PHYSICAL REVIEW VOLUME 160, NUMBER 3 15 AUGUST 1967

Optical Properties of Germanium in the Far Ultraviolet

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(Received 7 April 1967)

Reflectance measurements for Ge films evaporated *in situ* are reported for 16 wavelengths between 490 and 1610 Å, corresponding to photon energies of 25.2 and 7.7 eV. Measurements were taken after 3-min exposures to ambient pressures of 5×10^{-7} Torr. Reflectance values at a number of angles of incidence were used to compute the optical constants: the refraction index n, the extinction coefficient k, and the real and imaginary parts of the frequency-dependent dielectric constant $\epsilon(\omega)=\epsilon_1+i\epsilon_2$. Values are also presented for the characteristic electron energy-loss functions, i.e., the volume loss, $-\mathrm{Im}\epsilon^{-1}$, and the surface loss, $-\mathrm{Im}(\epsilon+1)^{-1}$. The quantity $-\mathrm{Im}\epsilon^{-1}$ peaked at 16.1 eV and had a half-width of 3.9 eV. Electron oscillator strengths, summed between 8 and 25 eV, gave a $\hbar\omega_p$ value of 13.7 eV. The present data are in better agreement with the accepted plasma theory than are previous data. Some changes of optical characteristics caused by exposure to ambient pressures and air are presented.

INTRODUCTION

MEASUREMENTS of the reflectance of Ge films evaporated *in situ* for up to eight different angles of incidence between 20° and 80° were made at sixteen wavelengths ranging from 490 to 1610 Å. These were used to calculate the refraction index n, the extinction coefficient k along with the real and imaginary parts of the frequency-dependent dielectric constant. The specimens were exposed to ambient pressures of 5×10^{-7} Torr for approximately 3 min before measurements could be taken. Surface changes, presumably caused by oxidation, were monitored and seemed to provide the explanation of why previous investigators found lower reflectance than we. Comparison with the oscillator-strength sum rule indicated that our data were a reasonable approximation to what could be expected of the bulk properties. Summing electron oscillator strengths between $\hbar\omega_1=8$ eV and $\hbar\omega_2=25$ eV yielded a $\hbar\omega_p$ value of 13.7 eV, which, being the lower limit, was in reasonable agreement with the 15.6 eV obtained, if we assume that Ge behaves like a free-electron gas with four valence electrons per atom and the effective mass of the electron equal to the rest mass. Electron energy-loss functions computed from our reflectances have higher peak values than those obtained from previous optical data and are compared with the electron-scattering data.

APPARATUS

The apparatus has been described elsewhere[1] in greater detail. The main features were as follows: Ultraviolet radiation was produced in a duoplasmatron source that was modeled after the design of Samson.[2,3] Monochromatization was effected by a normal-incidence grating which had 600 lines per mm and was covered by an ultraviolet high-reflectance coating of MgF_2 on Al.[4] Target films were evaporated in an appendage of the system and transferred into the measurement chamber without breaking the vacuum. The ultraviolet light beam that was directed at the target film emerged from the monochromator with an angular divergence of 2° in the plane of incidence, which would not introduce a significant error. The incident as well as the reflected intensities were detected with a traveling photomultiplier, its signal being fed into and observed on an electrometer.

VACUUM PROCEDURE

The instrument was pumped by a differential pumping system consisting of 4 Hg-diffusion pumps that were separated from the high-vacuum side by refrigerated baffles and liquid-N_2 traps. These pumped the measurement chamber down to 1×10^{-6} Torr; then a Ti ion-getter pump was activated and further reduced the gauge reading to 5×10^{-7} Torr. The evaporation chamber, which could be separated from the measurement chamber by a valve, was pumped by an oil-diffusion pump and protected against back diffusion by a zeolite sieve trap. The chamber was provided with a liquid-N_2 finger, and a water-cooling sleeve surrounded the evaporation source. The evaporation chamber had no gauge, but pressure changes produced by valving it off from the measurement chamber indicated that the pressure was lower than in the measurement chamber.

Ge was evaporated from Ta boats onto glass slides about 20 cm above the boat level. During a typical evaporation, the gauge in the measurement chamber recorded pressures of about 2×10^{-6} Torr; the pressure in the evaporation chamber was undoubtedly higher. Pressure dropped to the background level within a few seconds of the evaporation.

MEASUREMENT PROCEDURE

In the course of an average run, 4–5 evaporations were made from a Ta boat onto one glass substrate at

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[1] L. Marton, J. A. Simpson, J. A. Suddeth, and L. B. Leder, *1961 Transactions of Eight Vacuum Symposium and Second International Congress* (Pergamon Press, Inc., New York, 1962), p. 633.

[2] J. A. R. Samson and H. Liebl, Rev. Sci. Instr. 33, 1340 (1962). We are grateful for additional information Dr. Samson conveyed to us in personal communications.

[3] We are indebted to Dr. H. A. Fowler for the design and building of the duoplasmatron.

[4] The coating was kindly prepared for us by Dr. George Hass of the U. S. Army Engineer Research and Development Laboratories, Ft. Belvoir, Virginia.

intervals of about an hour. At the completion of an evaporation, the specimen was lifted into the measurement chamber and latched onto a holding rod. The specimen could be retracted for monitoring the intensity of the incident light. Then the photomultiplier, which travels on a circle coaxial to the specimen holding rod, was set at a desired angle, the specimen was pushed into the beam and rotated until the signal of the reflected beam reached a maximum. Then the angular setting of the photomultiplier was changed and the reflected intensity recorded for another angle of incidence until reflectances had been measured for a set of 5–8 incident angles at one wavelength. This procedure took 2–3 min at each wavelength and the measurements could commence about 2 min after evaporation. The primary beam intensity was checked for drift before and after recording each set of reflected intensities. Measurements were continued for about an hour after evaporation to monitor changes of reflectance with time; during this hour some data were also taken at other wavelengths to check the reproducibility of time history, at identical wavelengths, for reflectances obtained from different evaporations. Measurements of the reflected intensities, at each wavelength, started from the higher incident angles. Data at higher angles of incidence, which could be taken faster, were more sensitive to contamination and had a correspondingly stronger effect on the subsequently computed optical constants than the values at smaller incident angles. Angular accuracy of the photomultiplier setting was estimated to be $\frac{1}{4}$°.

Deposition rates were determined by measuring the thickness of films deposited by evaporations of different durations. Thicknesses of two pairs of films produced, from one boat, by consecutive evaporations lasting 3 and 6 sec were determined with a Tolansky interferometer. These measurements indicated deposition rates of 230 and 320 Å per sec. Judging from these deposition rates and durations of the evaporation flashes, the thickness of the films used in reflectance measurements ranged from 400–1000 Å.

RESULTS AND DISCUSSION

The data shown on Fig. 1 were taken about 3 min after evaporation, using a different film at each wavelength. Curves drawn through the data points are for identification purposes. Variations in these measurements can be caused by slight differences in preparation parameters, pressure conditions, and times elapsed between evaporation and measurements. To these must be added the random errors in the photomultiplier angular setting and reading of the electrometer scale. Estimated limits of random errors were ±2% in each measurement, leading to a maximum error limit of ±3% in the reflectance values on Fig. 1. The data from repeated evaporations at one wavelength, and those of nearly equal wavelengths in regions of slowly changing reflectance, have fallen within the expected limits of consistency. The reflectance as a function of time was closely reproducible for any wavelength from different evaporations.

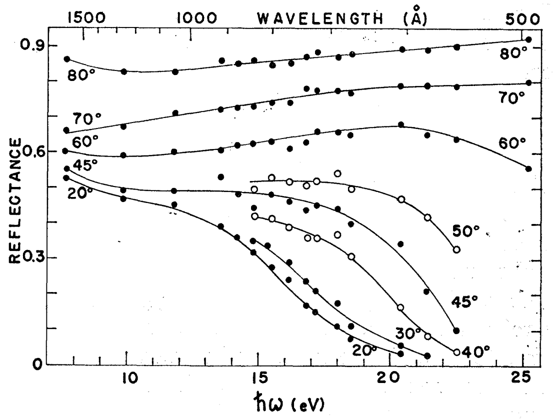

FIG. 1. Reflectance as a function of wavelength at different angles of incidence. Dots and circles indicate reflectance values at particular wavelengths and angles of incidence. Curves have been drawn to help identify the symbols with their proper angles of incidence.

The optical constants n, k, ϵ_1, and ϵ_2 were calculated with a computer [5] using all the reflectance values shown on Fig. 1, in the hope that the effect of random errors would be minimized by using many reflectance values. The "best" values obtained from these calculations are shown on Fig. 2. The polarization introduced by the grating is not known and the beam was assumed to be unpolarized in these calculations; changes up to 2% in n and k values were introduced by assuming 5% polarization.

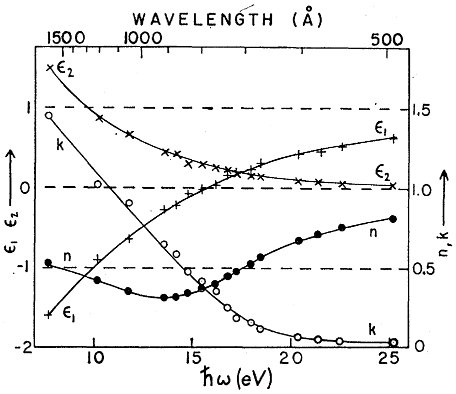

FIG. 2. Optical constants n and k and the real and imaginary parts of the complex dielectric constant $\epsilon(\omega)=\epsilon_1+i\epsilon_2$, as calculated from the reflectance values on Fig. 1. Closed circles indicate the refraction index n; open circles, the extinction coefficient k; plus signs, the real part of the dielectric constant; crosses, imaginary part of the dielectric constant.

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[5] The computer programs were written by Mrs. J. Shapiro of the National Bureau of Standards Far Ultraviolet Section. We are indebted to her and to Dr. R. P. Madden for their kind permission to use these.

Errors[6] of n and k caused by uncertainties in the reflectance values should be comparatively small in the short-wavelength region where reflectance varies steeply with the incident angle. The n value should be especially good as it depends mostly on the more precise reflectance values at the low angles of incidence. The probable error is greater for k, which depends strongly on the less precise reflectance values at high incident angles. The precision of both is smaller at long wavelengths, where the reflectance is a less sensitive function of the incident angle. At 16.8 eV, a 3% uncertainty in the reflectance at 20° and 80° leads to k values ranging from 0.19 to 0.28 and n values between 0.45 and 0.49.

In this wavelength region the earliest optical data on Ge were taken by Sabine[7] and Banning.[8] More recent measurements on exposed single crystal surfaces have been taken by Rustgi, Nodvik, and Weissler,[9] Philipp and Ehrenreich,[10] and Sasaki.[11] Measurements on films evaporated *in situ* have been reported by S. Robin-Kandare[12] and Madden.[13] Transmission data have been published by Hunter, Angel, and Tousey,[14] and LaVilla and Mendlowitz[15] have obtained values for optical constants from electron-scattering data.

Our n values were lower than those of other investigators. The changes due to contamination, as shown on Fig. 3, strongly suggest that lower n values are an indication of a cleaner surface and thus a criterion of better data. Sasaki had the lowest n values among the data published for the exposed and presumably contaminated surfaces. His n values are plotted on Fig. 3 and give some idea of the difference between exposed and freshly evaporated surfaces; additional discrepancy may be incurred from the different degrees of orientation of our specimens. Among the previously published data, the n values of Madden[13] for 584 and 735 Å, taken from films evaporated *in situ*, bear the closest resemblance to our values. In their analysis of available optical and electron-scattering data, LaVilla and Mendlowitz[15] came to the conclusion that consistency requirements predict lower n values than those observed by Sasaki[11] and Philipp and Ehrenreich.[10]

Our k values are almost identical to those of Madden in the short-wavelength end and in good agreement with those of Philipp and Taft[16] in the long-wavelength limit. The changes in n, as shown on Fig. 3, indicate that k is not so sensitive to surface contamination as n and the changes produced are not as systematic. This probably accounts for the better agreement of k values with the previous results, that our data display.

An attempt was made to eliminate the effects of the contaminating surface film by time extrapolation. We determined the optical constants of a Ge film that had been converted into GeO_2 by 30 h of heating in air at 375°C. Then we calculated[5] the reflectance characteristics of a thin-film combination with a substrate of optical constants shown on Fig. 2, covered by a layer of arbitrary thickness having optical constants of the heated specimen. Changes predicted by the addition of such layers were consistent with the observed changes with time in only a limited part of the spectrum, 12–16 eV. Consequently, the optical properties of the film contaminating the vacuum-evaporated samples were not identical with those of a specimen heated in air, and extrapolation to an atomically clean surface was not feasible from these data. Using GeO_2 data of Madden,[13] which have n values identical to ours but slightly higher k at the three available wavelengths, did not yield a better agreement with the observed changes. This is expected, as the contamination may be of a complex nature. GeO_2 has two crystalline forms, which may have different optical properties, a film only a few Å thick may have a different density than a thicker film, and the situation may be further complicated by the presence of adsorbed oxygen. In the region of the lowest n values, near 14 eV, where maximum change occurs with time, the changes were consistent with growth of a layer having the properties of our heated specimens. At $\hbar\omega = 14$ eV the optical constants of our air-heated specimen were $n = 0.66$ and $k = 1.2$. Calculations made by assuming a 5 Å oxide layer with these optical properties superimposed on our best data yielded characteristics in agreement with those observed 10 min after evaporation; a 10 Å layer gave results similar to those observed 30 min after evaporation. Although this agreement may be fortuitous, it may also give a rough estimate of the surface cleanness and oxidation rate.

For most of the energy range, above 12 eV (below 1000 Å in wavelength), our reflectances are higher than those reported by other investigators. However, at wavelengths above 1000 Å our reflectances are lower than those reported by Madden[13] for 1215 Å and by S. Robin-Kandare[12] for the range of her measurements, 1100–2000 Å. There is strong evidence that our lower reflectances are the result of slower evaporation speeds. We have noticed that in the long-wavelength region increased deposition rates increase the reflectance, a fact also reported by the above authors. Our evaporation speeds of 200–300 Å/sec were slower than the 500 Å/sec rate used by Madden; thus it is not surprising that our reflectance values were also lower.

Dependence of reflectance on evaporation speed indicates that intrinsic differences in the films result from

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[6] W. R. Hunter [J. Opt. Soc. Am. **55**, 1197 (1965)] gives illustrations of the errors involved.

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[8] M. Banning, J. Opt. Soc. Am. **32**, 98 (1942).

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[12] S. Robin-Kandare, doctoral dissertation, University of Paris, 1959 (unpublished).

[13] R. P. Madden, in *Physics of Thin Films*, edited by G. Hass (Academic Press Inc., New York, 1963), Vol. 1.

[14] W. R. Hunter, D. W. Angel, and R. Tousey, Appl. Opt. **4**, 891 (1965).

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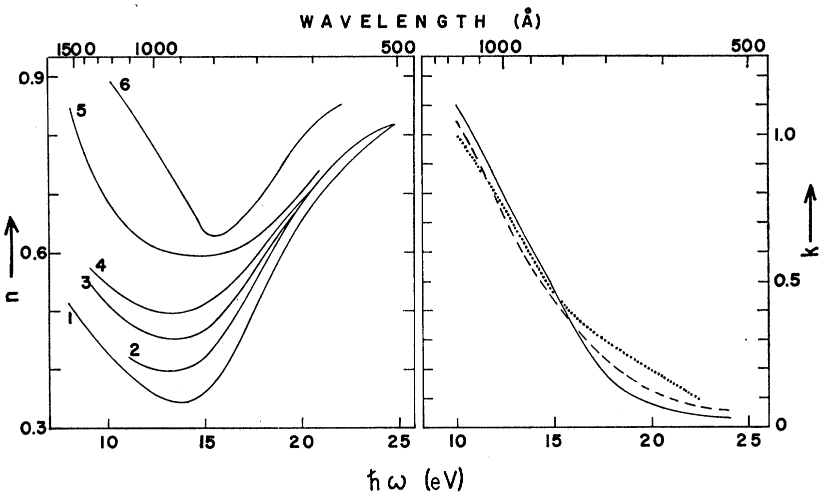
[16] H. R. Philipp and E. A. Taft, Phys. Rev. **113**, 1002 (1959).

FIG. 3. Changes produced in n and k by exposure of the specimen to vacuum and air. For the n plot: Curve number 1, n values computed from reflectance measured 3 min after evaporation; 2, 10 min after evaporation; 3, 30 min after evaporation; 4, 20 h after evaporation; 5, after 2 months exposure to air; 6, data of Sasaki. For the k plot the solid line is computed from data taken 3 min after evaporation; broken line is from measurements taken after 20-h exposure to vacuum; dotted line indicates the values after 2-months exposure to air. Below 16 eV, Sasaki's k values are higher than any of our curves, but closely follow our broken line at higher energies.



differences in the preparation conditions. These differences are probably caused by variation in the density and degrees of orientation, which we were unable to determine. However, by increasing the evaporation rate we were able to measure increased reflectance for the long wavelengths but not for the short ones. Thus the optical properties at short wavelengths seem less affected by the preparation conditions. This, however, has not been established unequivocally, since we were unable to separate the effect of surface contamination from those of the preparation conditions.

A check for our data is provided by the oscillator-strength sum rules. Our data did not cover an adequate range to sum the optical oscillator strength, but most of the electron oscillator strength, given by the relation[17]

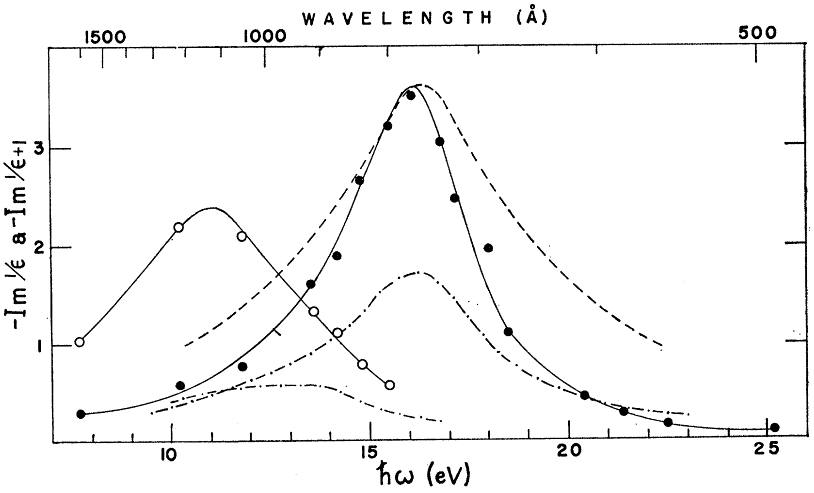
$$-\hbar^2\int_{\omega_1}^{\omega_2}\omega\,\mathrm{Im}\frac{1}{\epsilon}d\omega=\tfrac{1}{2}\pi\hbar^2\omega_p^2$$

was within the frequency range of our data. Substituting our $-\mathrm{Im}\epsilon^{-1}$ values from Fig. 4 and summing from $\hbar\omega_1=8$ eV to $\hbar\omega_2=25$ eV yielded $\hbar\omega_p=13.7$ eV. This value must be considered a lower limit because surface contamination has been observed to decrease the apparent oscillator strengths and a small contribution to the sum is expected from beyond our cutoff points. Thus our data are in reasonable agreement with $\hbar\omega_p=15.6$ eV obtained by assuming that the valence electrons of Ge behave like a free-electron gas with four electrons per atom. The most conspicuous change with time is the rise of n. If we were to assume n values lower by 0.05 throughout the range of our data, $\hbar\omega_p$ becomes 14.6 eV; lowering n by 0.1 raises $\hbar\omega_p$ to 16.1 eV. These figures give an approximate indication of the accuracy of our data and suggest that the chief residual systematic error was too high by a value of n.

CORRELATION WITH ELECTRON-SCATTERING DATA

Optical constants are related to the energy losses experienced by fast charged particles traversing the

FIG. 4. The characteristic electron-energy-loss functions. Closed circles indicates values of $-\mathrm{Im}\epsilon^{-1}$ and open circles those of $-\mathrm{Im}(\epsilon+1)^{-1}$ as computed from our data. Lines accompanying these symbols are calculated from the n and k curves on Fig. 2. Broken line indicates Swanson's electron-energy-loss line shape with the maximum normalized to 3.6. Dashed and dotted line represents the $-\mathrm{Im}\epsilon^{-1}$ and $-\mathrm{Im}(\epsilon+1)^{-1}$ values of Sasaki.



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[17] U. Fano, Phys. Rev. 103, 1202 (1956).

material. In the 10–30-eV range the energy is usually lost by exciting collective oscillations of the electron gas, and the excitation probability is directly proportional to $-\mathrm{Im}\epsilon^{-1}$.[18–21] The position of the $-\mathrm{Im}\epsilon^{-1}$ peak is associated with the density of the electron plasma, and the half-width is simply related to the plasmon decay time.

Figure 4 shows the values for $-\mathrm{Im}\epsilon^{-1}$ and the surface loss function[22] $-\mathrm{Im}(\epsilon+1)^{-1}$ as calculated from our n and k points on Fig. 2; lines accompanying these values are calculated from the n and k curves. Calculations made from the data taken at various times after evaporation indicated that contamination decreases the height and increases the width of the $-\mathrm{Im}\epsilon^{-1}$ peak. Also included are Sasaki's values[11] for these functions and the characteristic electron energy-loss curve of Swanson.[23] Normalization for the latter was achieved by setting the peak value equal to our $-\mathrm{Im}\epsilon^{-1}$ maximum. It can be seen that Swanson's curve with a half-width of 6.5 eV is considerably broader than ours. We have observed that contamination increases the $-\mathrm{Im}\epsilon^{-1}$ half-width; thus improved optical measurements are not expected to be in closer agreement with Swanson's data. Swanson estimated the film thickness to be several hundred angstroms, contaminating surface layers may have seriously affected the electron energy-loss spectrum of so thin a film and may be the primary cause of disagreement between our respective data.

Our highest $-\mathrm{Im}\epsilon^{-1}$ value occurs at a spectral line situated at 16.1 eV. The spectral lines are too far apart for a precise determination of the peak position, but symmetry of the other points suggests that it is quite close to the 16.1-eV line. Electron-energy-loss peaks reported in the literature[23–26] range from 15 to 18 eV; the more recent measurements give results in the 16 ±0.5-eV range. In some recent measurements the peak position has been found to depend on the crystalline form of the specimen. Richter and Rukwied[25] and Zeppenfeld and Raether[26] found the energy-loss peaks of crystalline specimens to be about 0.5 eV higher than those of the amorphous samples. Zeppenfeld and Raether also calculated the $-\mathrm{Im}\epsilon^{-1}$ curve according to a method given by Raether.[27] For crystalline specimens they found the $-\mathrm{Im}\epsilon^{-1}$ peak at 16.1 eV with a height of 5.4 and half-width of 3.4 eV; for the amorphous case the figures were 15.8, 3.8, and 4.0 eV, respectively. Half-width of the peak in $-\mathrm{Im}\epsilon^{-1}$, which we obtained, is almost identical to what they found for the amorphous case. Our $-\mathrm{Im}\epsilon^{-1}$ peak value of 3.5–3.6 is slightly lower, but it should be remembered that the contamination which occurred between evaporation and measurement probably lowered the $-\mathrm{Im}\epsilon^{-1}$ values. The peak position, however, shows closer agreement with the crystalline films of Zeppenfeld and Raether, whereas it is highly unlikely that our films were crystalline.

Excitation probability of the transverse or surface plasmon, given by $-\mathrm{Im}(\epsilon+1)^{-1}$, would have a maximum at $\hbar\omega_p/\sqrt{2}$.[28] In electron-scattering studies, Powell[24] has observed this peak at 11.2 eV. Values calculated from the n and k curves were in substantial agreement with that, although our ill-defined k in that region prevented a sensitive determination of the peak position. As in the case of $-\mathrm{Im}\epsilon^{-1}$ our value for $-\mathrm{Im}(\epsilon+1)^{-1}$ is considerably higher than those reported by previous investigators.

In a recent article, Bardasis and Hone[29] have postulated many-body effects to bring the predictions of a theoretical model into better agreement with the data of Philipp and Ehrenreich.[10] Our present data are closer to the predictions of their uncorrected model than to the results of Philipp and Ehrenreich. Our measurements demonstrate that, because of surface contamination, optical data of exposed specimens, such as those of Philipp and Ehrenreich, are expected to deviate from the predictions of a model which is valid for the bulk material. Ascribing this discrepancy to many-body effects may be unjustified.

CONCLUSION

We have measured the reflectance of Ge films evaporated *in situ* in the 490–1610 Å wavelength range. Internal evidence indicates the data to be a considerable improvement over previously published results, mostly because of improved vacuum conditions. In addition to higher reflectances, our maximum values of $-\mathrm{Im}\epsilon^{-1}=3.5$ and $-\mathrm{Im}(\epsilon+1)^{-1}=2.4$ are much higher than those computed from the optical data of previous investigators. Our $-\mathrm{Im}\epsilon^{-1}$ half-width of 3.9 eV is narrower than those found in previous optical measurements.

We have also observed that the reflectance of germanium in this wavelength range is quite sensitive to surface contamination. Thus we have not succeeded in determining the clean-surface properties but expect to have attained a good approximation to them. Our data, in spite of being limited by surface contamination, yielded an electron energy-loss line shape that was comparable to the best electron-scattering data.

ACKNOWLEDGMENTS

We would like to express our gratitude to Dr. H. A. Fowler for help in conducting the experiment and advice in preparing the manuscript. We are indebted to N. Swanson and Dr. H. Mendlowitz for interesting discussions and to Dr. R. E. LaVilla for numerous edifying discussions and a critical reading of the manuscript.

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