know, they are found only in Cr-doped crystals. It is quite possible that the 0.52 eV threshold is simply due to electron excitation from the 0.90 eV level. (Note that 0.90 + 0.52 = 1.42 eV, the room-temperature bandgap.) The peak at 0.87 eV has a resonance shape, as seen in the spectrum for sample A, and is likely due to an internal Cr transition, for which the upper level is in resonance with the conduction band.

There is no clear indication, in the PC spectra, of the previously discussed level at 0.69 eV from the valence band, although the rise in $\hat{\sigma}_A$, just before the 0.87 eV peak, may be due to this. Another threshold, at 0.56 eV, may be present in the PC data, but this is uncertain.

The PME data complement the PC data in that they are more sensitive to minority carrier excitation. Thus, for example, $I^A_{PME}$ shows a sharp threshold at 0.90 eV, which is consistent with our interpretation of this as a hole excitation, since sample A is quite "n-type". Only a shoulder appears at this energy in $\hat{\sigma}_A$. Similarly, the PME spectrum in sample B, a "p-type" sample, clearly indicates a known electron excitation at about 1.0 eV, whereas the sample A PME spectrum does not show this.

As mentioned before, $I_{PME}$ is quite sensitive to $\alpha$, if $\alpha L \ll 1$, and this is clearly seen for near-bandgap photoexcitation by comparing the PME spectra with the $\alpha$ spectrum for "pure" GaAs, which was obtained from Ref. 5. Above the bandgap, evidently $\alpha L \gg 1$, because both $\hat{\sigma}$ and $I_{PME}$ are nearly constant, at least compared to $\alpha$. For sample B, a lifetime of $6 \times 10^{-9}$ sec. is calculated from Eq. 5, under the assumption that $\alpha L_o \gg 1$, and this is consistent with the values calculated from both Eqs. 3 and 4, by using the estimated $I_o$. For sample A, however, no such consistency exists, probably because $\tau_n \neq \tau_p$. The use of Eq. 3 alone gives a value $\tau_{nA} \simeq 2 \times 10^{-7}$ sec, calculated by assuming that $\mu_n\tau_n \gg \mu_p\tau_p$. For the extrinsic region, rough values of $\alpha$ can be calculated from Eq. 7 by making reasonable approximations for the unmeasured quantities. For example, at 1.0 eV we find $\alpha_A \simeq 5$ cm$^{-1}$ and $\alpha_B \simeq 9$cm$^{-1}$. Literature

values, at this energy, range from 2-12 $cm^{-1}$.

The PH data are shown in Fig. 3 along with $\mu_n$ data. The dark Hall coefficients are negative so that a decrease in $-R_o\sigma_o$ indicates a more p-type sample. For sample A the PH spectrum is quite flat, because electrons continue to dominate. For sample B, however, the effects are quite

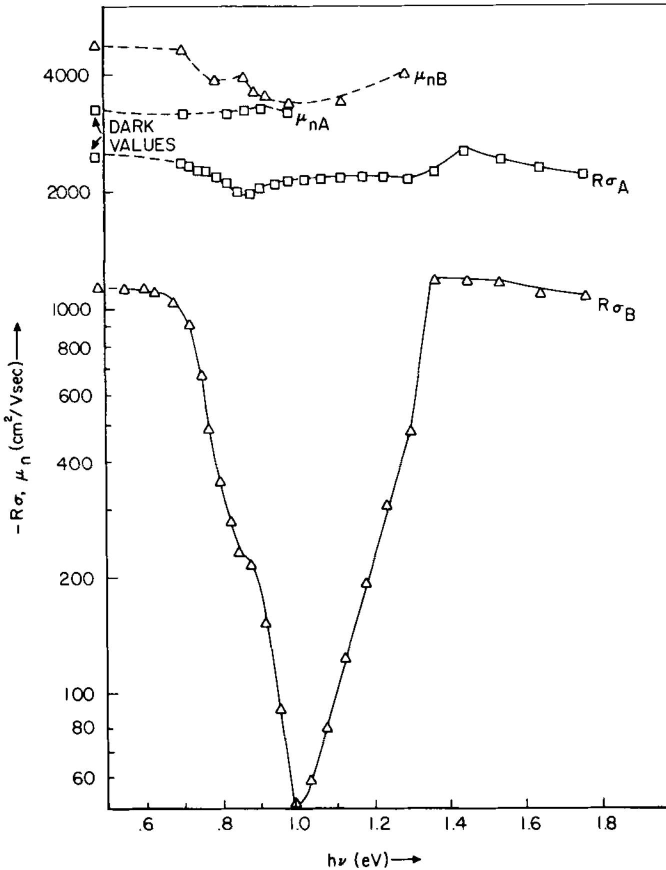


Fig. 3. The spectral dependences of the "apparent" mobility ($R\sigma$) and the actual electron mobility ($\mu_n$) for GaAs:Cr samples A and B. The light intensity was held constant. Also shown are the dark values of $R\sigma$ and $\mu_n$.

dramatic. According to Eq. 2, a decrease in $-R\sigma$ can be due to a decrease in n/p or a decrease in $\mu_n/\mu_p$. Usually the former is assumed, but as the $\mu_n$ data show, the latter is also quite important in sample B. The decrease in $-R\sigma_B$ at 0.7 eV is likely due to hole excitation from the 0.69 eV acceptor, which diminishes $\mu_{nB}$, as expected, and the decrease in $-R\sigma_B$ at 0.9 eV is similarly due to hole excitation from the 0.90 eV acceptor. Above 1.0 eV strong electron excitation begins to dominate.

Thus, the room-temperature energy diagram, which emerges from the above data, has Cr acceptor levels at 0.52 and 0.73 eV from the conduction band, and an excited state, associated with the 0.73 eV level, in resonance with the conduction band. It may also be noted that a room-temperature deep-donor level, ascribed to oxygen, has been seen at about 0.65 eV from the conduction band (6).

## Discussion

Certain of the measured electrical parameters have practical significance. For example, a plot of $\rho_o$ vs $N_{Cr}$, the Cr concentration as determined by spark-source mass spectroscopy (SSMS) (7), has a maximum at $N_{Cr} \simeq 1 \times 10^{17} cm^{-3} \simeq 2$ ppmA. This $\rho_{max}$ is near the theoretical maximum of about $2 \times 10^9 \Omega$-cm. Such information should be useful to the manufacturers. Another relationship of interest is between $R_o\sigma_o$ (dark) and $N_{Cr}$, as shown in Fig. 4. This indicates that adding more Cr makes the crystals more p-type, as would be expected. The large scatter in the data is due to the uncertainty in the SSMS results, which are accurate only to within about a factor three. The line drawn through the points has no theoretical significance and should not be considered as a "universal" curve to determine $N_{Cr}$ from $R_o\sigma_o$. Each letter in Fig. 4 denotes a particular manufacturer.

An often-applied measure of substrate quality is the layer-conversion propensity (LCP), which relates to the formation of a thin, conducting layer under high-temperature annealing conditions(8), such as those experienced in ion-implantation or VPE sample preparation. Preliminary data indicate correlations between the sheet resistance after anneal, i.e., the measure of the LCP, and (1) the sheet resistance before anneal, (2) $N_{Cr}$ (3) $R_o\sigma_o$ (dark), and

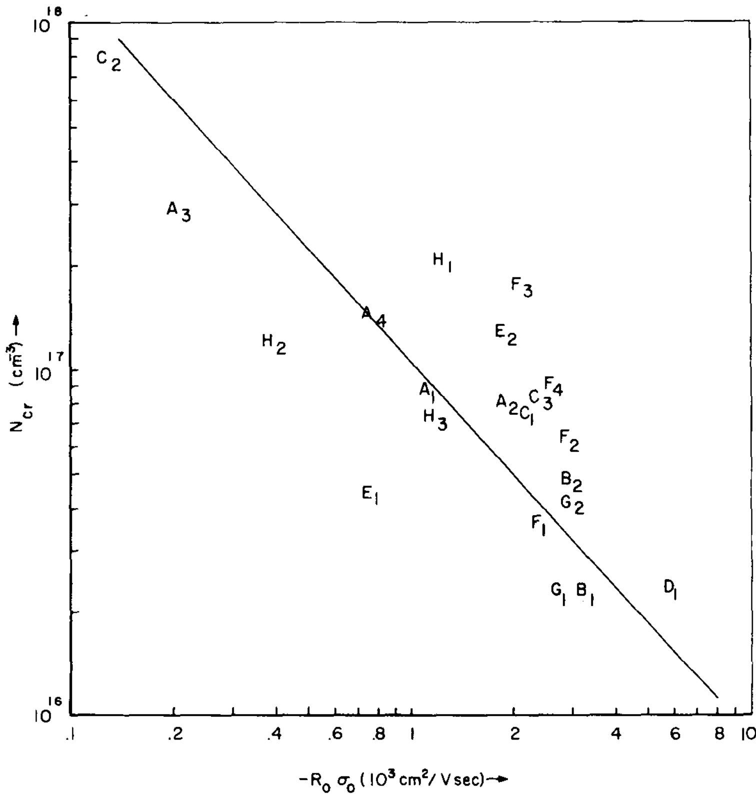


Fig. 4. The relationship between the Cr concentration, as measured by spark-source mass spectroscopy, and the "apparent" Hall mobility in the dark. The solid line is simply a least-squares fit to the points and has no theoretical significance. Each letter denotes a particular manufacturer.

(4) the PC at 0.7 eV. Other correlations may exist, also, but confirmation must await further studies, including the standardization of capping procedures, to eliminate that as a source of variation.

In summary, it appears that certain easily measurable parameters, such as the photoconductivity and photo-Hall mobility, may be useful as indicators of GaAs substrate

quality. Further research needs to be carried out, and we have attempted to include in this paper the relevant theoretical basis to aid in such research.

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