Seventh Quarterly Report

on

Amorphous Semiconductors

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1. INTRODUCTION

This seventh quarterly report, submitted in compliance with contract No. NASw-934, covers the period from 3 February 1966 to 2 May 1966. Continued progress has been made in both the theoretical and experimental work.

During the past quarter, the major effort has been in the determination of the refractive index for a large number of points between approximately 0.5μ and 6μ. The data shows that there is a sharp rise in refractive index as the band edge is approached. Additional work has been done on the interpretation of the absorption coefficient.

As has been previously reported (5th quarterly report) the examination of the structure of amorphous films has been proceeding and a preliminary report on the density of atoms in such films is reported at this time.

2. AMORPHOUS SEMICONDUCTING BORON THIN FILMS

2.1 Index of Refraction of Amorphous Boron Thin Films

The real part of the index of refraction of vacuum-deposited amorphous boron films was calculated from 0.475 μ to 4.8 μ. The films were deposited on both fused silica and Irtran-2, an Eastman Kodak product composed of polycrystalline ZnS. Transmission curves of the boron on quartz films were obtained by using the Cary 14 spectrophotometer (figure 1) (0.19 μ-2.5 μ) and the transmission curves of boron on Irtran-2 were recorded on the Beckman 5-A spectrophotometer (figure 2) (2 μ-16 μ). The Irtran-2 was used in the near infrared because it has a relatively flat transmission out to 13 μ. The index was calculated from the position of the interference fringes using the equation below.

$$\eta \lambda = 2 \mu t \tag{1}$$

or, solving for μ,

$$\mu = \frac{\eta \lambda}{2 t} \tag{2}$$

where

μ = the real part of the index of refraction

η = the order of interference

λ = the position of the interference maximums in the transmission curve

t = the film thickness.

The order of interference was estimated by assuming that μ, the index of refraction, did not change with wavelength. This approximation is fairly good for wavelengths of two microns or higher, but becomes increasingly less good as the wavelength drops below two microns. The approximation is obtained by applying equation (1) to two fringes,

$$\eta \lambda_1 = 2 \mu t \tag{3}$$

$$(\eta+1) \lambda_2 = 2 \mu t \tag{4}$$

Dividing equation (3) by equation (4),

$$\frac{\eta \lambda_1}{(\eta+1) \lambda_2} = 1$$

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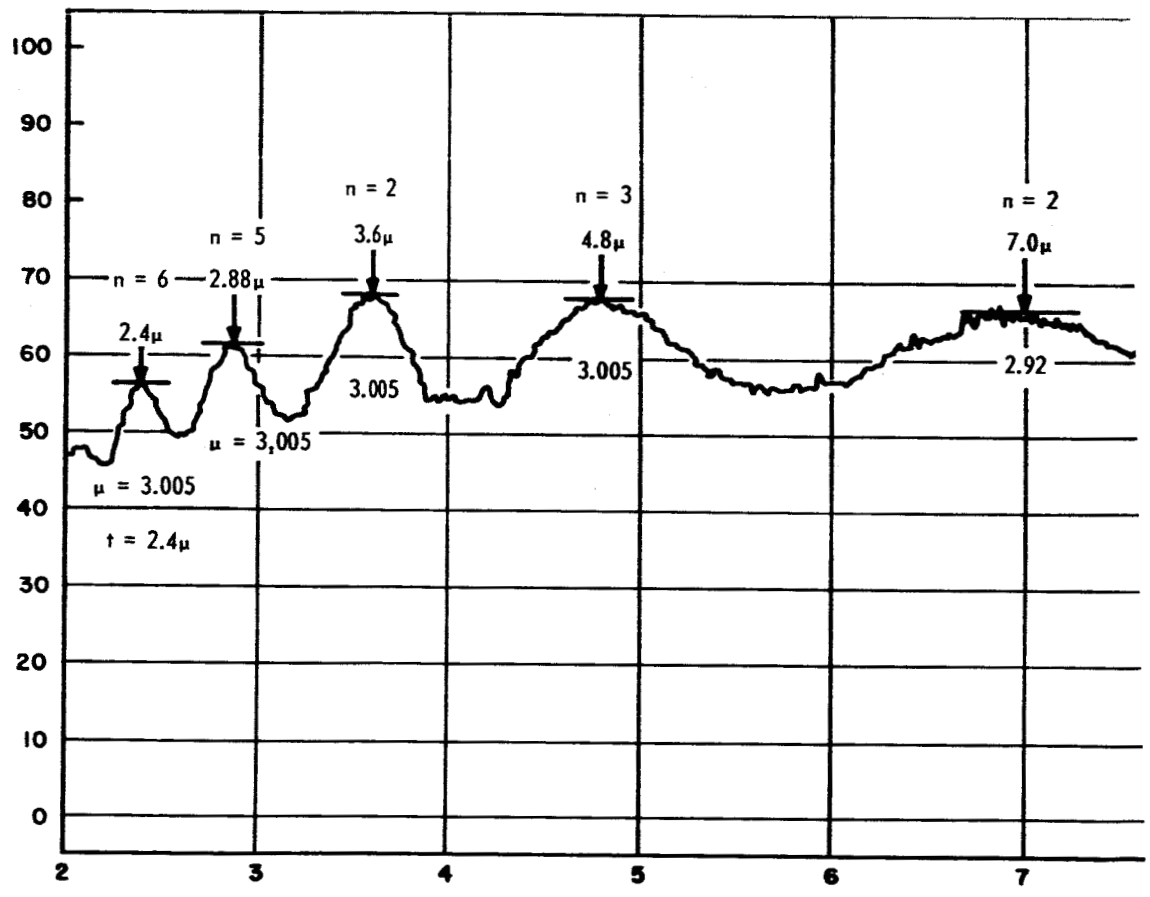
100
90
80
70
60
50
40
30
20
10
0
2
3
4
5
6
7
n = 6
2.4μ
n = 5
2.88μ
n = 2
3.6μ
n = 3
4.8μ
n = 2
7.0μ
μ = 3.005
t = 2.4μ
μ = 3,005
3.005
3.005
2.92

5-1

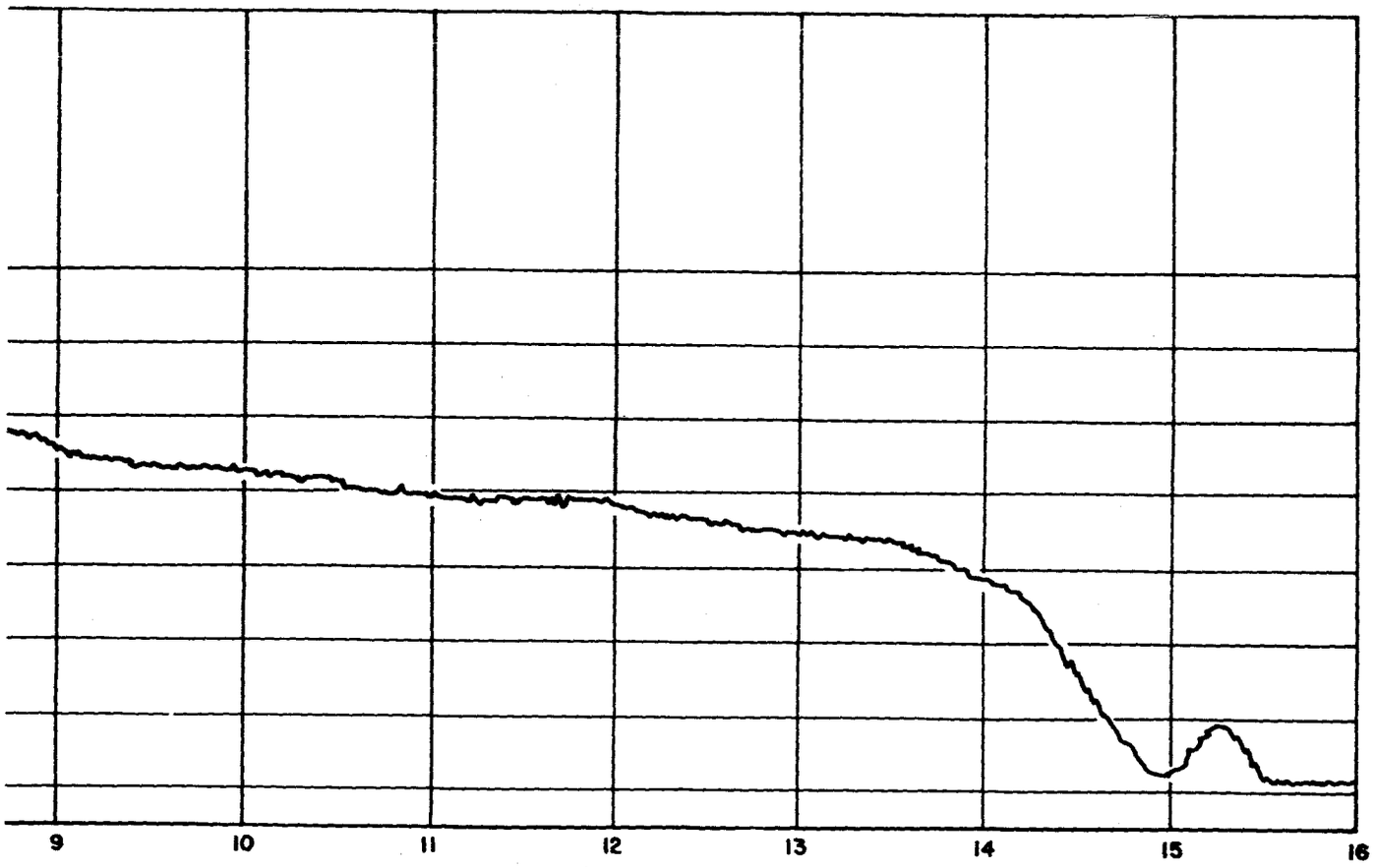

Figure 1. Transmission of Boron Thin Films Showing Interference Phenomena. Boron Film on Quartz in the Range 0.19 μ to 2.5 μ

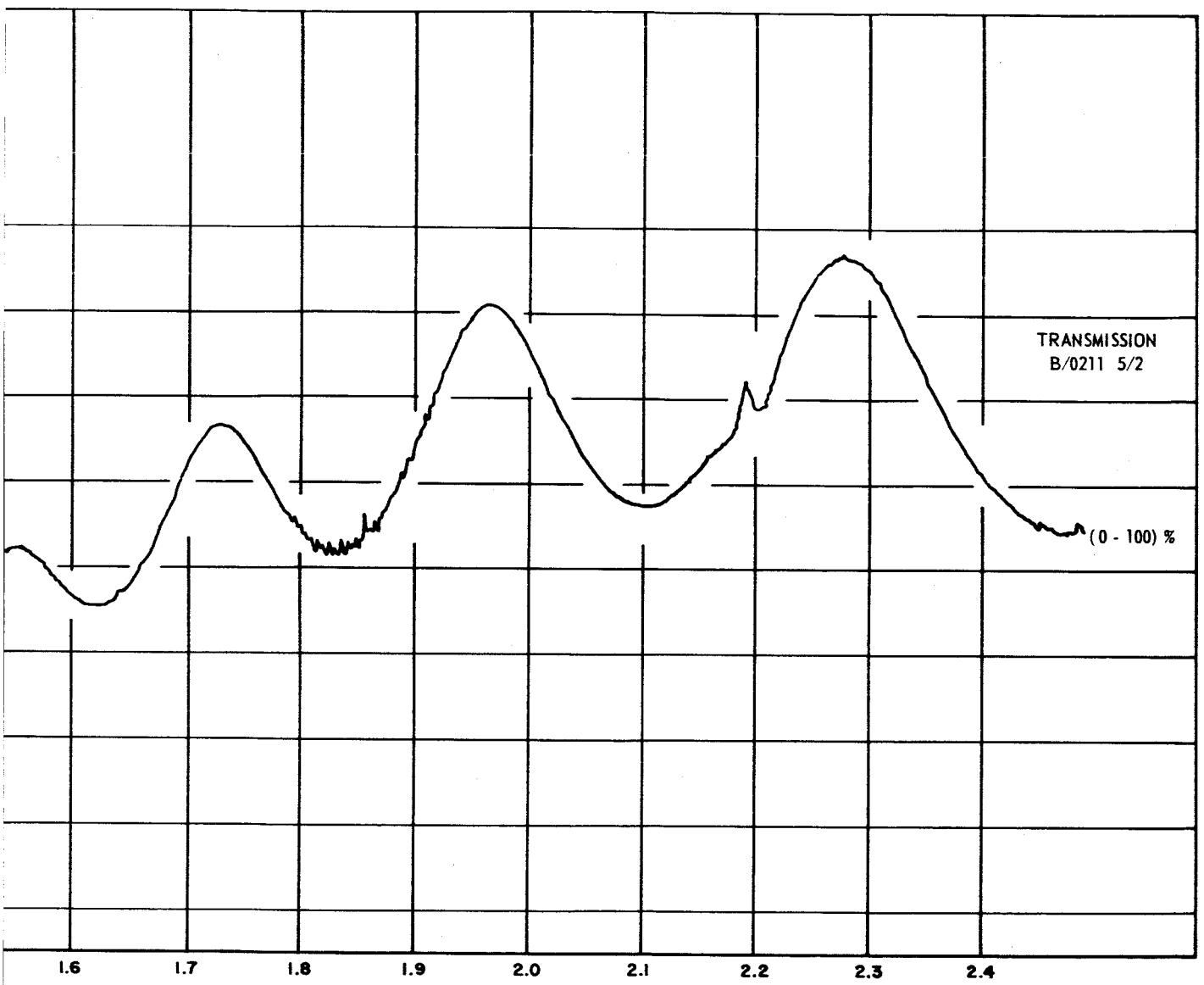

Figure 2. Transmission of Boron Thin Films Showing Interference Phenomena. Boron Film on Polished Irtran-2 in the Range 2 μ - 16 μ

And solving for η,

$$\eta \lambda_1 = (\eta + 1) \lambda_2$$

$$\eta \lambda_1 = \eta \lambda_2 + \lambda_2$$

$$\eta (\lambda_1 - \lambda_2) = \lambda_2$$

$$\eta = \frac{\lambda_2}{\lambda_1 - \lambda_2} \quad \text{where } \lambda_1 > \lambda_2 \tag{5}$$

and thus we obtain a quick method for estimating the order of interference.

The thicknesses of very homogeneously deposited films were measured by a Zeiss interference microscope, and the index of refraction was calculated using equation (2)

$$\mu = \frac{\eta \lambda}{2 t} \tag{2}$$

For other films, less homogeneously deposited, the thicknesses were calculated by solving equation (2) for t,

$$t = \frac{\eta \lambda}{2 \mu} \tag{6}$$

and using a value for μ calculated for the more homogeneous films. The film thickness was calculated for one wavelength and this value for thickness was then used in subsequent calculations for μ. The results are plotted in figure 3. The data as determined by Gebhardt[1] and Morita[2] are also given for comparison.

2.2 Absorbance of Amorphous Boron Thin Films

The absorbance of vacuum-deposited amorphous boron films was obtained from 0.16 μ to 2.0 μ. All the films used were boron deposited on quartz several hundred angstroms in thickness. The recording down to 0.2 μ was done on the Cary 14 spectrophotometer; and the recording down to 0.16 μ on the Beckman DK-2. Previously we had corrected the transmission data for reflection by the use of the formula

$$T = \frac{(1 - R)^2 e^{-\alpha d}}{1 - R^2 e^{-2\alpha d}} \tag{7}$$

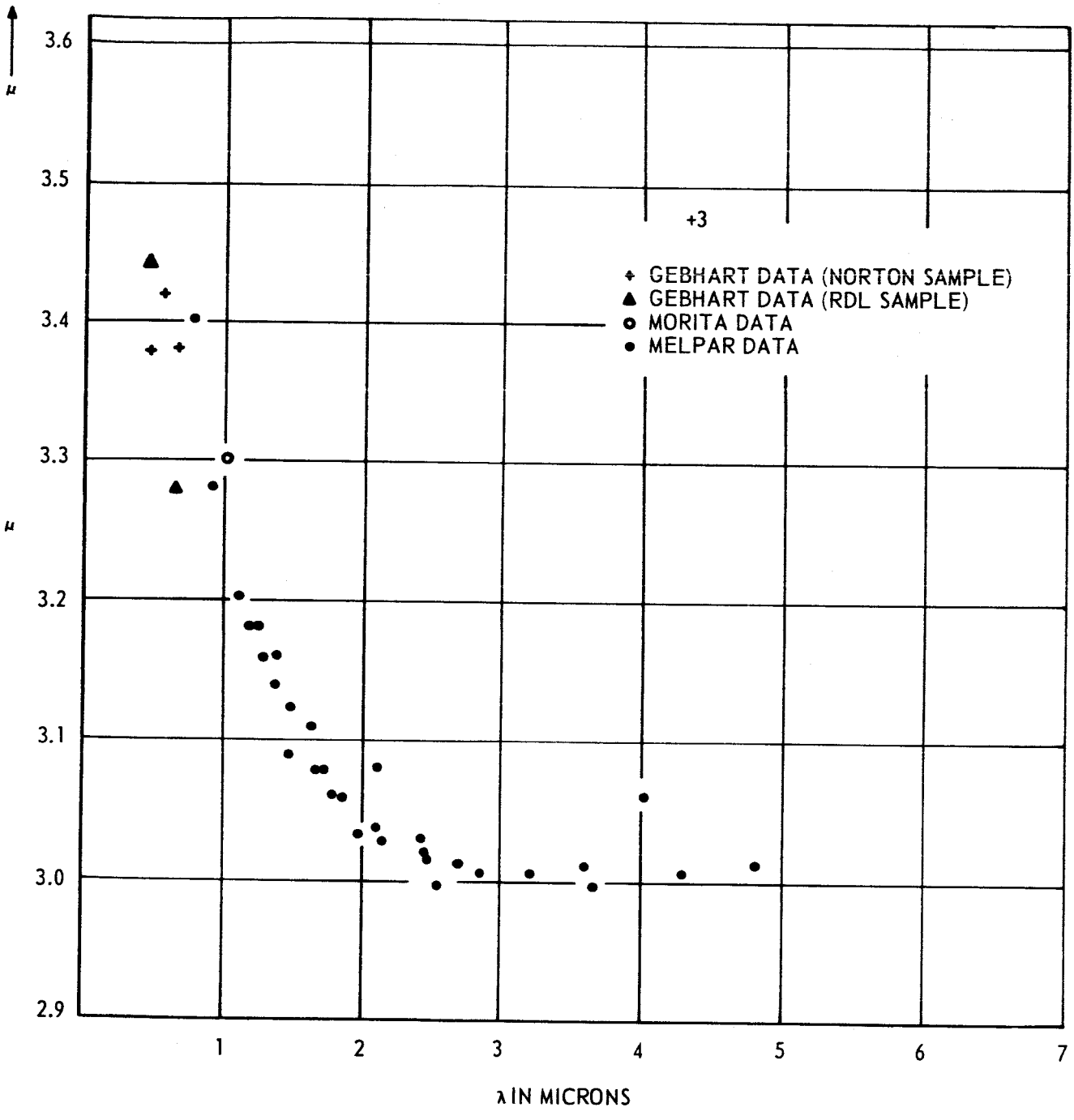

Figure 3. Index of Refraction Versus Wavelength

(See Sixth Quarterly Report, Sec. 2.1) which also takes multiple reflections within the film into account. For the reflection coefficient R, we took the constant value of 0.29 throughout the entire range. This is somewhat unsatisfactory since one would expect R to change rapidly as the regions of high absorption are approached. Presently, we have followed a procedure which eliminates the reflection correction as explained below.

The calculations were based upon equation (8) which relates the transmission, T, to some function of reflectance, F(r); the absorption coefficient α, and the thickness, t.

$$T = F(r)\, e^{-\alpha t} \tag{8}$$

Assuming F(r) at a given wavelength to be the same for films of different thicknesses, we have for 2 films:

$$T_1 = F(r)\, e^{-\alpha t_1} \tag{9}$$

$$T_2 = F(r)\, e^{-\alpha t_2} \tag{10}$$

Dividing equation (9) by equation (10), we have

$$\frac{T_1}{T_2} = \frac{e^{-\alpha t_1}}{e^{-\alpha t_2}} = e^{-\alpha(t_1 - t_2)} \tag{11}$$

and taking the natural logarithm and solving for α,

$$\ln \frac{T_1}{T_2} = -\alpha\,(t_1 - t_2) \tag{12}$$

$$\alpha = \frac{1}{t_1 - t_2} \ln \left[\frac{T_2}{T_1}\right] \tag{13}$$

We obtain equation (12) which allows us to determine the absorption coefficient at any wavelength of a deposited material by measuring the transmission ratio of 2 films of different and known thicknesses at that wavelength. The method therefore gives us the absorption coefficient of a film whose thickness is equal to the difference in thicknesses of the two films. These calculations were done for the Beckman DK-2 readings.

A slightly different approach was used with the Cary 14 spectrophotometer measurements. When recording with the linear slidewire, the Cary reads out I/I_o or, stating the result in terms of transmission, T/T_o, where T is the

transmission through the sample side of the spectrophotometer and T_o is the transmission through the reference side. However, when recording with the nonlinear slidewire, the Cary reads out $\log_e (T_o/T)$. Therefore, to read out $\log_e (T_2/T_1)$ as in equation (12), film No. 2 should be placed in the reference side and film No. 1 in the sample side. In order to give a positive (and hence on scale) reading, the thickness of film No. 2 (in reference side) should be less than the thickness of film No. 1 (sample side). This method has the enormous advantage of recording $\log_e T_2/T_1$ directly.

2.3 Results and Discussion

As was stated in the last quarterly report, we have succeeded in obtaining films of ultra-pure boron. The purity of these films was indicated by the absorption spectra in the far infrared. We have now obtained the absorption spectra of these pure films in the near ultraviolet, visible and near infrared regions, by a novel method which eliminates the reflection correction as explained in the previous section. The absorption data has been obtained for very thin films varying in thickness between 100 and 500 Å. One such curve for a 400 Å thick film is shown in figure 4 (strictly speaking, the difference in thicknesses of two films is equal to 400 Å). The absorption curve differs considerably from those reported previously. The following features of the spectrum are worth noting.

(a) A broad absorption band extending over nearly 2 ev with a maximum at about 1.65 ev. The rise in absorption between 0.6 and 1.6 ev appears linear; that is, it does not fit direct or indirect, allowed or forbidden transitions. The absorption coefficient in this region is very high, though the rise with increasing energy is slow. Comparing our values with the reported single crystal data,[3] we observe a value for the absorption coefficient, α, at 0.6 ev which is three orders of magnitude higher than that for a single crystal. On the other hand, from single crystal data, α increases by nearly two orders of magnitude as energy increases from 0.6 to 1.6 ev, while, in our case, the absorption coefficient is only three times as large at 1.6 ev. Even though one would expect higher values of α for amorphous films, due to lack of long range order, our observed values seem unusually large.

(b) A minimum in absorption is noticed at approximately 2.55 ev, beyond which the absorption increases again. Gaulé et al.[4] have reported such a minimum at approximately the same energy for single crystal boron, though they failed to observe such a dip in absorption for a 0.8 μ thick film. It is not known whether their data is corrected for reflection. We did not observe the minimum for data which was not corrected for reflection. The value of adsorption coefficient in this region is comparable to that reported for a single crystal.

The absorption coefficient α seems to fit the expression valid for direct transitions in the region 2.85-3.25 ev. This is shown in figure 5 and one obtains an intercept of 2.6 ev showing existence of a direct transition at this energy value.

Figure 4. Absorption Coefficient α of a Thin Boron Film as a Function of Energy

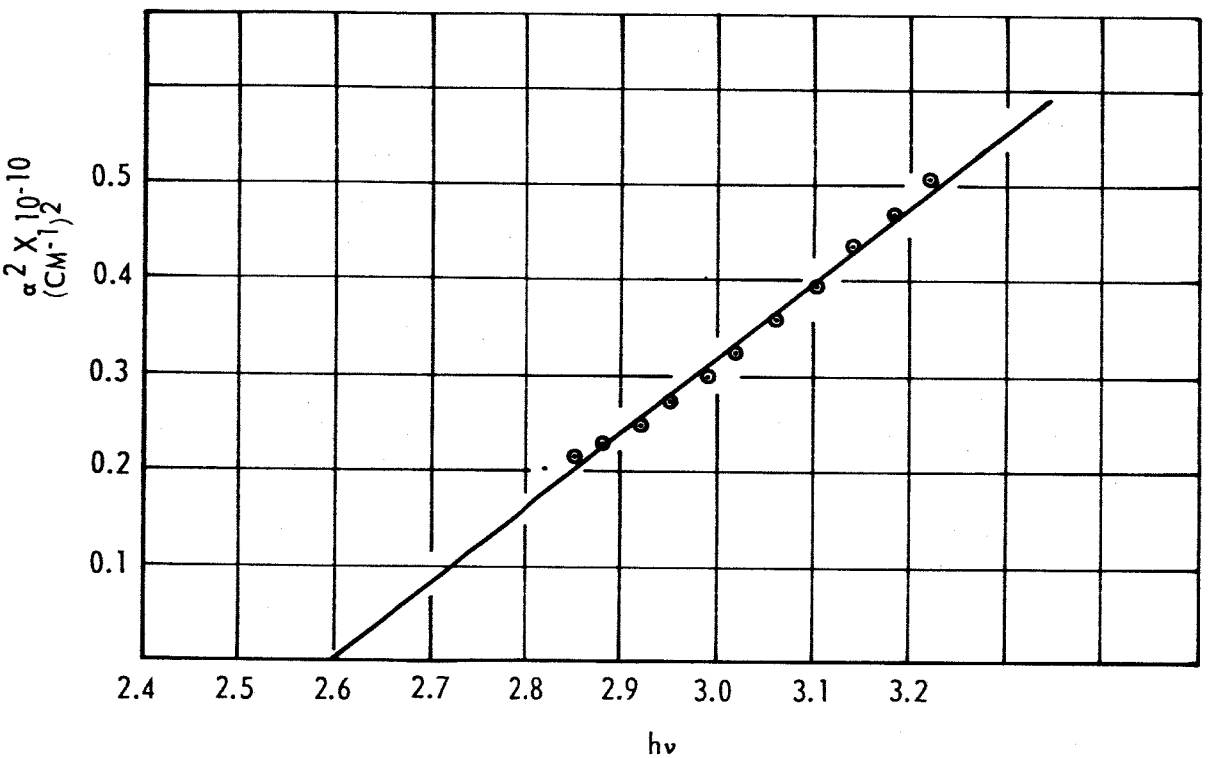

Figure 5. α^2 Versus Energy for a Thin Boron Film

A possible qualitative explanation of the above observations is offered below. Borland[5] has shown that for a one-dimensional disordered lattice, all the eigen-states of the system are localized. Although no such complete treatment exists for a disordered three-dimensional lattice, it is confidently believed that a part of the states in such a system are localized. Such a belief is strengthened by the work of Banyai[6] for amorphous germanium and Hartke and Regensburger[7] for amorphous selenium. In both cases the experimental results are explicable in terms of band theory where one incorporates the existence of traps, i.e., a localized level in the forbidden region of the energy band spectrum. A broad optical absorption edge is observed for amorphous selenium which has been explained[6] in terms of two types of transitions, one involving the transition between localized levels, which are necessarily observed at energies which are lower than the value of the band gap for a single crystal, and another type of transition between the non-localized levels. The individual absorption due to two types of transitions is obtained from the total absorption by measuring the photoconductivity of amorphous selenium which is normalized to unity at energies about an electron-volt above the value of the band gap for a single crystal.

A similar explanation is possible for our results but this can only be confirmed by studying the variation in photoconductivity of amorphous Boron with energy. The lack of long-range order in a system will create localized levels above and below the otherwise sharp band edges in a crystal. That is, the density of states in the neighborhood of a band edge is now modified with a nonvanishing value of density of states in the otherwise forbidden part of the energy spectrum. The transitions between these levels will account for the high value of absorption which is observed at low energy values. The maximum observed at 1.65 ev which is close to the value reported for band gap of a single crystal will seem to indicate that the density of states near the band edges is still relatively high.

The rise in absorption beyond 2.55 ev can be explained as due to a new transition either somewhere else in the Brillouin zone or between deeper levels. The fact that this minimum is not affected by the amorphous nature of the system will seem to indicate that disorder does not influence the deeper levels. That is to say the density of states is mainly affected in the neighborhood of the band edges.

3. STRUCTURE OF AMORPHOUS THIN FILMS

The most general technique for studying the arrangement of atoms in matter is the determination and interpretation of the scattering of radiation by the matter in question. The radiation is chosen so that its wavelength is comparable to the dimensions of structure to be detected, and regularities of structure produce diffraction maxima and minima in the measured variation of scattered intensity with angle. It is convenient to discuss the intensity function, s, in terms of a measure of the scattering angle defined as $(4\pi \sin\theta)/\lambda$, where $\theta = \varphi/2$ = one-half the scattering angle, and s has the dimensions of reciprocal length. The relations between structure and scattered intensity then depend on trigonometric functions, sin (rs), where r is a distance in the structure.

We have worked with films of boron, germanium, and silicon. When only one type of atom is involved, as in these structures, a scattering function D(s) characteristic of an isolated atom can be separated. It can be shown[8] that scattered intensity I(s) is related to the density $\rho(r)$ of atoms at a distance r from the average atom by the equation

$$s\left[\frac{I(s)}{D(s)} - 1\right] = \int_0^\infty 4\pi r\left[\rho(r) - \rho_o\right] \sin(rs)dr$$

where ρ_o is the average density for the whole structure. If we define

$$I_m(s) = \left[\frac{I(s)}{D(s)} - 1\right]$$

then a Fourier inversion yields

$$4\pi r\left[\rho(r) - \rho_o\right] = \frac{2}{\pi}\int_0^\infty s\, I_m(s) \sin(rs)\, ds\ .$$

For an isotropic material the statistical information conveyed by $\rho(r)$ is all the information obtainable by intensity measurements.

The intensity function I_m oscillates about zero with decreasing amplitude as s increases, and the integral over s can be terminated at some upper limit s_o. The resolution of the structure investigation depends on the high-frequency components of the variation of $\rho(r)$ with r, which are contributed by the functions $sI_m(s)\sin(rs)$ at high values of s. The resolution in r is thus of the order of π/s_o.

Studies of solids and liquids have generally been made with Xrays or neutrons in the wavelength range 0.7-1.6 Å. The absolute maximum for s_o is then about 25, and the usual value is 15 or less. For thin films the use of electron diffraction is preferable because the scattering is more intense and wavelengths of the order of 0.05 Å can be used. The technique has been intensively developed for study of the structure of gas molecules. Values of s_o ranging from 30 to 60 are considered necessary for such work.

Instruments for examination of solids by electron diffraction usually are limited to lower s values because the precise measurement of closely spaced, sharp diffraction maxima from crystalline samples is usually most important. To obtain wide-angle measurements of the diffuse patterns from amorphous thin films we have installed a simple modification in the JEM-6A electron microscope, by which the camera length is almost halved and $s_o = 45$ can be attained. The patterns were recorded in a series of graded exposures to permit all portions to fall within the measurable range of photographic density.

The boron and germanium plates have been measured. This was done with a recording microdensitometer having a linear density scale with a range of 0-2.0. The recorder charts were translated to digital records on punched cards by a commercial data-processing firm. Further processing of these data was done with an IBM 7094 computer.

The curves and functions derived from them were represented by values at a set of uniformly spaced points. The initial density values were obtained by four-point interpolation from the original data. Logarithms of the density values were calculated and plotted mechanically. The curves were intercompared to detect disagreements, and those segments were selected that appeared to give the best representation of the intensity curve over the full range of angles. Additive corrections were applied to make adjacent segments match exactly. The final s_o values of the data used were 20.5 for boron and 29.6 for germanium.

The intensity I(s) should approximate the atomic intensity function D(s) more and more closely as s increases, the absence of high-frequency components in the function $(\rho(s) - \rho_o)$ being implied by the finite size of atoms. The D(s) functions were approximated by choosing 10-15 points on the combined intensity curve to represent a mean of the rapid oscillations and using four-point interpolation.

Fourier transforms were obtained with a computer routine specially coded in FORTRAN. The functions $I_m(s)$ were found to give smooth transform curves, but the transforms of the functions $s\,I_m(s)$ showed the usual rapid oscillations due to termination. This problem is generally encountered because multiplication by s increases the contribution from the high-angle portion of the intensity curve. The effect was mitigated by multiplying $I_m(s)$ by an artificial temperature factor of the form $\exp(-Bs^2)$ representing the effect of a random oscillation of all atoms about their mean positions.

The value of B was chosen so that $s_o \exp(-Bs_o^2) = 1$, i.e., the function I_m was unchanged at its upper termination. This procedure gave the curves shown in figure 6 for boron and germanium. The curve for germanium may be compared with the radial distribution curve obtained by Richter and Breitling from X-ray measurements[10]; the positions of all peaks are in good agreement.

The present curves require refinement by proper adjustment[11] of the so-called "background" curve D(s) to give linearity in the range of r below the nearest-neighbor peak. In this region $\rho(r) = 0$, and the calculated function must equal $-4\pi r\rho_o$. When the adjusted radial distribution curves are available, this slope will provide a basis of reference for the estimation of the coordination numbers by integration over the first peak. When the entire sequence of measurement and computation procedures has been proved by successful application to the determination of the radial distribution function for boron and redetermination of that for germanium, these techniques will be applied to patterns of silicon already recorded and to other amorphous thin films.

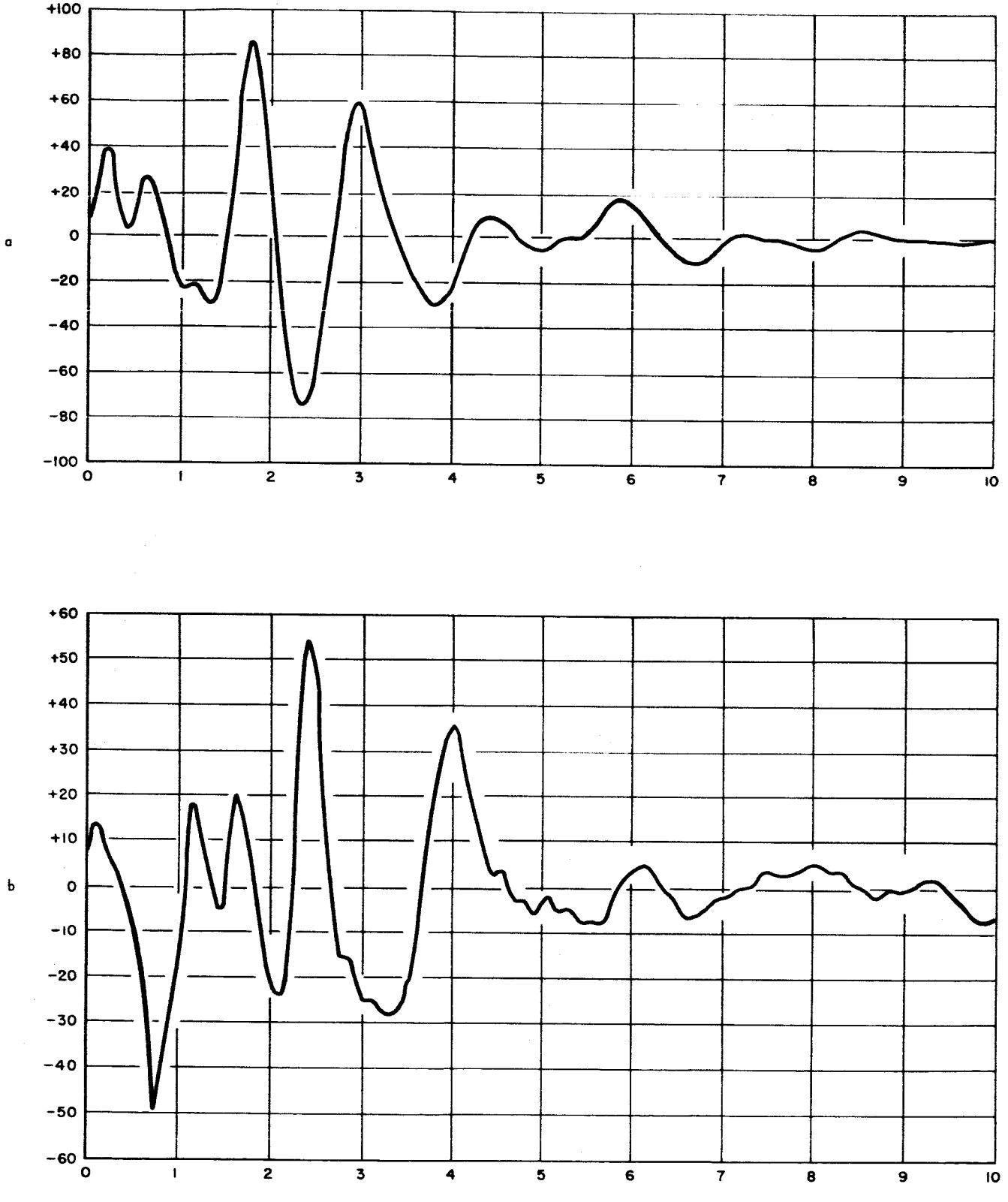

Figure 6. Calculated $(\rho(r) - \rho_0)$ With an Artificial Temperature Factor: (a) for a Boron Thin Film; (b) for a Germanium Thin Film

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5. SUMMARY

During the past quarter, the optical properties of amorphous boron thin films have been rechecked because of the improvement in the character of the films as reported in the last quarter. With the increased purity of the films, there is a greater surety of accuracy in these measurements and at this time we are reporting on the refractive index, absorptance, and absorption coefficient. The characterization of structure of amorphous thin films has continued and is nearing completion for boron and germanium.

In the next quarter, it is expected that the optical properties of boron films in the visible and infrared to 16 μ will be completed and that photoconductivity measurements will be made to confirm the explanation of band structure presented in this report. The work on film structure will be continued and a final determination of nearest neighbor concentrations may be possible.

Senior personnel who have participated in this work during the past quarter are Dr. Charles Feldman, Dr. Kishin Moorjani, Dr. Fred Ordway, and Mr. William Zimmerman III.

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