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Optical Constants of Germanium: 3600 A to 7000 A

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The optical constants of single-crystal Ge, obtained from the ellipticity of reflected polarized light, exhibit two maxima. The real part of the index of refraction has maxima of 5.66 at 6000 A and 4.24 at 3900 A. The extinction coefficient has a maximum of 2.3 at 4900 A and another, just outside the range of the measurements, at about 3100 A with a value of about 3.3. The data are consistent with the Kramers-Kronig relations, and it is concluded that the absorption curve has only two maxima and rapidly approaches zero beyond 2500 A. There are significant differences between the five published measurements of the optical constants of Ge in the visible. Of the two previous works that used single-crystal material, the present results disagree with one and agree with the other which, however, covers over 700 A of the visible.

INTRODUCTION

THE optical constants of single-crystal Ge have been obtained in the wavelength range 3600–7000 A from measurements of the state of polarization of reflected polarized light. The need for accurate values in the visible and ultraviolet became apparent when plots of data from the several reports in the literature showed disagreements both as to the magnitudes and the characteristics of the wavelength dependence of the optical constants. These discrepancies are attributed to the fact that three[1–3] of the five measurements were made on evaporated films whose optical constants may differ not only from bulk material but also from film to film, depending upon method of preparation and history.[3] Of the two previous measurements on single crystals, one[4] gives reliable values but is limited to wavelengths longer than 6300 A and only the absorption coefficient was measured. The remaining literature report gives constants measured by reflection from single-crystal material.[5] The gross lack of agreement of these results with the present measurements may be caused by a relatively thick oxide film on the surface used by these workers, which was not taken into account in calculating optical constants. The large effect of even very thin films on the values of optical constants calculated from reflection data is shown in this report and was taken into account in designing the experiment and in calculating the results of the present measurements.

PRINCIPLES

Consider a beam of plane polarized monochromatic light in 45° azimuth obliquely incident upon a reflecting surface. This beam may be resolved into two in-phase orthogonal plane wave components of equal amplitude—one in the plane of incidence the other normal to it. After reflection these components will in general be out of phase by the angle Δ and the ratio of their amplitudes (parallel to perpendicular) will be reduced to the value $\tan\Psi$. The angles Δ and Ψ are the experimental quantities of the present work. Their magnitudes depend only upon the angle of incidence and the optical constants of the reflecting substance *if the reflecting surface is film-free*. The dependence is expressed by[6]

$$\frac{1-e^{i\Delta}\tan\Psi}{1+e^{i\Delta}\tan\Psi}=\left(\frac{n^2-k^2-\sin^2\phi-i2nk}{\tan\phi\,\sin\phi}\right)^{\frac{1}{2}}, \tag{1}$$

where ϕ is the angle of incidence and the complex index of refraction is

$$\bar{n}=n-ik. \tag{2}$$

k is often called the extinction coefficient and is related to the absorption coefficient by $k=\alpha\lambda/4\pi$. Separating the real and imaginary parts of Eq. (1) yields

$$n^2-k^2=\tan^2\phi\,\sin^2\phi\frac{(\cos^2 2\Psi-\sin^2 2\Psi\,\sin^2\Delta)}{(1+\sin 2\Psi\,\cos\Delta)^2}+\sin^2\phi, \tag{3}$$

$$2nk=\tan^2\phi\,\sin^2\phi\frac{\sin 4\Psi\,\sin\Delta}{(1+\sin 2\Psi\,\cos\Delta)^2}. \tag{4}$$

n and k are calculated from Eqs. (3) and (4) using experimental values of Δ and Ψ.

Both Δ and Ψ are affected by the presence of a surface film according to the equations

$$\delta\Delta=\alpha L, \tag{5}$$

$$\delta\Psi=-\beta L, \tag{6}$$

where L is film thickness and the coefficients α and β are functions of n, k, ϕ and the index of refraction of the film. Equations (5) and (6) are valid for $L<100$ A. The functions α and β for Ge have been given previously.[7] Their magnitudes are such that a 10 A oxide film on Ge causes calculated k values to be too large by from 2% to 30% in the range of k values reported here. Calculated n values are correspondingly too small

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[1] W. H. Brattain and H. B. Briggs, Phys. Rev. **75**, 1705 (1949).
[2] H. M. O'Bryan, J. Opt. Soc. Am. **26**, 122 (1936).
[3] A. H. Gebbie, Ph.D. thesis, Reading, 1952 (unpublished).
[4] W. C. Dash and R. Newman, Phys. Rev. **99**, 1151 (1955).
[5] D. G. Avery and P. L. Clegg, Proc. Phys. Soc. (London) **B66**, 512 (1953).
[6] R. W. Ditchburn, J. Opt. Soc. Am. **45**, 743 (1955).
[7] R. J. Archer, J. Electrochem. Soc. **104**, 619 (1957).

by from 0.6% to 5%. It is clearly necessary to take into account the effect of surface films in evaluating optical constants from reflection data by applying to the experimental measurements the corrections given by Eqs. (5) and (6).

The apparatus for measuring Δ and Ψ is shown schematically in Fig. 1. Incident elliptically polarized light is obtained with this arrangement, the ellipticity depending upon the orientations of the wave plate and the polarizer. These orientations are adjusted so that the incident ellipticity is just compensated by the phase difference Δ caused by reflection. The reflected beam is then plane polarized and can be extinguished by properly orientating the analyzer. Δ and Ψ are calculated from the extinction orientations by equations which will be given after specifying the necessary definitions and conventions. The orientation, P or A, of the polarizer or analyzer is the angle the electric field vector of a transmitted beam makes with the plane of incidence. The magnitude and sign of this angle is given by a conventional Cartesian coordinate system with the x axis in the plane of incidence, the y axis normal to it and the z axis coinciding with the beam. The direction of propagation is the positive z direction. The orientation, Q, of the mica wave plate is the angle made by its fast axis with the plane of incidence in the above coordinate system. The relative retardation δ, of the wave plate is the phase difference, produced by transmission through the plate, between two plane waves whose electric field vectors coincide, respectively, with the fast and slow axis of the plate. If the orientation of the wave plate is set at $Q=\pm 45°$ any phase change Δ can be compensated regardless of the value of δ, e.g., the mica sheet need not be a quarter-wave plate. The following relations are easily derived between Δ and Ψ and P, A, and δ.

$$\tan\Delta = \sin\delta \cot 2P, \tag{7}$$

$$\cos 2L = -\cos\delta \cos 2P, \tag{8}$$

$$\tan\Psi = \cot L \tan A = \tan L \cot A', \tag{9}$$

$$\tan^2\Psi = \tan A \tan A'. \tag{10}$$

Primed and unprimed quantities refer, respectively, to the cases $Q=-45°$ and $Q=+45°$. Tan$L$ is the ratio of the parallel to the perpendicular amplitudes in the incident beam.

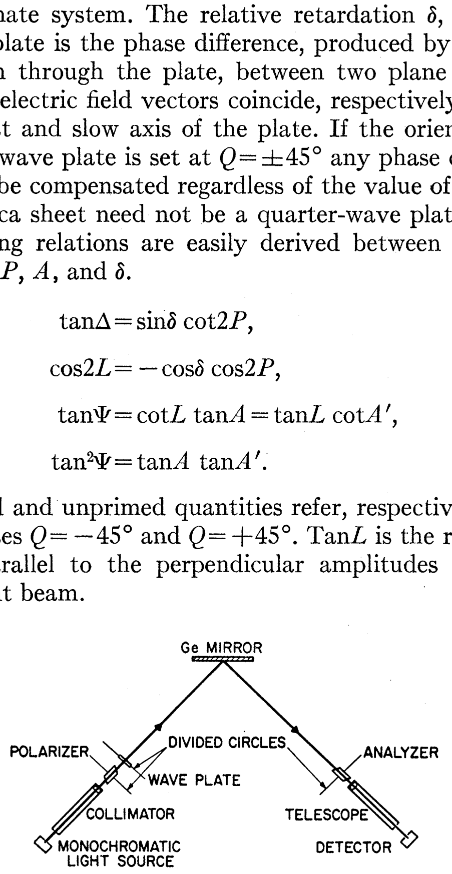

FIG. 1. Schematic representation of ellipsometer.

The relative retardation of the wave plate is a function of wavelength according to the equation

$$\delta = (2\pi/\lambda)d(n_0 - n_E), \tag{11}$$

where d is the thickness of the mica sheet. The dispersion of the difference between the indices of refraction for the ordinary and extraordinary beams is known to vary approximately linearly with wavelength. It is not necessary to measure $\delta(\lambda)$ independently since Eqs. (7) through (10) can be solved for Δ and Ψ without knowing δ. The procedure is to calculate Ψ from A and A' using Eq. (10). Then δ, calculated from Eq. (8), is used in Eq. (7) to find Δ. One such series of measurements throughout the wavelength range of interest, of course, yields the function $\delta(\lambda)$, and subsequent measurements can be performed at single Q settings. In agreement with Eq. (11) and the linearity of the dispersion of $(n_0 - n_E)$, δ was found to vary linearly with λ^{-1}.

TECHNIQUE

The polarizing spectrometer (Fig. 1) is a specially made Gaertner ellipsometer with glass lenses and quartz Glan-Thompson polarizing prisms mounted in rotatable divided circles which allow the orientations P and A to be read to ±0.01°. The mica wave plate is similarly mounted and is contained between glass slides. Extinction settings were obtained by using a photomultiplier microphotometer as the detecting element and employing a special technique (to be described elsewhere) that allows extinction settings to be made with a precision equal to that to which the divided circles can be read. A Gaertner quartz prism monochromator in conjunction with tungsten and mercury arc lamps constituted the monochromatic light source.

The presence of glass in the optical train limits the measurements to wavelengths longer than 3600 A. The long-wavelength limit, about 7000 A, is determined by the sensitivity of photomultiplier tubes.

The Ge mirror was mounted at the axis of the spectrometer in a metal cell through which clean dry nitrogen flowed at a rate of two liters per minute. To obviate the problem of strain double refraction in glass windows, the two windows in the metal cell were uncovered and served as outlet ports for the flowing nitrogen.

Measurements were made on both mechanically polished and etched 6 ohm-cm, single-crystal, p-type Ge mirrors. The polished mirrors were boiled in benzene and refluxed over acetone for several hours before being used. Immediately before the measurements they were rinsed for 15 seconds in HF followed by several rinses in redistilled acetone. This treatment was to assure a minimum oxide film thickness.[7] The etched surfaces were prepared by agitating polished mirrors in a mixture consisting of 4 parts HF and 21 parts HNO_3 for twenty seconds. While etched surfaces were not nearly as flat as the polished ones (as judged by the

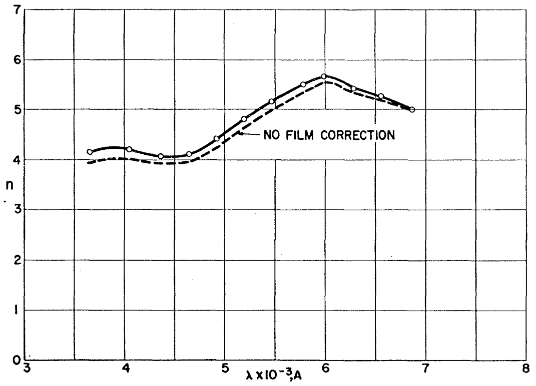

FIG. 2. Real part of index of refraction as function of wavelength. Broken curve fits data before film thickness correction is made.

sharpness of the collimator pin hole image seen with a Gauss eyepiece at the telescope), they were adequate for making the measurements.

The surfaces were very stable in the nitrogen environment. Three hours after the HF treatment, or the etch, film thickness increased by only 0.7 A as compared to an increase of 6 A when identically treated specimens were exposed to air.[7]

The solution of Eqs. (3) and (4) for Δ and Ψ gives two equations which define two mutually orthogonal families of circles in the p, q plane for constant Δ and Ψ, respectively.

$$p^2-q^2-\sin^2\phi=n^2-k^2,\quad pq=nk.$$

A nomograph was constructed on this principle from which p and q could be immediately read from pairs of values Δ, Ψ. The solution of a simple quadratic equation then yielded n and k. The errors in n and k taken from the nomograph were both about ±0.013 throughout the range of n and k measured.

Of considerable importance in evaluating n and k are the corrections to Δ and Ψ which must be made to compensate for the effect of a surface film. Three types of films could be present: a physically adsorbed film, e.g., water, a chemically adsorbed film or surface compound, e.g., oxide, and a Ge surface phase with optical properties different from the subphase, e.g., a mechanically damaged layer. In the present system, a physically adsorbed film may be discounted. The fact that polished and etched surfaces give identical values for the optical constants throughout the range measured precludes an optically different Ge surface phase. It is certain, however, that there is a surface oxide film. The approximate thickness and index of refraction of this film were obtained from some preliminary measurements of Δ and Ψ for a Ge mirror immersed in a series of organic liquids of different index of refraction. From the characteristics of plots of Δ and Ψ against ambient index of refraction, one is able to obtain 1.9±0.2 for the index of refraction of the oxide film and a value 10 A±4 A for the thickness of the oxide film on HF-rinsed surfaces in nitrogen. The principles of this analysis and the results of the experiments will be published when more comprehensive measurements have been made. These values for film thickness and index of refraction were used in Eqs. (5) and (6) to correct the experimental values of Δ and Ψ before n and k were calculated.

RESULTS

The results of the measurements and calculations are presented in Figs. 2 and 3. Each point in both plots is the average of three values—two from separate experiments on different mechanically polished mirrors and one from measurements on a etched mirror. The average of the average deviation of each set of three points from the mean is about 0.03 for both n and k. There is, therefore, close agreement between the optical constants for mechanically polished and etched surfaces. The experimental data are corrected for a 10 A oxide film before calculating optical constants. The broken curves are those upon which the values fall without the film correction.

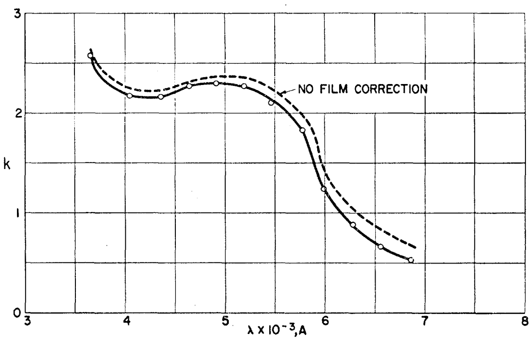

FIG. 3. Extinction coefficient (imaginary part of index of refraction) as function of wavelength. Broken curve fits data before film thickness correction is made.

An uncertainty of ±4 A in the thickness correction introduces an inaccuracy of about 0.1% in n and 10% in k at 7000 A. The inaccuracy is less for k and more for n at shorter wavelengths. This source of error outweighs those due to experimental and computational errors, which may be neglected.

The measurements reported here were made at an angle of incidence of 70°. Measurements at 60° and 75° for $\lambda=5461$ A gave values for n and k identical to those at 70°. It may be concluded therefore, that the measured values of the optical constants do not depend on the angle of incidence, as has sometimes been reported.[8]

DISCUSSION

Five previous workers have measured the optical constants of Ge in, or in part of, the wavelength range

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[8] R. M. Emberson, J. Opt. Soc. Am. 26, 443 (1936).

covered in the present work. All of these measurements are plotted in Figs. 4 and 5. The gross lack of agreement is apparent.

Of the various measurements, only two were made on bulk germanium. The rest used evaporated films. The most recent work is that of Dash and Newman[1] who measured by transmission the absorption coefficient of single crystalline plates. Their results extend only to about 6300 A from the infrared, but the values in the visible agree most closely with the present work. The agreement is good because the error in the transmission measurements, estimated by Dash and Newman to be about 20%, is largest in this range.

The other single-crystal work is the reflection measurements of Avery and Clegg.[3] The characteristics of their curves agree qualitatively with the present ones, but the magnitudes of the two sets of values disagree by about 30–40%. They do not specify the cleanliness of their surfaces, and did not correct their data for film effects. In view of this fact, it should be mentioned that a 40 A oxide film on the mirrors used in the present experiments would have affected the reflection parameters in such a way that optical constants calculated without correcting for the film effect would roughly agree with those of Avery and Clegg. This statement is only true for that part of their data at wavelengths greater than 4000 A. At shorter wavelengths the sign of the difference in magnitude for k is wrong for compensation by a film thickness correction. It may be significant that Avery and Clegg changed their measuring technique at 4000 A.

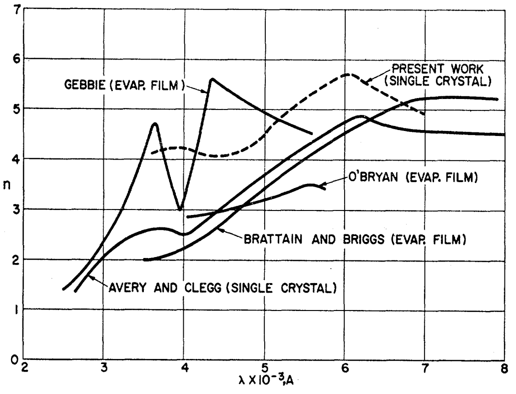

FIG. 4. Comparison of present with previous values for the real part of the index of refraction as function of wavelength.

Because of the probable differences in the optical constants of bulk material and evaporated films, an analysis of the discrepancies between the present results and the three sets of measurements[1–3] on films will not be given. It is clear from Figs. 4 and 5 that there are significant differences both in the characteristics of the curves and in the magnitudes of the optical constants between the various film results and between these results and those of the present work. Close agreement exists between the extinction coefficients of Gebbie and the present work. Gebbie's films were known to be crystalline.

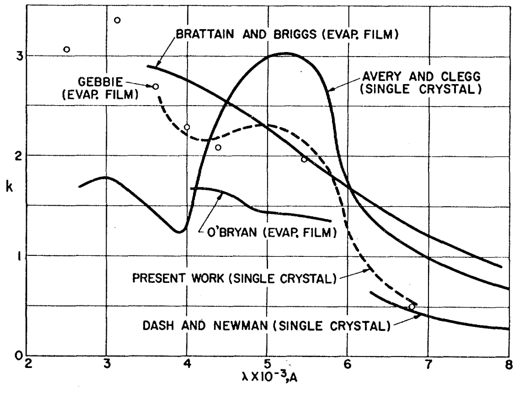

FIG. 5. Comparison of present with previous values for the extinction coefficient as function of wavelength.

The extinction coefficient curve, Fig. 3, suggests two absorption maxima with the data terminating short of the second peak. A more complete curve can be obtained by extrapolating the present data with suitably adjusted values from previous measurements. In particular, comprehensive data for the quantity $n\alpha$ are desired. Reliable values for this function in the infrared can be obtained by combining the α data of Dash and Newman with the n values of either Brattain and Briggs or Avery and Clegg. For the ultraviolet, α can be obtained from Gebbie's curve. n values in the ultraviolet have been chosen by extrapolating the curve of Fig. 2 parallel to the n curve of Avery and Clegg. The justification for this latter procedure is the fact that the two curves are approximately parallel in the visible. The resultant $n\alpha$ *versus* λ curve is shown in Fig. 6—the extrapolated portions are broken lines.

A test of the degree to which this curve gives the complete absorption curve for Ge can be had by apply-

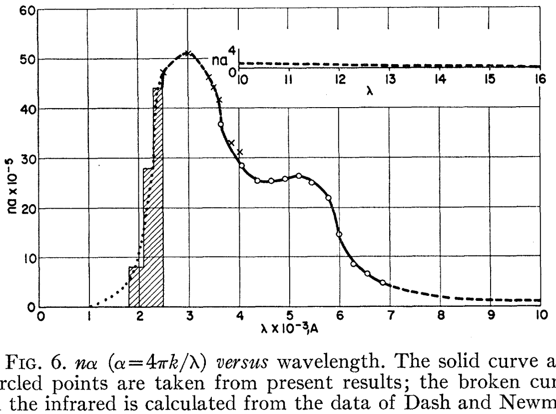

FIG. 6. $n\alpha$ ($\alpha = 4\pi k/\lambda$) *versus* wavelength. The solid curve and circled points are taken from present results; the broken curve in the infrared is calculated from the data of Dash and Newman and of Brattain and Briggs; the broken curve in the ultraviolet is from Gebbie's k values combined with n values obtained by extrapolating the curve of Fig. 2. The crosses represent the latter calculated points.

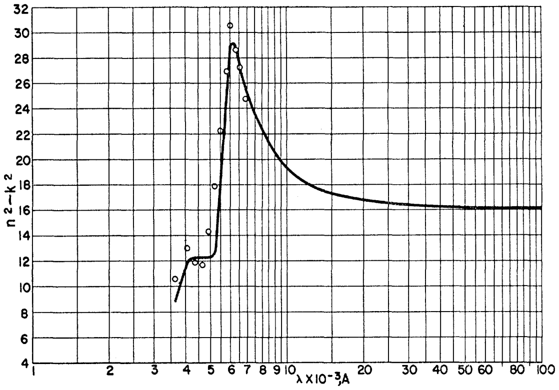

FIG. 7. Comparison of experimental values for the real part of the dielectric constant, n^2-k^2, with values calculated from the Kramers-Kronig relation.

ing the Kramers-Kronig relation[9–12] between the real and imaginary parts of the complex dielectric constant in the form

$$\pi^2(\epsilon_0-1)=\int_0^\infty n\alpha d\lambda, \qquad (12)$$

where ϵ_0 is the statical dielectric constant. $\epsilon_0=16$ for Ge. Graphical integration of the extrapolated $n\alpha$ curve up to the last point at 2500 A gives the value $\epsilon_0=14.3$, which is 11% smaller than the accepted value. In order for the integral to agree with the accepted value, the curve must encompass the additional area shown shaded in Fig. 6. It may be concluded therefore that the curve rapidly approaches zero beyond 2500 A and that the data of Fig. 6 give a nearly comprehensive absorption curve for Ge if the short-wavelength extrapolation is valid.

In its general form, the Kramers-Kronig relation between the real and imaginary parts of the dielectric constant is

$$n_1^2-k_1^2-1=\frac{\lambda_1^2}{\pi^2}\int_0^\infty \frac{n\alpha}{\lambda_1^2-\lambda^2}d\lambda. \qquad (13)$$

Thus, given the function $n\alpha$ at all wavelengths, the corresponding quantity n^2-k^2 can be calculated for any wavelength. As a check of the consistency of the experimental data and the validity of the extended $n\alpha$ curve, an n^2-k^2 curve, in the range of the present experiments and at longer wavelengths, was obtained by integrating Eq. (13). The function $n\alpha(\lambda)$ was obtained from Fig. 6 by using the final extrapolation beyond 2500 A shown. The result is Fig. 7 where the n^2-k^2 curve calculated from the Kramers-Kronig relation is compared with experimental values from Figs. 2 and 3. The agreement between the experimental points and the calculated curve is satisfactory in view of the fact that the curve, in the range of most of the experimental data and at shorter wavelengths, is strongly dependent on the shape of that part of the $n\alpha$ curve at shorter wavelengths than 3600 A where the present experimental values end. The long-wavelength tail of the curve should be as accurate as the experimental values since the integral beyond about 1 micron is nearly independent of the shape of the extrapolated part of the $n\alpha$ curve and depends principally on the total area under that curve.

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[9] H. A. Kramers, Atti Congr. Fis., Como (1927), p. 545.

[10] R. Kronig, J. Opt. Soc. Am. **12**, 547 (1926).

[11] J. H. Van Vleck, Massachusetts Institute of Technology Radiation Laboratory Report No. 735, 1945 (unpublished).

[12] T. S. Moss, Proc. Phys. Soc. (London) **B66**, 141 (1953).