

Optical Constants of Silicon in the Region 1 to 10 ev

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The reflectance, $|r(\lambda)|^2$, of single crystal silicon was measured in the range 1 to 11.3 ev. The phase, $\theta(\lambda)$, was computed from these data using the Kramers-Kronig relation between the real and imaginary parts of the complex function $\ln r = \ln|r| + i\theta$. The optical constants, n and k , were then determined from the Fresnel reflectivity equation. The real part of the refractive index, n , shows a sharp maximum of magnitude 6.9 at 3.3 ev. The extinction coefficient, k , shows maxima of magnitude 3.1 at 3.5 ev and 5.1 at 4.3 ev; optical absorption above 3 ev is associated with the onset of strong direct transitions. The results indicate that much useful information, applicable to band structure calculations for both silicon and germanium, could be obtained from limited reflectance studies (2 to 5 ev) on Ge-Si alloys.

INTRODUCTION

THE energy band structures of silicon and germanium are fairly well understood.¹ As additional experimental data are obtained, revisions and refinements may be made. One important source of such information is found in optical absorption studies. By applying the Kramers-Kronig relation to normal incidence reflectance data, information concerning optical transitions can be obtained in regions of the absorption spectrum not conveniently studied by direct transmission measurements. A previous paper has presented these data for germanium.² They are discussed in a recent letter by J. C. Phillips³ in terms of the energy band models for this crystal.

It is the purpose of this paper to present similar data for silicon. As in the case of germanium, there appears in the absorption spectrum sharp structure indicating the position of strong direct optical transitions. This absorption in silicon presumably occurs above the minimum direct energy gap, which has been tentatively in-

ferred from transmission studies.⁴ The results of the present work suggest that reflectance studies on mixed silicon-germanium crystals would be particularly rewarding in elucidating various aspects of the energy band picture of both silicon and germanium.

REFLECTANCE MEASUREMENTS

The procedures employed in these measurements have been described in a previous paper.² Reflectance data for etched silicon samples at 300°K are shown in Fig. 1. The uncertainty in the value of reflectance is estimated, from repeated measurements on different samples, to be less than 5% in the region 1 to 7 ev. Above 7 ev, the inaccuracy may be larger.

No corrections were made in these data for the possible presence of an oxide layer on the crystal surface. Values of reflectance measured immediately after etching and again at a later time were not significantly different in the spectral region below 7 ev. At higher energy, differences were observed. Aged samples showed a much more rapid drop in reflectance with increasing $h\nu$ than that given in Fig. 1. At 11.3 ev these values ranged from 35% for a sample measured immediately after

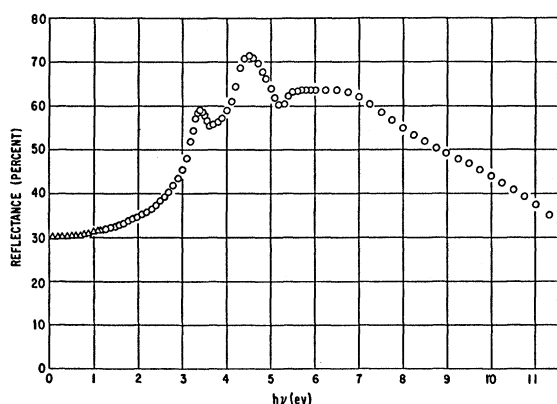


FIG. 1. Spectral dependence of the reflectance of Si. Below 1.2 ev, these values are calculated from direct measurements of index of refraction. [See C. Salzberg and J. Villa, *J. Opt. Soc. Am.* **47**, 244 (1957)].

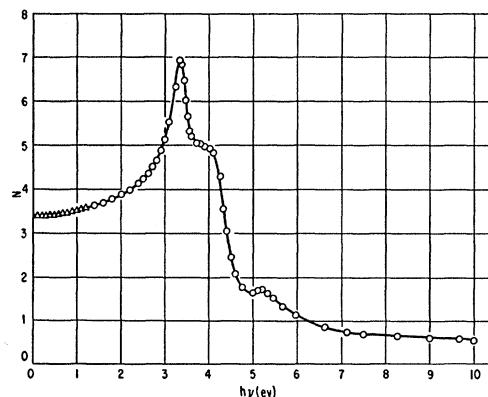


FIG. 2. Spectral dependence of the real part of the index of refraction of Si. Below 1.2 ev, the values are taken from the literature. [See C. Salzberg and J. Villa, *J. Opt. Soc. Am.* **47**, 244 (1957)].

¹ J. C. Phillips, *Phys. Rev.* **112**, 685 (1958); F. Herman, *Revs. Modern Phys.* **30**, 102 (1958).

² H. R. Philipp and E. A. Taft, *Phys. Rev.* **113**, 1002 (1959).

³ J. C. Phillips, *J. Phys. Chem. Solids* **12**, 208 (1960).

⁴ W. C. Dash and R. Newman, *Phys. Rev.* **99**, 1151 (1955).

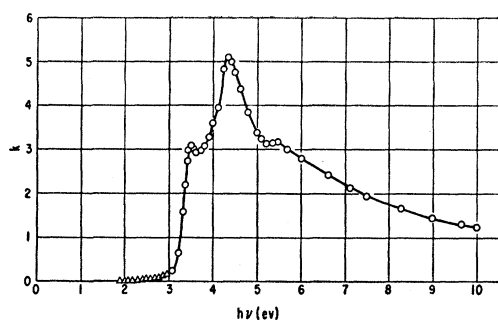


FIG. 3. Spectral dependence of the extinction coefficient (the imaginary part of the index of refraction) of Si. The absorption data of Dash and Newman (see reference 4) are plotted below 3.0 ev.

etching to 20% for a sample exposed to room air for a period of months. The results obtained immediately after etching are believed more significant for the purposes of the present investigation.

The data of Fig. 1 are in rough accord with measurements of reflectance appearing in the literature⁵ although there are differences in some details.

RESULTS AND DISCUSSION

Values for n and k derived from the reflectance data of Fig. 1 are shown in Figs. 2 and 3.⁶ Values of absorption constant, $\alpha = 4\pi k/\lambda$, are shown in Fig. 4. There are two salient features in this curve. First, the absorption rises rapidly just above 3 ev and goes through a maximum near 3.5 ev.⁷ Second, there is a relatively sharp peak near 4.3 ev.

The position of the minimum direct energy gap in silicon has been tentatively inferred from transmission studies⁴ to be near 2.4 ev.⁸ In Fig. 4 the rise in absorption just beyond 3 ev is related to the onset of strong direct optical transitions. It may conceivably be as-

⁵ S. Robin-Kandare and B. Vodar, *Compt. rend.* **248**, 1965 (1959); S. Robin-Kandare, M. Damany, and L. Tertian, *J. phys. radium* **20**, 504 (1959); V. S. Vavilov, A. A. Gippius, and M. M. Gorshkov, *J. Tech. Phys. (U.S.S.R.)* **28**, 254 (1958) [translation: *Soviet Phys. (Tech Phys.)* **3**, 230 (1958)].

⁶ The details relating to this calculation are given in reference 2. Beyond 11.3 ev, the reflectance was linearly extrapolated in a plot of $\ln R^{\frac{1}{2}}$ vs $\ln h\nu$ to 15% at 15 ev, 0.71% at 30 ev, and to 0.014% at 120 ev.

⁷ The nature of this peak as derived in this paper depends on the exact way in which R varies with $h\nu$ in this region. Since some error in reflectance measurements may be present, an alternative method for evaluating n and k in this spectral region was employed for purposes of comparison. These measurements were kindly performed by D. T. F. Marple using the procedures described in S. Roberts, *Phys. Rev.* **114**, 104 (1959). His results are substantially the same as those in Figs. 2 and 3.

⁸ At 77°K there is observed in the absorption spectrum near 2.4 ev a small step which disappears when the sample is warmed to 300°K. Dash and Newman made the suggestion that this structure may be associated with the onset of direct transitions. This step is not present when a small amount of germanium is added to the crystal (see reference 11). Although the above interpretation appears plausible, it should probably be treated with caution until more complete information is available. Experiments on mixed crystals may throw light on this problem.

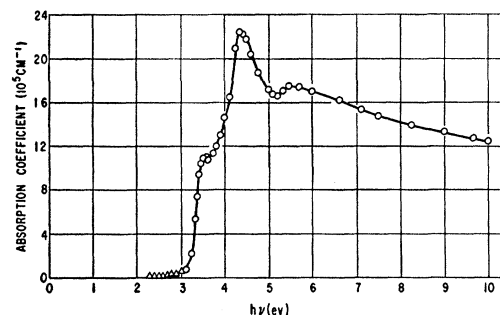


FIG. 4. Spectral dependence of the absorption coefficient ($\alpha = 4\pi k/\lambda$) of Si.

sociated with the direct gap $L_{8'} \rightarrow L_1$ located at $k = \pi a^{-1}$ (111), following the interpretation that has been given to similar structure appearing in the absorption spectrum of germanium near 2.3 ev.³ It is also interesting to note that the absorption peak at 4.3 ev in the curve for silicon is roughly coincident with structure in germanium.

There are additional experiments⁹ which could throw considerable light in the interpretation of these curves. Germanium and silicon are miscible in all proportions, and form a continuous series of solid substitutional solutions of fixed crystal structure over the entire composition range.¹⁰ Detailed transmission studies have shown that the primary absorption mechanism near the threshold of optical absorption is the same for germanium-silicon alloys as for pure germanium and silicon, namely, phonon-assisted indirect electronic transitions.¹¹ However, it is possible to follow the threshold for direct transitions only in germanium-rich alloys since structure associated with these transitions vanishes when the silicon concentration exceeds about 10 mole %.

The present results suggest that higher energy absorption processes should be evident throughout the entire range of alloy composition, since these transitions are strong in both the pure crystals. This information could be obtained from reflectance spectra measured over a limited energy range, say 2 to 5 ev.¹² Such results would be of considerable interest in understanding these materials.

ACKNOWLEDGMENTS

We are indebted to Dr. D. T. F. Marple for obtaining independent optical measurements in a critical region of the absorption spectrum and to Dr. H. Ehrenreich for many stimulating discussions and pertinent suggestions concerning this work.

⁹ The authors are grateful to H. Ehrenreich for suggesting this approach.

¹⁰ E. R. Johnson and S. M. Christian, *Phys. Rev.* **95**, 560 (1954).

¹¹ R. Braunstein, A. Moore, and F. Herman, *Phys. Rev.* **109**, 695 (1958).

¹² Dr. J. Tauc has informed us that interest in this problem has previously arisen in his laboratory; International Conference on Semiconductor Physics, Prague, August 1960 (to be published).