conditions.

$$\langle E_{s\parallel}(0)E_{s\parallel}(t)\rangle_{\rm av}=\frac{1}{\tau_1+\tau_2}\{\tau_1\langle E_{s\parallel}(0)E_{s\parallel}(t)\rangle_{{\rm av}\ p_1(0)=1}+\tau_2\langle E_{s\parallel}(0)E_{s\parallel}(t)\rangle_{{\rm av}\ p_1(0)=0}\}$$
$$=E_{s\parallel}{}^2\frac{W_1W_2}{(W_1+W_2)^2}\exp[-(W_1+W_2)t]. \quad \text{(A8)}$$

In terms of Eqs. (3) and (4), we have

$$\frac{W_1W_2}{(W_1+W_2)^2}=\frac{1}{4\cosh^2(\epsilon_s/2kT)}. \quad \text{(A9)}$$

We now find

$$\langle E_{s\parallel}(t')E_{s\parallel}(t'+t)\rangle_{\rm av}=\frac{E_{s\parallel}{}^2}{4\cosh^2(\epsilon_s/2kT)}\exp(-|t|/\tau_s), \quad \text{(A10)}$$

where τ_s is the correlation time of the sth hopping pair, and is given by

$$1/\tau_s=W_1+W_2=\frac{E_1{}^2}{\pi\rho_0 s^5\hbar^4}W^2\epsilon_s\coth(\epsilon_s/2kT). \quad \text{(A11)}$$

PHYSICAL REVIEW VOLUME 153, NUMBER 3 15 JANUARY 1967

Use of Thin Films in Determining the Optical Constants of PbS from 1 to 5 eV

PAUL R. WESSEL
U. S. Naval Ordnance Laboratory, Silver Spring, Maryland

(Received 5 February 1966; revised manuscript received 30 August 1966)

Reflectance and transmittance measurements have been made on four epitaxial thin films of PbS ranging in thickness from 260 to 830 Å, in the spectral region from 1 to 5 eV. The optical constants of each film have been derived in order to demonstrate the usefulness of the data obtained from such thin samples. The results are self-consistent and are in good agreement with the bulk optical constants obtained by Avery. The uncertainty in the magnitude of the optical constants derived from thin-film data is approximately equal to the uncertainty in the data themselves if the film thickness is accurately known. The thin-film approach to the derivation of optical constants is shown to be superior to the use of dispersion relations in many cases. The problems and advantages encountered in the use of thin-film samples are discussed.

I. INTRODUCTION

PREVIOUS investigations[1,2] have indicated that reliable optical data could be obtained from thick epitaxial films of the semiconducting lead salts. In this study the reflectance R and the transmittance T of four very thin films (thickness, τ, from 260 to 830 Å) have been measured. The results have been used to derive the optical constants. Samples of widely different thicknesses were included so that any significant thickness dependence of the derived optical constants would be apparent.

The experimental procedure and the equipment used are described in Sec. II. The reflectance and transmittance data from four samples are given in Sec. III. In Sec. IV the method by which the optical constants are derived from the data is described and the results obtained from the calculations are presented. The implications of these results concerning the further use of thin films and the value of this method of deriving the optical constants compared to the use of dispersion relations are discussed in detail in Sec. V.

II. EXPERIMENTAL PROCEDURE AND EQUIPMENT

The epitaxial thin film samples of PbS used in this study were prepared in the manner described by Schoolar.[3] Each sample was checked for the presence of pinholes or surface cloudiness before the measurements were made. Thicker samples prepared in this manner ($\tau>0.3\,\mu$) have been shown to be excellent single crystals from back-reflection Laue patterns, and do have electrical properties comparable to the bulk material. These tests cannot be applied to very thin samples due to the interference of the rocksalt substrate in the Laue patterns, and the interference of cleavage steps in electrical measurements. Hence, there is no prior basis for assuming that such thin films have optical properties comparable to the bulk material.

Measurements of R^2 and T were made with the optical system which is shown schematically in Fig. 1. The output of a modified Perkin-Elmer model 12B double-pass monochromator was used to obtain data at each 0.1 eV, beginning at 1.0 eV and ending at 5.0 eV.

[1] P. R. Wessel *et al.*, Bull. Am. Phys. Soc. 8, 517 (1963).
[2] R. B. Schoolar, Bull. Am. Phys. Soc. 8, 516 (1963).
[3] R. B. Schoolar and J. N. Zemel, J. Appl. Phys. 35, 1848 (1964).

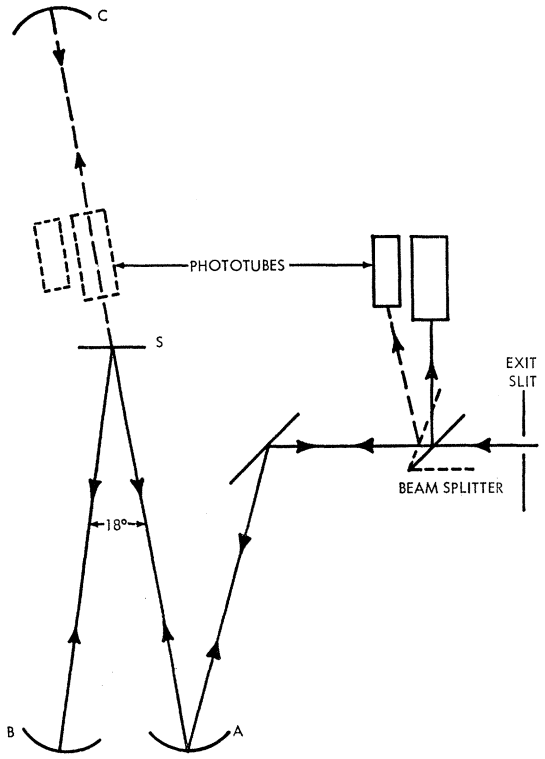

FIG. 1. Schematic of the optical system. The position of the photomultiplier tubes is shown for reflectance (solid outline) and transmittance (broken outline) measurements. The sample position is denoted by S and the positions of the identical spherical mirrors by A, B, and C.

The sample was mounted on a precision ball-bearing slide assembly. It moved in a vertical plane and was equipped with rigid mechanical stops at each end of its travel. With the slide down, the sample intercepts the beam coming from the spherical mirror A and reflects it to the spherical mirror B. The beam then returns along the same path and is directed to the proper photomultiplier tube by the beam splitter. With the sample holder in the up position the beam passes through an open aperture to a third spherical mirror C, from which it returns along the same path to the beam splitter and the detectors. In measuring the square of the reflectance a mask was placed behind the sample to prevent any of the transmitted radiation from returning through the sample to the detectors. Transmittance data was obtained by placing the phototubes between the sample and mirror C while mirror B was covered.

With this optical system the beam striking the detector is never inverted, thus avoiding a possible source of error. A small error will still result due to the distortion of the beam by the uneven cleavage surfaces of the rocksalt substrates and the irregularity in the response of different areas of the photocathodes. Since the sample is located at the focal point of each of the spherical mirrors, alignment problems are minimized. The only motion involved in making a measurement is that of the sample holder, which can be controlled with great precision. No appreciable error is expected from movement of the sample. The weakness of this optical system is that the reflectance results depend on the relative reflectivities of the mirrors B and C. These mirrors were standard Perkin-Elmer spherical mirrors and their reflectivities throughout the measurement region were found to agree within an experimental error of about 2%.

III. DATA

The reflectance and transmittance curves for the films of 260, 430, 490, and 830 Å thickness are shown in Figs. 2 and 3. Data points at odd tenths of an eV have been omitted so that the error limits on points at even tenths of an eV, for which the optical constants were calculated, might be shown more clearly.

The 260 and 490 Å films had very bright smooth surfaces. The error in R was taken to be $\pm 2\%$ at most points, corresponding to errors of 1% in reproducibility, 1% in photomultiplier response, and 2% in mirror reflectivities, for a maximum error of $\pm 4\%$ in the measured quantity, R^2. The error in T was taken from

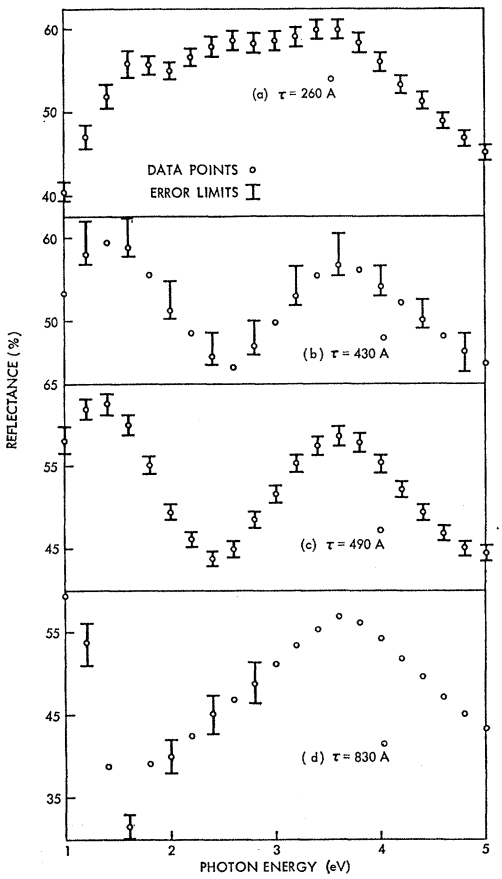

FIG. 2. Reflectance data. At each point for which the optical constants were calculated, limit marks are used to show the maximum error in the data.

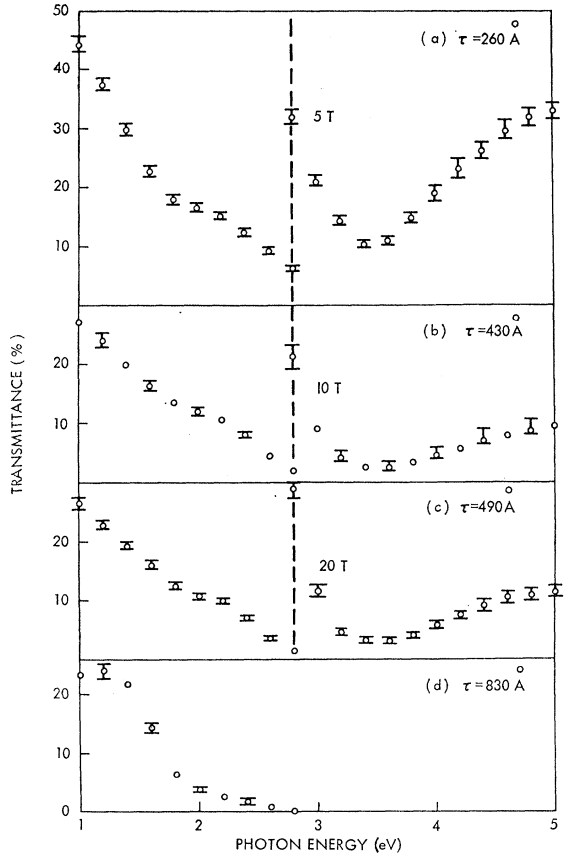

FIG. 3. Transmittance data. The transmittance data are shown in the same manner as the reflectance data in Fig. 2, except for a scale change at 2.8 eV. From 2.8 to 5.0 eV, the points plotted are $5T$, $10T$, and $20T$ for the 260-, 430-, and 490-Å films, respectively.

3 to 10%, depending primarily on the magnitude of the transmittance, since a transmittance of 20% can be measured with much greater precision than one of 0.2%. The signal level due to scattered light was measured at many points in order to assess its importance. The level was found to be approximately 0.1% for reflectance measurements and less than 0.02% for transmittance. The data were corrected for the presence of scattered light wherever it was significant. The measurements on these films were made immediately after the films were removed from the vacuum system in which they were grown.

The 430 and 830 Å films were not of the same high quality as the two mentioned above. In particular, a slight frosting of the back surface of the substrate of the 430 Å film indicated that it had been exposed to moisture. This was expected to lead to losses of both reflected and transmitted radiation and the error limits were changed accordingly. A limited amount of data was obtained from the 830 Å film since the transmittance beyond 2.8 eV was too small to be measured.

In addition to the above, measurements were made on a film approximately 80 Å thick and the reflectance of a film 1.4 μ thick was also measured. Part of the data obtained from the thin film was inconsistent and the transmittance of the thick one could not be measured. The only use made of these data is in the discussion.

IV. CALCULATIONS

A. Film Thickness

A major problem in any optical study involving the use of thin films is the determination of film thickness. An independent measure of thickness is highly desirable in such cases but for very thin films on crystalline substrates many of the conventional methods of thickness determination cannot be used.

Optical-interference methods cannot be used because of the unevenness of the substrate. Weighing or quantitative chemical analysis will be too inaccurate owing to the small amount of material present. Colorimetric analysis or radioactive tracer techniques may be successfully employed but are complicated and difficult to use. A quartz-crystal resonance device could also be used but was not available.

In view of these problems, it was felt that the use of the equations given by Hall and Ferguson[4] and the carefully obtained optical constants of Schoolar and

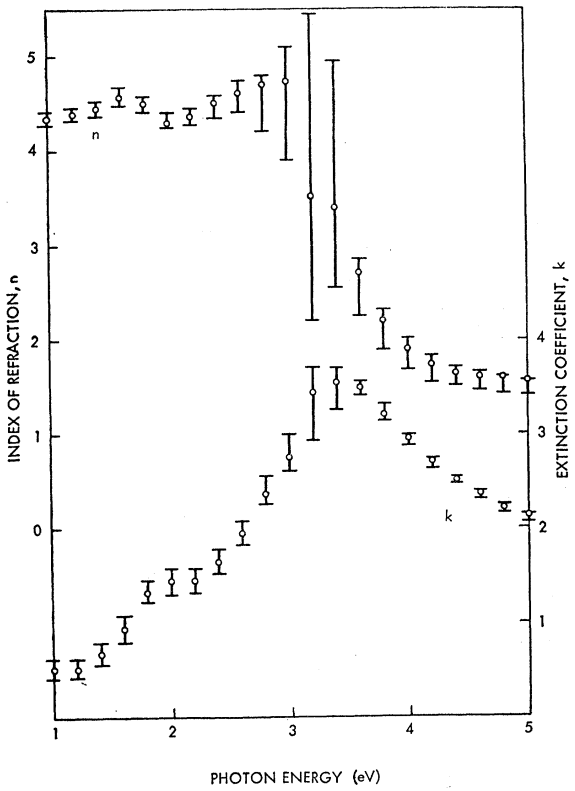

FIG. 4. The index of refraction n and extinction coefficient k obtained from the data for the 260-Å film.

[4] J. F. Hall, Jr., and W. F. C. Ferguson, J. Opt. Soc. Am. 45, 714 (1955).

Dixon[5] would provide the most accurate consistent means of determining the film thicknesses. The thickness was calculated for each film from the experimental reflectance and transmittance data at 1.2 eV.

The obvious problem here is that thickness dependence of the optical constants at 1.2 eV would lead to erroneous thicknesses for the films. Keeping this problem in mind we proceeded to derive the optical constants throughout the spectral region under consideration and found them to be remarkably self-consistent. Any large thickness dependence of the optical constants could be expected to interfere with the consistency of the results since the reflectance and transmittance are complex functions of the optical constants, the thickness, and the wavelength of the incident radiation. The data obtained in this study are insufficient to provide absolute proof of the thickness independence of the optical constants but does indicate that this effect is at least small. A comparison of the optical constants obtained for a given set of experimental data at two different thicknesses indicates that a change in thickness of 10% will necessitate changes of opposite sign ranging from 0 to 10% in both n and k. The magnitude of the change is, of course, a function of the thickness and of the energy of the incident radiation. It was also observed that changing the assumed thickness by as much as 10% resulted in several data points which could not be matched in the calculations with any reasonable values of the optical constants.

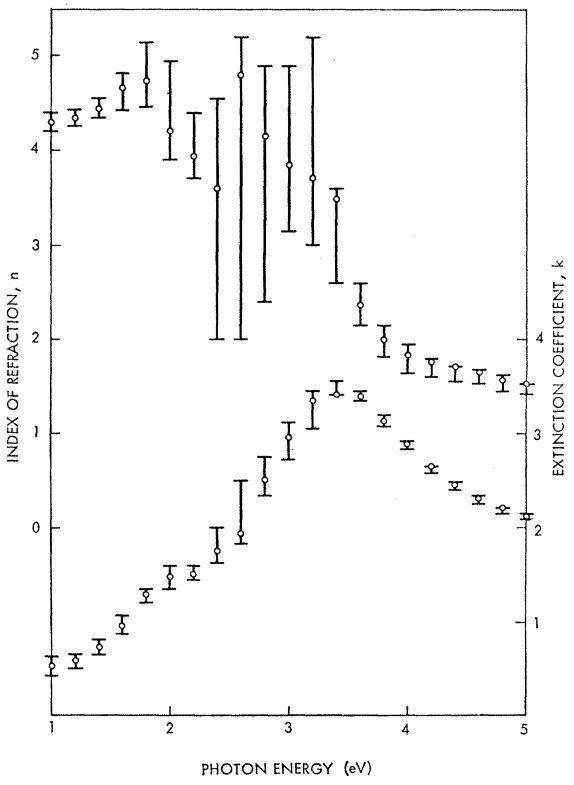

FIG. 5. The index of refraction n and extinction coefficient k obtained from the data for the 490-Å film.

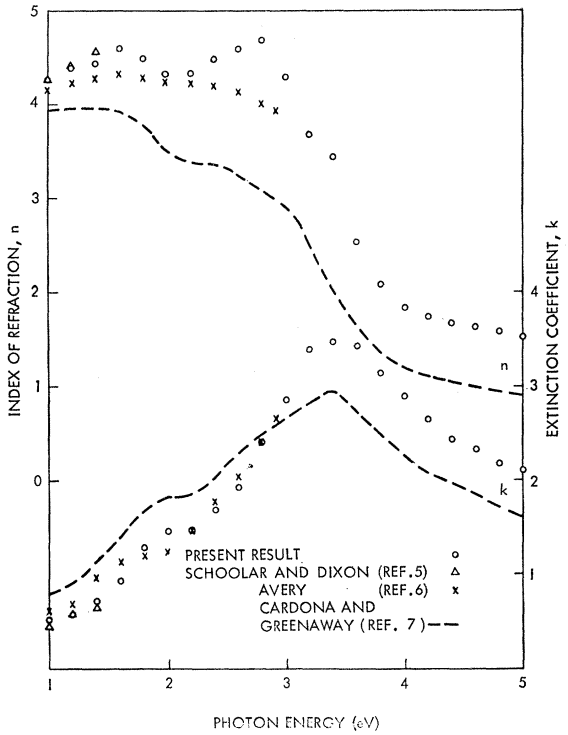

FIG. 6. The optical constants of PbS obtained by previous investigators compared with the present results.

B. Optical Constants

Using the calculated thicknesses, and the data and error limits shown in Figs. 2 and 3, we have determined the optical constants which correspond to the data. The limiting values of n and k have been determined from the maximum error in the data.

The optical constants obtained for the 260 and 490 Å films are shown in Figs. 4 and 5. The greater errors associated with the data from the 430 and 830 Å films led to somewhat broader limiting values of the optical constants. In each case where they were calculated they were generally in excellent agreement with the results given for the other two films and serve to reinforce the conclusion that the optical constants show no appreciable dependence on thickness. The large uncertainty in the determination of n near 3 eV will be discussed later.

Values of the optical constants have been obtained by taking the average of the points shown in Figs. 4 and 5, except where one film gave an obviously more certain result that single point was used. These values are plotted in Fig. 6 along with the results of Schoolar

[5] R. B. Schoolar and J. R. Dixon, Phys. Rev. 137, A667 (1965).

and Dixon,[5] Avery,[6] and Cardona and Greenaway.[7] The excellent agreement with the results of Ref. 5 is expected since they were used as a starting point for determining the film thickness. The most significant result of this comparison is the very good agreement obtained with the data of Avery. His optical constants were obtained from measurements made on single crystals of the bulk material. The excellent agreement with the present thin film results over most of the energy range indicates that they can be applied directly to the bulk material.

The poor quantitative agreement with the results of Cardona and Greenaway is probably due in part to the different methods used for the derivation of the optical constants, and in part to rather large differences in the measured reflectivity of PbS.

V. CONCLUSIONS AND DISCUSSION

From the data collected during this investigation we have been able to reach the following conclusions:

(1) The optical constants obtained from thin epitaxial films of PbS are nearly independent of thickness and may be applied to the bulk material. This conclusion is substantiated by comparing the data obtained from the various films, and by the agreement between the present results and those of Avery. The normal incidence reflectivity calculated from the derived optical constant also agrees very well with the measured reflectivity of a 1.4-μ thick film. The optical constants obtained from the data on the 80 Å film did not agree with the remainder of the data beyond 3 eV, indicating the existence of a lower limit for useful film thicknesses.

(2) Generally, the allowed range of magnitude for the optical constants is about the same as the error involved in the measurement of the reflectance and transmittance, i.e., $\pm 5\%$ or less, if the thickness can be obtained accurately. This is true except near 3 eV where the index of refraction is practically indeterminate.

The reason for this indeterminancy can best be illustrated by solving the normal-incidence-reflectivity equation for n, from which we obtain

$$n=\frac{1+R}{1-R}\pm\left[\left(\frac{1+R}{1-R}\right)^2-(1+k^2)\right]^{1/2}. \qquad (1)$$

When the quantity under the radical is very small a 2% change in R, with k held constant, may be sufficient to change the value of the radical from 0.1 to 0.7. Thus a small uncertainty in the reflectivity can lead to a large uncertainty in the index since we have the additional problem of deciding which sign to place in front of the radical. This is precisely what occurs in the case of PbS. The two roots of Eq. (1) are equal somewhere near 3 eV, but without absolute precision in the measurements we cannot determine exactly where this point is located. We are therefore unable to make a very precise determination of the index in this region on the basis of thin film data.

The presence of interference phenomena also reduces the accuracy with which the optical constants can be determined. Since the location of such phenomena is dependent on the film thickness one might expect the region of inaccuracy to shift with the film thickness. This was actually observed, the determination of n from the 830 Å film data being rather poor even at 1.2 eV, while the 490 Å film gave reasonably good results to 2.2 eV, and the 260 Å film to 2.8 eV. This result implies that the best determination of the optical constants can be obtained by using the data from one relatively thick film and one very thin one.

(3) The use of thin-film optical data for the derivation of optical constants is superior to the use of dispersion relations in several respects. To be used successfully, the dispersion method requires accurate measurement of the reflectivity over a wide energy range and extrapolation of the reflectivity beyond the range of measurement. The first requirement can be met only if very extensive optical equipment is available and the second can severely limit the accuracy of the final result. In contrast to this, to derive the optical constants at a given energy from thin film data, one need only measure the reflectance and transmittance at that energy and have a reasonable approximation to the film thickness and the index of refraction of the substrate.

In summary, the present work has shown that the use of thin film samples can be of great value in many optical studies, but that an independent, accurate measure of sample thickness is necessary to obtain the maximum amount of information from the data.

ACKNOWLEDGMENTS

I wish to thank J. R. Dixon for his continuing interest and assistance in all phases of this program. I also wish to thank R. B. Schoolar and E. G. Bylander for preparing the samples, and J. N. Zemel and H. R. Riedl for many interesting discussions of the general physical properties of PbS.

[6] D. G. Avery, quoted by T. S. Moss, *Optical Properties of Semiconductors* (Academic Press Inc., New York, 1959).

[7] M. Cardona and D. L. Greenaway, Phys. Rev. 133, A1685 (1964).