OPTICAL PROPERTIES OF THIN GERMANIUM FILMS

By R. E. Denton* and S. G. Tomlin*

Abstract

The refractive and absorption indices of thin amorphous germanium films have been obtained from measurements, at normal incidence, of reflectances and transmittances over a wide range of wavelengths. The optical constants derived were in general agreement with the results of Tauc *et al.* (1964) except in the long wavelength region beyond the absorption edge. The absorption followed the law for indirect transitions from 0·72 to 1·1 eV, and the same law, but with a change in the slope of the curves, from 1·1 eV to the limit of our measurements at about 1·5 eV. The results are consistent with the view that the energy band structure of amorphous germanium is not essentially different from that of the crystalline material, except that the random structure eliminates the restriction that allows only direct transitions with the result that the absorption law for amorphous films is of the same form as for indirect transitions in crystals.

I. Introduction

Reviews of methods of determining the optical constants of thin films by Abelès (1963) and Rouard and Bousquet (1965) show the advantages of procedures based on measurement of the reflectance R and transmittance T at normal incidence. The calculation of the refractive index n and absorption index k from the measured values of R and T has been a formidable problem because of the very complicated relations between these quantities, and the existence of multiple solutions to the relevant equations. It has been shown by Denton, Campbell, and Tomlin (1972) that the calculations are much simplified by using expressions for $(1 \pm R)/T$ rather than those for R and T, and that the correct choice from the multiple solutions can be made unambiguously, together with an accurate determination of film thickness, provided measurements are made over a sufficiently wide range of wavelengths. The same paper also discusses the application of rigorous formulae, for a double layer film, to the investigation of thin surface layers and shows how to allow for the effects of such layers.

Several studies of the optical constants of germanium films (Brattain and Briggs 1949; Lukes 1960; Tauc *et al.* 1964, 1966; Grant and Paul 1966; Wales, Lovitt, and Hill 1967; Donovan, Spicer, and Bennett 1969; Tauc 1970) have yielded discrepant results due in part to the use of approximate formulae, or perhaps the wrong choice from multiple solutions, and also the lack of means of allowing for thin surface layers. In this paper we present results for amorphous films of germanium based on the use of rigorous formulae according to the methods discussed by Denton, Campbell, and Tomlin (1972).

* Department of Physics, University of Adelaide, Adelaide, S.A. 5001.

II. Experimental Method

The germanium films were deposited on optically flat quartz wedges in a conventional vacuum system in which the pressure during evaporation did not exceed 10^{-5} torr. The reason for using wedges is that light reflected from the back face of the substrate is deflected out of the optical path of the reflectometer so that multiple reflections within the substrate cannot affect measurements. At the same time the angle of the wedge is so small that transmission across the back face is given sufficiently accurately by the transmittance formula for normal incidence.

Table 1
CALCULATED AND MEASURED THICKNESSES OF GERMANIUM FILMS
d_1 is the thickness of the surface layer and d_2 the thickness of the germanium film alone

Film No.	Calculated d_1 (Å)	Calculated d_2 (Å)	$d = d_1 + d_2$ (Å)	Measured d (Å)
GE3	—	—	—	510 ± 25
GE4	10 ± 3	997 ± 3	1007 ± 6	1020 ± 23
GE5	$0-2$	1098 ± 10	1098 ± 12	—
GE6	$0-5$	1130 ± 5	1130 ± 10	1147 ± 35
GE7	$0-5$	1425 ± 20	1425 ± 25	—
GE8	10 ± 5	1750 ± 20	1760 ± 25	1743 ± 46

The substrate was rotated during an evaporation to improve the uniformity of film thickness. If this was not done it was found that closure of the dispersion curve (see Denton, Campbell, and Tomlin 1972) could not be achieved owing to insufficient uniformity of film thickness. The substrate temperature could be maintained at any desired temperature between room temperature and 700°C.

The measurements of optical reflectance and transmittance were made with a reflectometer slightly varied from the design of Strong (Kuhn and Wilson 1950). Full details of the apparatus and measuring procedures are given by Denton (1972).

Measurements of film thickness were made by the Tolansky method of fringes of equal chromatic order, following the procedure described by Campbell (1967).

III. Results for Amorphous Films

Films of germanium evaporated on the substrates at room temperature were found to be amorphous by X-ray diffraction. The experimental refractive and absorption index curves were very similar for all the films prepared provided the film thickness exceeded 400 Å. Results for two of the six films studied have been presented by Denton, Campbell, and Tomlin (1972, Figs. 5 and 6) and these illustrate the degree of closure of the dispersion curves achieved and the estimated errors. Six such results were obtained for films of thicknesses 510 to 1760 Å. Except in the case of the thinnest film, for which there were no multiple solutions within the wavelength range covered, the calculated n and k values were obtained by use of the double film formulae (Denton, Campbell, and Tomlin), with the closure criterion to determine the thickness of the film and of the oxide layer, if present. These thicknesses are given

in Table 1 together with the value measured directly by interferometry. For the thinnest film a direct measurement of thickness was used in the formulae for finding n and k.

Figure 1 shows the averaged dispersion and absorption curves from the six films, with the vertical bars indicating the limits within which the individual curves lay. The variations between the results from different samples are probably no more than is to be expected from imperfect control of evaporating conditions during the preparation of the films.
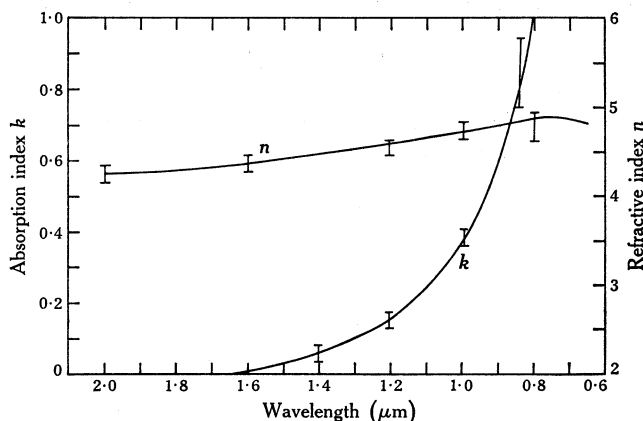

Fig. 1.—Average dispersion and absorption curves from six different germanium films. The vertical bars show the ranges within which the individual curves fell.

The calculated thicknesses of the surface films given in Table 1 are between 0 and 5 Å in three cases and about 10 ± 5 Å in the remaining two, although the films were subjected to the same treatment. The reasons for this discrepancy are not clear. It may be due to some small systematic error in the measurement of R and T, or to increasing thicknesses of oxide layers on exposure to the air, for which we have some evidence worthy of further study.

IV. Discussion

The theory of absorption processes in crystalline materials is treated in detail by a number of authors (e.g. Smith 1961). It is shown that for direct transitions, involving only a photon–electron interaction, the periodicity of the crystal lattice imposes certain selection rules which lead to the relation

$$(EnK)^2 \propto E-E_g, \tag{1}$$

where E is the photon energy, E_g is the band gap at the centre of the Brillouin zone, $K = 4\pi k/\lambda$, and n and k are the refraction and absorption indices at the wavelength λ corresponding to energy E. For indirect, or phonon-assisted, transitions in crystals the rule for allowed transitions is relaxed with the result that

$$(EnK)^{\frac{1}{2}} \propto E-E'_g, \tag{2}$$

where E_g' is the minimum gap between the conduction and valence bands, which is not at the centre of the Brillouin zone for germanium.

In the case of amorphous materials it might be expected that if the energy band structure is substantially unaltered then the indirect transitions will occur as for the crystalline material, and the formula for direct transitions will not apply because this results from a selection rule which depends upon the periodic crystal structure. When this rule is relaxed and all direct transitions which conserve energy are considered, instead of only those allowed in the perfect lattice, it has been shown by Tauc *et al.* (1964) that a relation of the same form as (2) results, namely

$$(EnK)^{\frac{1}{2}} \propto E - E_g, \tag{3}$$

where E_g is the band gap defined above. The constants of proportionality in the two expressions are, of course, different.
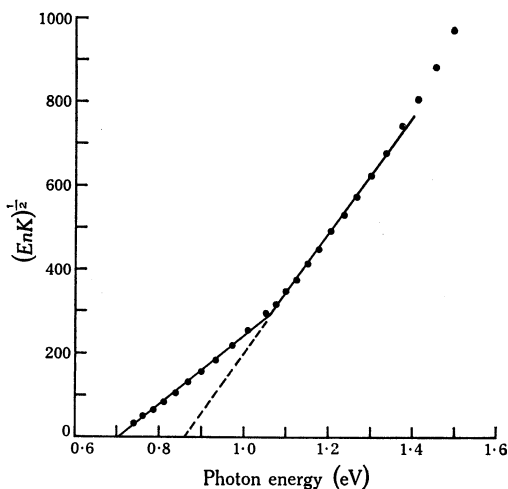

Fig. 2.—Plot of $(EnK)^{\frac{1}{2}}$ against $E - E_g'$ for the lower part of the curve, and against $E - E_g$ for the upper part. The intercepts on the axis give the energy gap values quoted in the text for amorphous germanium films.

From Figure 2, where $(EnK)^{\frac{1}{2}}$ is plotted as a function of photon energy E, it is evident that the results do fit the relations (2) and (3) above. The intercepts on the E axis give $E_g' = 0\cdot71$ eV and $E_g = 0\cdot86$ eV, which may be compared with $0\cdot72$ and $0\cdot89$ eV respectively obtained by Tauc *et al.* (1964), who used different methods of determining the optical constants of their films. For single crystal germanium the corresponding values are $0\cdot62$ and $0\cdot81$ eV. Thus the optical properties of these amorphous films support the view that the change from the highly ordered crystal structure to the random amorphous form has relatively little effect upon the electronic energy band structure.

V. Acknowledgments

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