the data of Table IV and the result of Mohyuddin and Douglas.

The data presented here indicate that the second, high-temperature peak in binary sodium silicate glasses is due to the stress-induced relaxation of singly bonded oxygen ions. The results are not unequivocal, however. As they stand, they do not rule out the possibility of cooperative sodium ion motion in which two or more sodium ions move together. Since dielectric relaxation measurements in binary alkali silicates show no evidence of any maxima except that which is clearly attributed to sodium ions,[16–18] the centres causing the mechanical relaxation must be unpolarized. It is improbable that two sodium ions would always move in such a fashion as to remain unpolarized.

At the temperatures where the second peaks appear, the sodium ions in these glasses are relatively mobile. It is probable that their presence should be taken into account here. It is not clear, however, how these should be inserted into the model. Further work, both experimental and theoretical, is needed on this problem.

6. SUMMARY

In summary, the high-temperature peak in binary sodium silicate glasses is apparently due to stress-induced, nonbridging oxygen ion diffusion. The evidence indicates that free, unoccupied sites are thermally generated in these glasses above 250°C. Below this temperature, $\sim 10^{12}$ free sites/cm^{13} are frozen into the structure.

ACKNOWLEDGMENT

The author gratefully acknowledges the aid and encouragement he has received from Dr. R. H. Redwine while preparing this paper.

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Use of the Faraday Effect to Determine Electron Concentrations and Concentration Profiles in n-GaAs

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The use of the Faraday rotation for determining the electron concentration and the electron concentration profile in n-GaAs with $n=10^{15}$ to 10^{18} cm^{-3} has been investigated. It is shown that correction can be made for the errors in the measurement introduced by multiple reflections and that accurate subtraction of the interband contribution to the total rotation will yield a well-defined value of the free-carrier contribution.

1. INTRODUCTION

The Faraday effect is the rotation of the plane of polarization of a light beam on passing through a material due to a magnetic field applied parallel to the propagation direction of the light. The angle of rotation, θ, is proportional to both the magnetic field strength B and the optical path length d, i.e.,

$$\theta = VBd, \tag{1}$$

where V, the Verdet constant, is the characteristic rotation of the material per unit field strength and per unit length.

The theory of the Faraday effect in semiconductors has been treated by various authors[1–3] in terms of two additive contributions. One of these, usually called the interband Faraday effect, arises from the differences in probability for the various virtual transitions of valence electrons from the Zeeman split Landau levels of the valence band to those of the conduction band. This effect causes a difference in the dispersion of the refractive index for the two senses of circular polarization which results in a Faraday rotation. The effect is large for wavelengths corresponding to the bandgap energy and decreases as the wavelength increases. The other contribution to the Faraday rotation is associated with the dielectric dispersion due to the free carriers and arises from the virtual transitions of conduction electrons to the Zeeman split Landau levels of the conduction band. Under the condition that the frequency of the radiation is large compared to the cyclotron resonance and collision frequencies, as is normally the case in the ir region of the spectrum, the Verdet constant for this free-carrier Faraday rotation is given, in mks units,[1] by

$$V_{\mathrm{FC}} = N\lambda^2/m^{*2}n\cdot e^3/8\pi^2c^3\epsilon_0, \tag{2}$$

where λ is the wavelength; N, the free-carrier concentration; m^*, the effective mass; n, the refractive index; and e, the electronic charge.

In n-type GaAs, the interband and free-carrier rotations are of the same sign. Thus the observed total rotation is found to be large at wavelengths near the bandgap, to decrease to a minimum, and then again to in-

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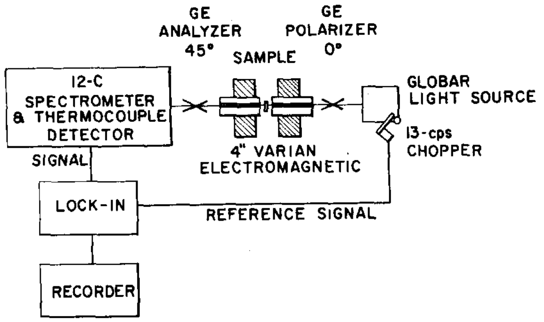

FIG. 1. Faraday rotation apparatus.

crease as the wavelength increases. At sufficiently long wavelengths, this latter increase is found to be proportional to λ^2. In this region, the interband effect is evidently negligible and the total rotation is that given by Eq. (2). Various authors[4–6] have used the magnitude of the rotation in this range to determine the effective electron mass in GaAs. It is the purpose of this paper to describe the effectiveness with which Faraday rotation measurements may be combined with established values of effective mass to yield reliable determinations of carrier concentration. The small effective mass of electrons in GaAs make the method particularly applicable to *n*-type GaAs because it results in a strong dependence of the free-carrier Faraday rotation on the electron concentration.

The results show that Faraday effect measurements can give equivalent information to Hall measurements over a wide range of electron concentrations. They are in many respects simpler to make in that they require no electrical contacts and make no special demands on sample geometry which may interfere with subsequent use of the specimen for other purposes. The results also demonstrate the use of the method to determine the electron density in a localized region and thus to obtain a profile of the variation of electron density with position within a specimen.

2. EXPERIMENTAL METHODS

The apparatus used in the determination of the Faraday rotation is shown schematically in Fig. 1. Radiation from a globar source is chopped at 13 Hz and passed through a Brewster-angle germanium plate polarizer. The resulting polarized beam passes through the sample by way of axial holes in the pole pieces of an electromagnet between which the sample is located. It then passes through a second germanium polarizer, oriented at 45° to the first, into a 12-C Perkin–Elmer beam spectrometer with a thermocouple detector. A lock-in detector detects the thermocouple output synchronous with the light chopper and drives a recorder. The Faraday effect at a given magnetic field strength is measured by recording the relative intensities of the light reaching the detector for the two directions of magnetic field, i.e., for the two senses of Faraday rotation. If I_+ is the larger intensity and I_- the smaller, the magnitude of the Faraday rotation, θ, is given by

$$\sin 2\theta = (I_+ - I_-)/(I_+ + I_-). \quad (3)$$

DeMeis[7] has analyzed the effect of imperfect polarizers on Faraday rotation measurements of this kind. His result corresponds to multiplication of the right-hand side of Eq. (3) by the factor $(1+f)/(1-f)$, where f is the ratio of the transmitted light intensity with the polarizers crossed to that with polarizers parallel. For our polarizers, f was in the range 0.01 to 0.02. No correction was made to our measurements for this effect. The sensitivity of the method depends on the ratio of the minimum detectable difference between I_+ and I_- to their sum. Since the sum is proportional to the total intensity of the radiation, the sensitivity may be, in general, increased by increasing the incident intensity. The experiments were carried out at wavelengths of from 2 to 10 μ. It is estimated that the source-monochromator arrangement provided intensities of the order of a few microwatts. Under these conditions, rotations of about 0.1° could readily be detected. The samples were for the most part in the form of wafers about 1 mm thick with optically polished faces. The electromagnet provided fields strengths up to about 13 kG, making possible determination of Verdet constants of slightly less than 0.1°/kG·cm.

3. EXPERIMENTAL RESULTS

Five samples were studied in detail. These are samples 1 to 5 listed in Table I with their carrier con-

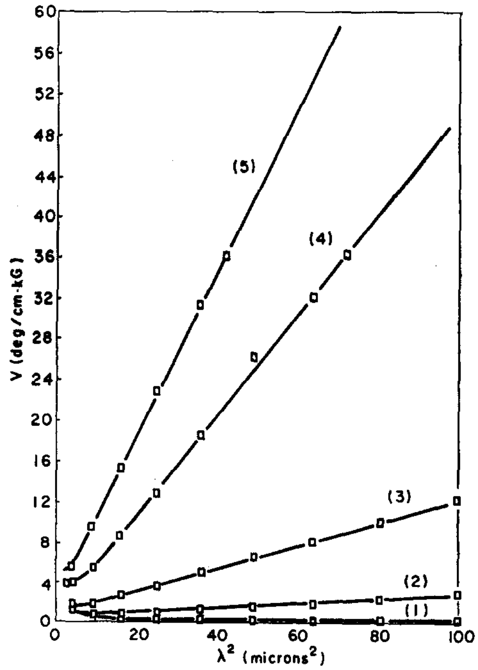

FIG. 2. Verdet constant in *n*-GaAs samples 1 to 5 as a function of the square of the wavelength.

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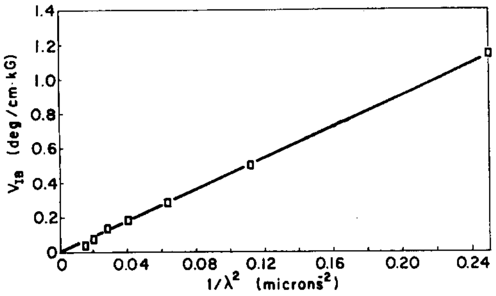

FIG. 3. Verdet constant in semi-insulating GaAs as function of reciprocal of the square of the wavelength.

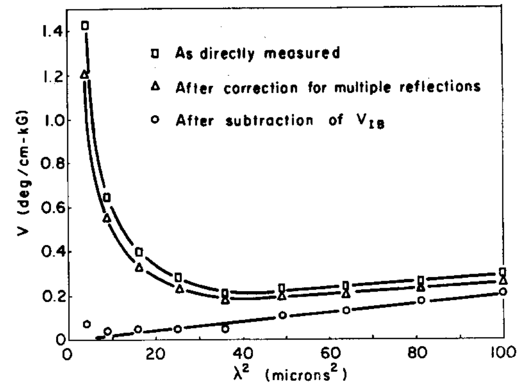

FIG. 4. Verdet constant in n-GaAs sample 1 as function of the square of the wavelength. □ directly measured; △ after correction for multiple reflections; ○ after subtraction of V_{IB}.

centrations as determined by Hall measurements on adjacent pieces. Also listed are the thicknesses of the specimens used for the Faraday effect measurements and the magnetic field strength used. The Verdet constants measured for these samples are plotted against the square of the wavelength in Fig. 2. The strong dependence of the rotation on carrier concentration is shown by the differences among these samples and is indicative of the sensitivity of the method in determining electron densities. The linear dependence of the Verdet constant λ^2 for samples of carrier concentration above 10^{17} cm^{-3} is apparent. This corresponds to the dependence predicted by Eq. (2) and indicates that here the interband rotation is negligible compared to the free-carrier rotation. The interband effect shows up in these samples as a departure from linearity at the shortest wavelengths. On the samples of lower carrier concentration, the interband effect is of greater relative significance, and more detailed analysis is required to isolate the free-carrier rotation.

Another deviation from the behavior predicted by Eq. (2) apparent in these curves is the failure of the straight-line portions to extrapolate to zero rotation at zero wavelength. It appears that the correct explanation of this effect is that given by DeMeis[7] and Piller[8] who ascribe it to the occurrence of multiple reflections in samples with plane parallel faces. The result is to yield an apparent rotation angle θ_m, different from the true value θ which would be obtained in the absence of reflections. Piller has derived the relation between θ_m and θ for the type of measurement made here using incoherent light, i.e., ignoring interference effects, as

$$\sin 2\theta_m = \sin 2\theta / (1 - 2R^2 e^{-2\alpha d} \cos 4\theta). \qquad (4)$$

Here R is the reflectivity and α the absorption coefficient of the material; the relation is valid when $R^4 e^{-4\alpha d} \ll 1$. Since R is approximately constant at 0.28 for GaAs in the ranges of wavelength and carrier concentration used here, this condition is satisfied in our experiments.

TABLE I. Samples and conditions used in Faraday effect measurements.

Sample No.	N (Hall effect)[a] (cm^{-3})	Sample length (mm)	Measuring field kG
1	2.4×10^{15}	1.055	12.50
2	1.8–4.2×10^{16}	1.205	12.70
3	1.5×10^{17}	0.897	13.30
4	6.5×10^{17}	0.536	9.80
5	1.3×10^{18}	0.560	8.65
6	1.2×10^{17}	0.870	8.7

[a] Measured by J. Black and S. Perkowitz.

Use of data such as that of Fig. 2 for quantitative determination of carrier densities depends on the ability to deduce accurately the free-carrier contribution to the measured rotation. To obtain this, the measured rotation angles were first corrected for the effect of multiple reflections using relation (4). Absorption coefficients for the wavelengths and carrier densities involved were estimated from the data of Spitzer and Whelan.[9] This procedure is not entirely rigorous since the absorption coefficient is not fully determined by N. However, assuming no very wide discrepancies in mobility, it should provide a reasonable value. Verdet constants derived from the corrected rotation angles were then assumed to be the sum of the free-carrier contribution V_{FC} and the interband contribution V_{IB}. V_{IB} was determined by direct measurement of a sample of semi-insulating GaAs, where the effect due to

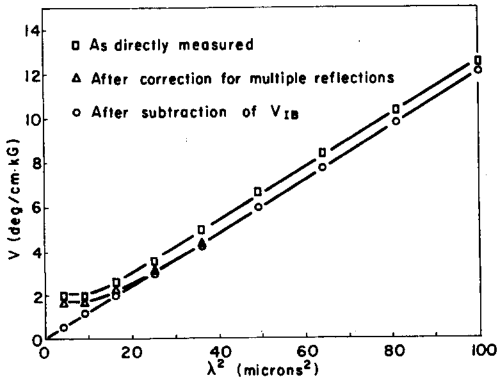

FIG. 5. Verdet constant in n-GaAs sample 3 as function of the square of the □ directly measured; △ after correction for multiple reflection; ○ after subtraction of V_{IB}.

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[8] H. Piller, J. Appl. Phys. **37**, 763 (1966).

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TABLE II. Comparison of carrier densities as determined by Faraday effect and Hall effect.

Sample No.	N(Faraday) (cm^{-3})	N(Hall) (cm^{-3})	m^*/m
1	2.3×10^{15}	2.4×10^{15}	0.072
2	3.0×10^{16}	$1.8\text{–}4.2\times10^{16}$	0.072
3	1.4×10^{17}	1.5×10^{17}	0.072
4	5.9×10^{17}	6.5×10^{17}	0.073
5	1.1×10^{18}	1.3×10^{18}	0.075

free carriers could be assumed negligible. The use of a sample about 7 mm thick with nonparallel sides gave an accurate measure of the Verdet constant free of the effects of multiple reflections. The results of this measurement are plotted against $1/\lambda^2$ in Fig. 3. The linear relation found in the range of 2 to 8 μ is in agreement with theoretical expectations for wavelengths long compared to that of the bandgap energy[2] and makes the extrapolation to longer wavelengths straightforward.

The apparent Verdet constants as measured, those resulting from the correction for multiple reflections, and the contribution remaining after subtraction of V_{IB} are plotted in Figs. 4 and 5 for two of the samples of Fig. 2. The corrections leave a straight line of zero intercept. This result is strong confirmation of the accuracy of the correction procedures and of the fact that the remaining rotation may be ascribed to the free carriers and represents V_{FC}. No significant effects of electron concentration[10] on the magnitude of the interband contribution were observed in the 2 to 10 μ region measured up to the largest electron concentrations used. The slope of this line permits calculation of the carrier density from Eq. (2). Such calculations were made for all the samples measured, using the effective masses given by Piller[11] and taking the refractive index as 3.3. The results obtained are given in Table II together with carrier densities resulting from measurement of the Hall effect. Also listed are the effective masses used in the calculation. Where a range is shown for the Hall concentration, it indicates the variation obtained from Hall measurements on different specimens.

The agreement between the Faraday- and Hall-effect measurements is entirely satisfactory, particularly in view of the fact that the measurements were not on the same specimens. This agreement, together with the internal consistency achieved in separating the free-carrier contributions (as illustrated in Figs. 4 and 5) from the raw data, shows that the Faraday effect can be successfully used as a valid means of measuring electron concentrations in n-type GaAs.

The routine use of the Faraday effect in this way does not require the extensive measurement of rotation at a variety of wavelengths as was done in the present work. Establishment of V_{FC} at any one wavelength is sufficient to determine the carrier density. It is, in fact, possible to reverse the correction procedures of the preceding paragraphs to yield a direct calibration between the apparent Verdet constant (calculated from θ_m) and the carrier density at any given wavelength. This procedure is illustrated in Fig. 6 for wavelengths of 5 and 10 μ. The solid curves represent the dependence of V_{FC} on N, the nonlinearity arising from the increase of effective mass at large electron densities.[11] The dashed curves give the sum of V_{FC} and of the V_{IB} appropriate for the particular wavelength. As can be seen, V_{IB} is negligible at sufficiently large carrier densities and becomes dominant at sufficiently low carrier densities at each wavelength. These curves represent the direct result of measurement under conditions where no correction for multiple reflections is required. The dotted curves represent the results of measurements in which the error due to multiple reflections is a maximum. This occurs for samples with parallel faces when the quantity $e^{-2\alpha d}\cos 4\theta$ in Eq. (4) is approximately unity. This causes the apparent rotation angle θ_m and hence the apparent Verdet constant V_m to be about 19% larger than the correct value. An appreciable error of the opposite sign cannot occur for practical values of magnetic filed strength because sufficiently large values of θ to change the sign of $\cos 4\theta$ arise only from carrier densities and sample lengths which make the exponential factor very small. Thus, without correcting for multiple reflections, experimental values of rotation should give Verdet constants falling between the dashed and dotted curves and under most circumstances will define N to about ±10%.

For greater precision, it may be noted that for fixed d and B, both θ and α become small at small N, giving results near the dotted curve. Both quantities increase with N so that, at sufficiently large N, results will correspond to the dashed curves which merge with the solid curves. The vertical arrows in Fig. 6 indicate the approximate range over which the transition from the dotted to dashed curve takes place under the conditions of the present work, i.e., d of the order of 1 mm and B of approximately 10 kG.

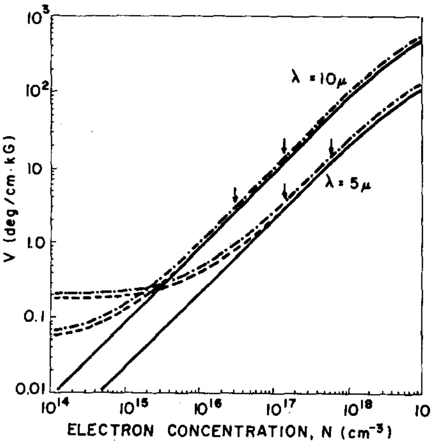

FIG. 6. Verdet constant as function of carrier density. Solid curve: V_{FC}; dash curves: $V_{FC}+V_{IB}$; and dotted curve: apparent $(V_{FC}+V_{IB})$ with maximum error due to multiple reflections. $\lambda=5\mu$ and 10μ.

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[10] B. L. Mitchell, E. D. Palik, and R. F. Wallis, Phys. Rev. Letters **14**, 827 (1966).

[11] H. Piller, J. Phys. Soc. Japan, Suppl. **21**, 206 (1966).

It may also be noted that the effect of multiple reflections may be eliminated by using wedge-shaped samples[7] as was done on the semi-insulating specimen in the present work. This, however, introduces a requirement on geometry which is often not compatible with the planned further experimental use of the specimen. In addition, on thin samples, it leads to an indeterminacy in d which may produce as serious an error. Calculation of the correction factor in specific instances is always possible, either from estimates of absorption coefficient as discussed earlier, or from a measured value on the specimen itself at the wavelength used.

5. RANGE OF APPLICABILITY OF FARADAY-EFFECT MEASUREMENTS

In the preceding section it is shown that Faraday-effect measurements may be readily used to determine electron concentrations in n-type GaAs over the range from about 2.3×10^{15} to 1.3×10^{18} cm^{-3}. In this section, consideration is given to the factors which ultimately limit the range of electron densities which may be measured by this method. At concentrations higher than those used here, there appears little problem because of the extremely large free-carrier rotations. The large absorptions at the longer wavelengths of such heavily doped materials preclude the use of even 10 μ for concentrations of the order of 10^{18} cm^{-3}. However, 5 μ is a useful wavelength for values in excess of this, and even shorter wavelengths could be used for larger concentrations if necessary.

The limitations at low carrier densities are more fundamental. There is first the interference of the interband Faraday effect. As the curves of Fig. 6 show, at any given wavelength, the total Verdet constant decreases with decreasing carrier concentration until it reaches the value corresponding to the interband effect at that wavelength. It then becomes insensitive to variations in carrier concentration. A rough measure of the lowest carrier concentration which can be determined at a given wavelength may be taken to be that at which the interband and free-carrier effects are equal. Reference to Fig. 6 shows that at 5 μ this occurs at about 8×10^{15} cm^{-3}, while at 10 μ it occurs at about 5×10^{14} cm^{-3}. The materials requirements for certain microwave applications of GaAs indicate a need to determine smaller carrier concentrations than this, but since the dependence of this crossover concentration on wavelength may be expected to go as λ^{-4}, this seems to pose no fundamental problem. Thus, with appropriate polarizers, measurements to at least 20 μ should be feasible, which would place this lower limit at about 3×10^{13} cm^{-3}. The ultimate limitation on wavelength is placed by the absorption associated with the fundamental lattice band centered at 36 μ.

A second difficulty associated with low electron densities is the small rotations obtained and the consequent requirement of highly sensitive techniques for accurate measurements. The method of measurement of intensity differences used in this work is both sensitive and convenient. As indicated earlier, for the sample dimensions and magnetic fields used, it provided ready measurement of Verdet constants to about 0.1°/kG·cm, corresponding, at 10 μ, to a carrier concentration of about 10^{15} cm^{-3}. If it is assumed that the present thickness of about 1 mm is one that is in general convenient and that magnetic fields substantially larger than those used here are not likely to be available, this limit may be reduced by an increase in wavelength or in the sensitivity of the measurement. Since the free-carrier rotation varies with the square of the wavelength, measurement at 20 μ with the same sensitivity as that achieved here would lower the limiting measurable concentration to below 3×10^{14} cm^{-3}. As pointed out earlier in connection with Eq. (3), the sensitivity of the present method should increase directly with increased intensity of the incident radiation. A factor of 3 or 4 in intensity at 10 μ should make possible measurements there to the limit of 5×10^{14} imposed by the interband effect. The use of lasers as sources (for example, the CO_2 emission at 10.6 μ or the H_2O emissions at 23 to 28 μ) would appear to be useful. However, the possible consequences of interference effects on multiple reflection of the coherent laser beam remain to be explored.

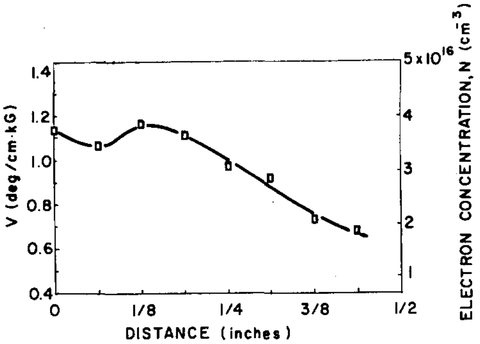

FIG. 7. Electron concentration profile in n-GaAs sample 2 vs distance across the sample.

6. DETERMINATION OF LOCALIZED CARRIER DENSITIES

In the preceding sections, the usefulness of the Faraday effect as a means of determining electron density in n-type GaAs has been described. The values which result represent an appropriate average over the volume of the crystal through which the beam passes. It is clear that by restricting the beam diameter so that it passes through only a limited region of the sample, determination can be made of the electron density in a correspondingly localized volume. Measurement at a series of points obtained by translation of the specimen in the beam will then give a profile of the variation of carrier density across the specimen. The possibility of obtaining such a profile in a simple and nondestructive manner is of great importance in view of the frequently encountered uncertainties as to the uniformity of doping

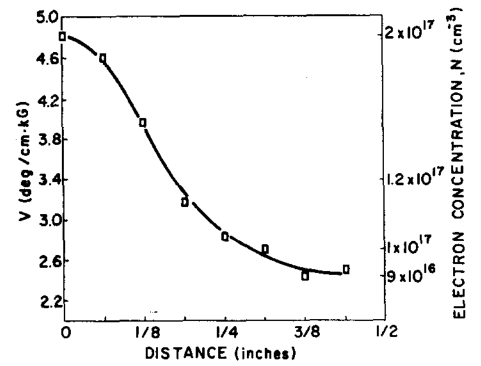

FIG. 8. Electron concentration profile in n-GaAs sample 6 vs distance across the sample.

across a slice cut from a single crystal ingot. It makes possible immediate rejection of material where the variations are intolerably large or the definition of specific regions where the carrier concentration falls within acceptable limits for application, for example, in a specific device.

In order to demonstrate the capability of obtaining a profile of carrier concentration vs position in a specimen of GaAs, measurements of the Faraday effect were made on the same apparatus as described earlier except that a shield with a restricted opening was placed between the sample and the analyzer so that the measurement reflected the properties of only the part of the sample directly in front of this opening. Because of limitations on the ir optics available and on the intensity of the beam the opening in the shield was $\frac{1}{8}$ in. in diameter. The wavelength used was 5 μ. The sample was mounted on a stage and translated laterally across the beam and measurements made at increments of $\frac{1}{16}$ in.

The results of this measurement are shown in Figs. 7 and 8 for samples 2 and 6. In each case the abscissa gives the distance along the sample. The ordinate is labeled on the left with the directly measured Verdet constant and on the right with the carrier concentration as read from the appropriate curve in Fig. 6. In each sample the variation of electron density with position is plainly seen. The range for sample 2 is from 1.9 to 3.9×10^{16} cm^{-3}, while that for sample 6 is from 0.9 to 2.0×10^{17} cm^{-3}. Two Hall measurements on a specimen adjacent to sample 2 gave carrier densities of 1.8 and 4.2×10^{16} cm^{-3} in remarkable and no doubt somewhat fortuitous agreement with the results of the Faraday measurement. The Hall data on the material of sample 6 yielded a carrier concentration of 1.2×10^{17} cm^{-3}, which is not far from the average value indicated by the Faraday measurement.

The resolution of the measurements reported here is quite limited owing to the relatively large beam diameter. They serve to illustrate, however, the ease with which the technique can be adapted to yield a quantitative profile of carrier-density variations. Increased resolution could readily be obtained with increased intensity and better focusing techniques. In this mode of application, the use of a laser source, suggested earlier in this paper, appears highly promising.

7. SUMMARY

The use of the Faraday effect as means of determining electron concentrations in n-type GaAs has been investigated. It has been shown that precise correction can be made for the errors in the measurement introduced by multiple reflections and that accurate subtraction of the interband contribution to the total rotation can be made to yield a well-defined value of the free-carrier contribution. Interpretation of this value by conventional theory using established values of effective mass has been shown to give reliable measurement of electron concentration. Calibration of the measured rotation as a function of carrier density, including the interband contribution and possible effects of multiple reflection, has been carried out. Measurements of electron densities above 10^{18} cm^{-3} indicate no particular upper limit to the range of applicability. Measurement down to approximately 10^{15} cm^{-3} has been demonstrated, and the conditions are indicated which should make possible measurement of densities at least an order of magnitude lower than this. The use of a small diameter beam to measure local electron densities has been demonstrated and also the application of this technique of localized measurement to obtain a profile of the variation of electron density with position across a sample.

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