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A contactless method for determining the spatial variation of the free carrier density in CdS is presented. The method involves the correlation of IR transmission with the free carrier density via the IR absorption coefficient. Preliminary measurements indicate a free electron density sensitivity of less than 5×10^{14} cm^{-3} and a spatial resolution which is limited only by the spot size of a CO_2 ($\lambda = 10.6 \mu$m) laser; this should be of the order of 100 μm. Experimental results indicate that the predominate scattering is due to impurity interaction at room temperature; this is indicative of the high degree of compensation in CdS.

INTRODUCTION

A contactless method for determining the spatial variation of the carrier concentration in semiconductor materials is of interest to permit the evaluation of the optical and electrical uniformity of CdS (as well as other semiconductors). Infrared absorption by free carriers has been demonstrated in semiconductors.[1] Fan et al.[1,2] developed the theory for infrared absorption by free carriers taking into account lattice and impurity scattering. Of most significance to this effort is the work performed by Jastrzebski, Lagowski, and Gatos[3] which involved the use of a scanning CO$_2$ laser to obtain spatial resolution of the impurity concentrations in silicon. Free electron absorption in CdS occurs in a range of wavelengths from 8 to 12 μm. Within this range of values either coherent or noncoherent radiation may be employed; both have been investigated.

THEORETICAL DISCUSSION

Consider electromagnetic radiation normally incident upon a lossy dielectric slab as shown in Fig. 1.

For monochromatic radiation it has been shown[4] that the transmission coefficient is given by

$$T = \frac{[(1 - R_{12})^2 + 4R_{12} \sin^2 \sigma_{12}] \exp(-\alpha d)}{[1 - R_{12} \exp(-\alpha d)]^2 + 4R_{12} \sin^2(\delta_{12} + K_2 d)\exp(-\alpha d)}, \tag{1}$$

where

$$R_{12} = \frac{(K_1 - K_2)^2 + (\alpha/2)^2}{(K_1 + K_2)^2 + (\alpha/2)^2}$$

and

$$\delta_{12} = \tan^{-1}\left(\frac{-K_1 \alpha}{K_1^2 - K_2^2 + (\alpha/2)^2}\right).$$

α is the absorption coefficient which is related to the complex conductivity (σ') by the expression

$$\alpha = \sigma' \sqrt{\mu/\epsilon}.$$

K_2 and K_1 are the propagation constants for the semiconductor and free space, respectively, given by

$$K_2 = \omega\sqrt{\mu_0 \epsilon_0 \epsilon_r}$$

and

$$K_1 = \omega\sqrt{\mu_0 \epsilon_0}.$$

The reflection coefficient is given by

$$R = \frac{R_{12}\{[1 - \exp(-\alpha d)]^2 + 4 \exp(-\alpha d) \sin^2 K_2 d\}}{[1 - R_{12} \exp(-\alpha d)]^2 + 4R_{12} \exp(-\alpha d) \sin^2 (\delta_{12} + K_2 d)}. \tag{2}$$
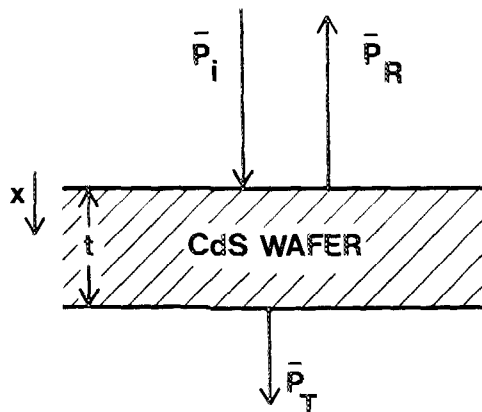
FIG. 1. A plane wave normally incident (P_i) upon a lossy dielectric slab. $P_t = TP_i$ is the transmitted wave and $P_R = RP_i$ is the reflected wave.

For the incoherent case, Eqs. (1) and (2) reduce to

$$T = \frac{(1 - R_{12})^2 \exp(-\alpha d)}{1 - R_{12}^2 \exp(-2\alpha d)}$$ (3)

and

$$R = R_{12}\left(\frac{1 + e^{-2\alpha d}}{1 + R_{12}^2 e^{-2\alpha d}}\right).$$ (4)

Whether the incident radiation is coherent or incoherent, the important link to be made is between the absorption coefficient and the free carrier density which provides a relative measurement of the impurity spatial variations.

The absorption coefficient α is a measure of the IR attenuation due to the free electron interactions with incident photons. The photon absorption by the free electrons is a two-step process which includes electron-phonon interac-

tions as a necessity for conservation of momentum. Lattice vibrations, impurities, and lattice defects (acting as scattering centers for the free electrons) give rise to absorption. These intravalley transitions represent small energy variations so that second-order perturbation theory[5-8] can be used to determine the transition probability for each of the scattering processes. For semiconductors, there are five scattering mechanisms which may be significant depending upon the crystal structure, defects and impurity concentrations. These mechanisms are acoustic phonon, optical phonon, polar optical phonon, piezoelectric, and charged impurity scattering. The absorption coefficients for these various mechanisms have been theoretically developed by a number of different investigators; Ridley[6] presents this information in a form that makes it easy to compare the various coefficients and to determine their wavelength and temperature dependence.

At room temperature, a calculation of the ratios of the absorption coefficients in CdS indicates that polar optical phonon scattering should dominate for intrinsic material and the ratio of the polar optical phonon absorption coefficient (α_{po}) to the ionized impurity absorption coefficient (α_I) is given by

$$\frac{\alpha_{po}}{\alpha_I} \approx \frac{10^{17}}{N_I},$$ (5)

where N_I is the ionized impurity concentration measured in numbers per cm^3. CdS, which is a wide band gap II-VI compound, tends to be heavily compensated.[9] Samples with free electron concentrations of the order of 10^{15} cm^{-3} can easily have ionized impurity concentrations in excess of $10^{17} cm^{-3}$. Therefore, it is quite likely that the materials tested in this report have a significant fraction of impurity scattering.

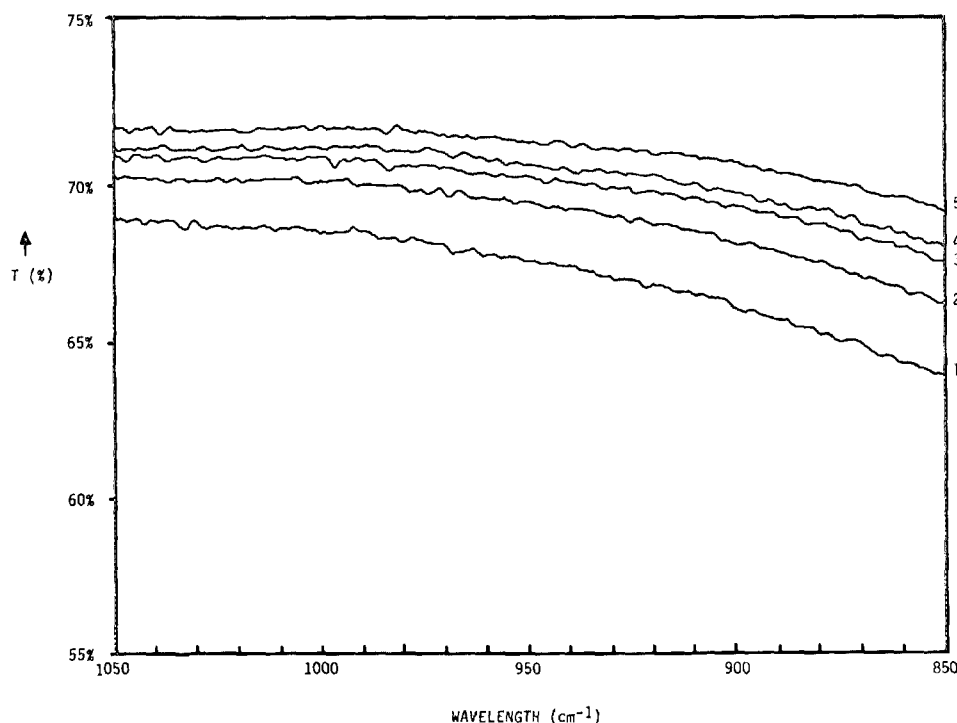If free electron absorption measurements are made sub-

FIG. 2. Experimentally obtained curves of the transmission coefficient vs wavelengths for five CdS wafers of varying resistivity.
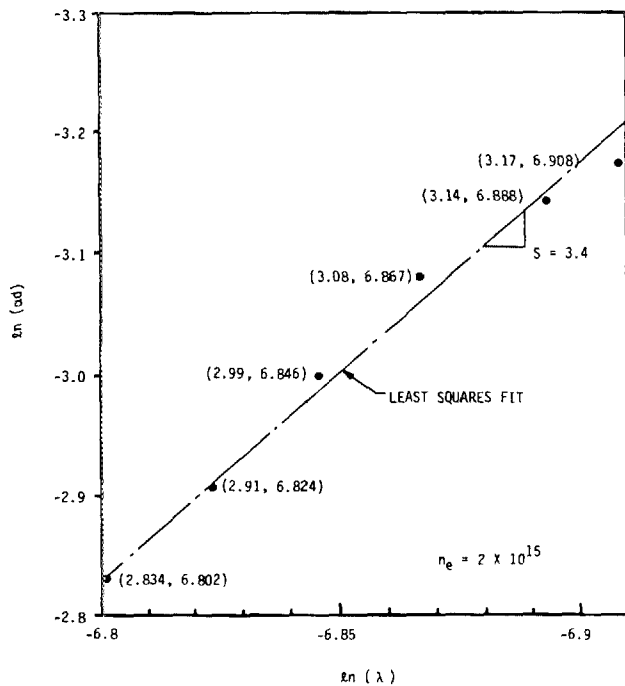
FIG. 3. $\ln(\alpha d)$ vs $\ln(\lambda)$ for sample no. 5 (the least-doped sample) indicating a wavelength dependence of $m = 3.4$ as determined from a least-squares fit to the data.

ject to the conditions that $\hbar\omega_v > \hbar\omega_0$. Where ω_v is the IR frequency and ω_0 is the optical phonon frequency then it is easily shown that[7]

$$\alpha_{op} = an_e\lambda^{2.5} \tag{6}$$

and

$$\alpha_I = bn_eN_I\lambda^{3.5}, \tag{7}$$

where a and b are combinations of the appropriate materials parameters, n_e is the free electron density, and λ is the IR wavelength. Thus, assuming that the other scattering mechanisms are negligible in CdS, the absorption coefficient should be of the form

$$\alpha_{CdS} = an_e\lambda^{2.5} + bn_eN_I\lambda^{3.5}. \tag{8}$$

EXPERIMENTAL OBSERVATIONS

For CdS wafers with $d = 0.1$ cm, the incoherent transmission coefficient is given by Eq. (3). Plots of T vs λ are shown in Fig. 2. Curves 1–5 are experimental curves as obtained from separate samples of CdS for which the resistivity (ρ) and mobility (μ) have been measured at room temperature.

Assuming that $T \to 0.75$ for lossless CdS over the range of our measurements allows us to approximate

$$\ln(T) \simeq \ln(1 - R_{12}) - \alpha d \simeq 0.288 - \alpha d \tag{9}$$

so that

$$\ln(\alpha d) = \ln[-\ln(T) - 0.288].$$

A plot of $\ln(\alpha d)$ vs $\ln(\lambda)$ is shown in Fig. 3 for sample no. 5. The least-squares fit to this curve indicates that

$$\frac{\Delta[\ln(\alpha d)]}{\Delta[\ln(\lambda)]} = 3.4.$$

Other calculations produce similar results indicating that the scattering is predominately due to impurity effects. Figure 4 is a plot of
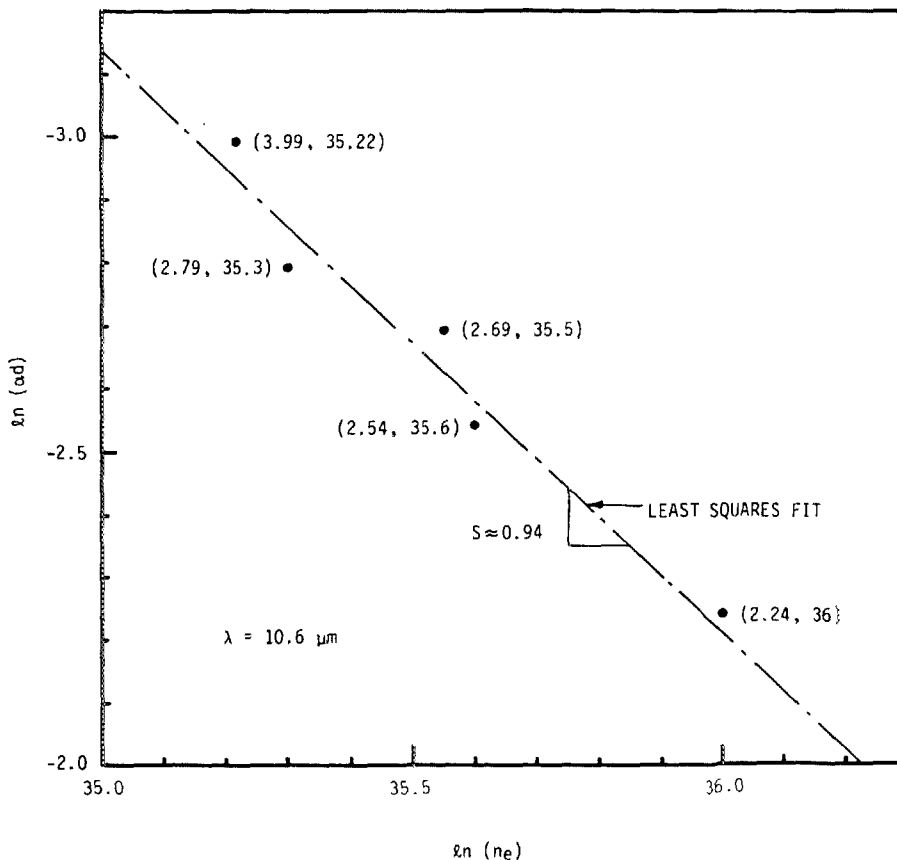

FIG. 4. $-\ln(\alpha d)$ vs $\ln(n_e)$ where αd was obtained from IR transmission data [Eq. (9)] and n_e was obtained from Hall measurements.

TABLE I. Comparison of free electron concentrations as obtained from Hall and free electron absorption data.

Sample no.	$\mu(\text{cm}^2/\text{V s})$ (300 K)	$n(10^{15}\text{ cm}^{-3})$ (Hall measure)	$n(10^{15}\text{ cm}^{-3})$ determined by IR	% variation (relative to Hall)
1	368	4.28	3.9	− 8.2
2	371	2.88	2.90	+ 0.7
3	372	2.63	2.58	− 5.8
4	374	2.22	2.37	+ 2.3
5	375	1.98	1.85	− 6.6

$$\ln[\,-\ln(T) - 0.288] \simeq \ln(\alpha d)\ \text{ vs }\ \ln(n_e)\,,$$

where n_e are Hall measured values, which show that

$$\frac{\Delta \ln(\alpha d)}{\Delta \ln(n_e)} = 0.94.$$

This substantiates the thesis that the absorption is directly proportional to the free carrier density. Tests on samples with resistivities ranging from 1 to $10^7\ \Omega$ cm indicate an ab-

sence of any characteristic lattice absorption in the 850–1050 cm^{-1} range of wave numbers. We have assumed that free electron absorption is the dominate mechanism over this range; the correlation between the IR measurements and the Hall measurements tends to substantiate this assumption.

Since

$$\ln\{\ln(T_{\alpha=0}/T)\} = \ln(A) + \ln(n_e) + m\ln(\lambda),\qquad (10)$$
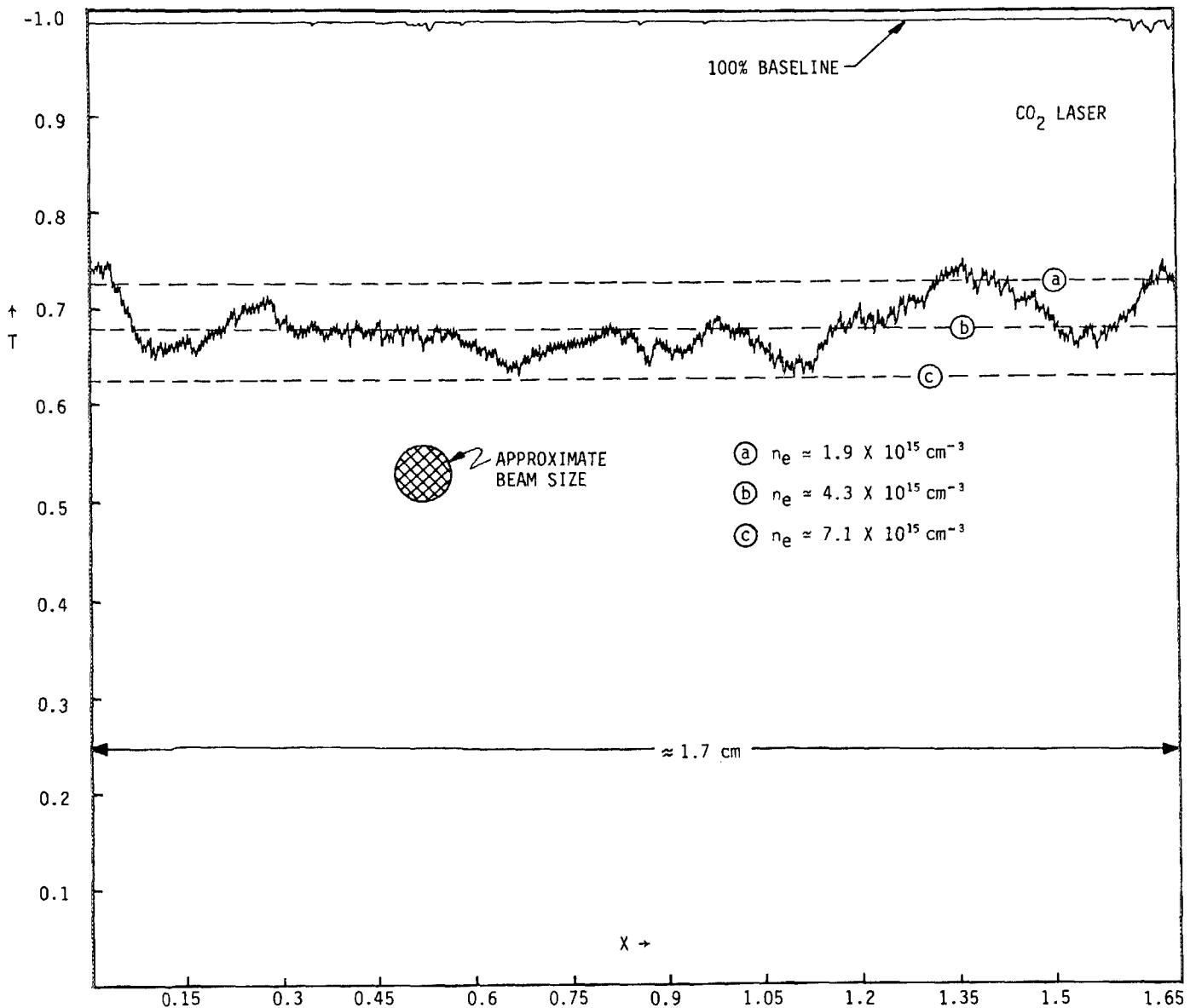

FIG. 5. 10.6-μm transmission scan on a wedge shaped sample with a 50 μm/cm taper. Resistivity variations of 2–10 Ω cm are indicated. The CO_2 beam was approximately 1 mm in diameter, wafer mean thickness was 1 mm.

m can be determined from

$$\ln[\ln(T_{\alpha=0}/T)] \quad \text{vs} \quad \ln(\lambda),$$

and n_e can be determined from

$$\ln(T_{\alpha=0}/T) \quad \text{vs} \quad n_e$$

measurements. Table I shows the results obtained from five samples tested using a value of 7×10^{-7} for A and using $\lambda = 10.6\,\mu\text{m}$ data.

In order to achieve the required spatial resolution, a coherent IR source has been employed. The transmission coefficient given by Eq. (1) has a phase factor which is a function of the material thickness.

Since

$$K_2 = \omega\sqrt{\mu\epsilon} = 2.2 \times 10^4 \ \text{cm}^{-1}$$

for CO_2 radiation at $10.6\,\mu\text{m}$, it is apparent from

$$K_2 d = 2\pi n$$

that the phase factor will go through a complete cycle for

$$\Delta d = 2\pi/K_2 \simeq 2.85 \times 10^{-4} \ \text{cm} = 2.85 \ \mu\text{m}.$$

This would imply that thickness variations of a fraction of 1 μm could lead to erroneous conclusions relative to free carrier densities. To avoid the complications of sorting out carrier density variations from thickness variations we have considered three approaches: (1) taper the sample thickness so that the thickness changes by more than 2.85 μm over a distance which corresponds to the IR beam size or (2) apply an antireflective coating to the sample surface, or (3) intentionally change the effective thickness of each sampled spot by rotating the sample through a small angle ($\sim 6°$) thereby insuring that the full range of values as described by Eq. (1) is obtained at each spot. The problem with approaches (1) and (2) is that special test sample preparations are required which would make routine nondestructive measurements difficult. Further, since no antireflective coating will be perfect, it would be difficult to obtain resolutions down to $10^{14} \ \text{cm}^{-3}$ range when using AR coatings.

As a check on the first approach, a sample was prepared for exposure in a CO_2 laser beam with a spot of 1-mm diameter; the sample was wedge shaped with a taper of 50 μm/cm. The result of a surface scan across a 1.7-cm section taken out of a 2-cm sample is shown in Fig. (5).

The resistivity values indicated are uncalibrated and are based on the results obtained from samples 1–5 as shown in Fig. (1). The significant result is that the predicted relationship between ΔT and Δn has been verified to be approximately linear such that for

$$\Delta T = 0.01, \quad \Delta n = 5 \times 10^{14} \ \text{cm}^{-3},$$

which is an easily achieved resolution.

A computer evaluation of Eq. (1) shown in Fig. (6) demonstrates the practicality of rotating the sample to obtain the transmission maximum at each sampled point. Using the parameters for CdS in Eq. (1), the value of the maxima of the curves (T_{max}) is given by

$$T_{max} = \frac{(1 - R_{12})^2 e^{-\alpha d}}{(1 - R_{12} e^{-\alpha d})^2}, \tag{11}$$

where

$$\alpha d = A\, n_e \lambda^m.$$

The fractional change in T_{max} as a function of n_e,

$$\frac{\Delta T_{max}}{T_{max}} = -\left(\frac{1 + R_{12} e^{-\alpha d}}{1 - R_{12} e^{-\alpha d}}\right) A\,\lambda^m \Delta n_e, \tag{12}$$

provides the best resolution for determining changes in n_e from changes in the transmission coefficient. This also is apparent from Fig. 6. The experimental apparatus for performing these measurements has not yet been assembled so that no data are available. However, preliminary results obtained by manually rotating the sample indicate the validity of this approach.
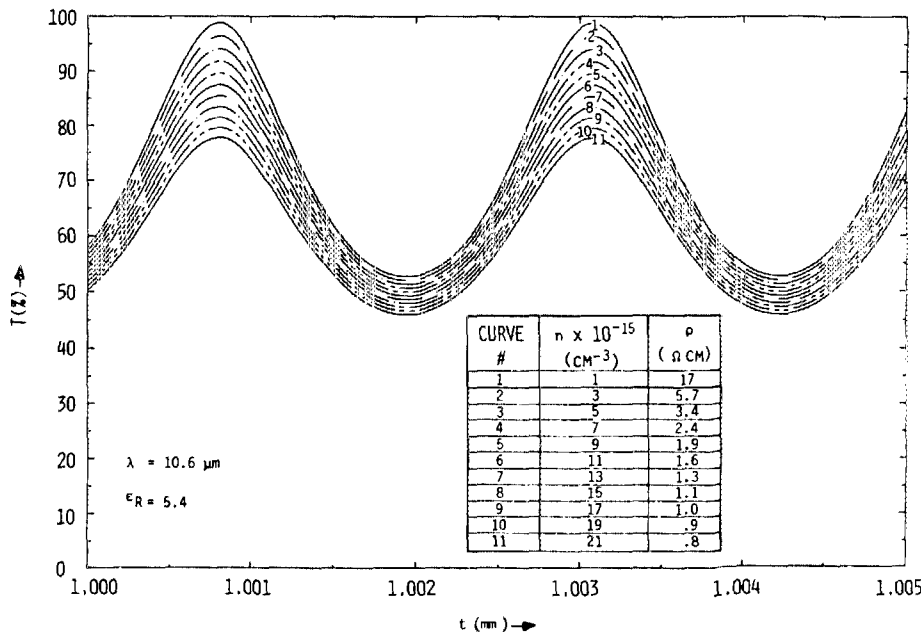

FIG. 6. Computer-generated curve showing the variation in transmission as a function of sample thickness.

CURVE #	n × 10⁻¹⁵ (CM⁻³)	ρ (Ω CM)
1	1	17
2	3	5.7
3	5	3.4
4	7	2.4
5	9	1.9
6	11	1.6
7	13	1.3
8	15	1.1
9	17	1.0
10	19	.9
11	21	.8

$\lambda = 10.6\,\mu\text{m}$

$\epsilon_R = 5.4$

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CONCLUSION

We have demonstrated the practicality of using IR transmission measurements to determine relative free carrier density variations across the surface of a CdS wafer. The most promising approach appears to be that of relating the variations in transmission maxima to the free carrier variations.

Correlation between the Hall measurement and IRFE measurements indicate a relative absence of other lattice absorption mechanisms over the range of wavelengths from 4 to 12 μm. The direct proportionality of the absorption coefficient to free electron density has been demonstrated and the wavelength dependence indicates impurity scattering as the dominate mechanism. A comparison to the theoretical expressions substantiates that CdS is heavily compensated; it would appear that IR transmission measurements can be used to directly determine the compensation ratio since impurity scattering is clearly dominant in CdS.

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