Optical Properties of Thin Germanium Films in the Wavelength Range 2000-6000 Å*

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Measurements have been made of the normal incidence reflectivity and transmissivity coefficients R and T of thin germanium films. Films were deposited in vacuo on fused quartz substrates where the crystalline perfectiveness of the film was controlled by varying the substrate temperature so that the effect of crystalline order on reflectivity could be observed. In addition, epitaxial films were grown on cleaved CaF_2 substrates to thicknesses in the range 100-3000 Å. Structure in the reflectivity and transmission spectra showed these films to possess bulk band properties. However, the amplitudes of R and T were affected by the presence of film surface roughness believed to originate from nucleation and growth phenomena. Also, compressive strain induced by the difference in thermal expansion coefficients between Ge and CaF_2 shifted interband transition structure to slightly higher energies. Values of the optical constants were deduced from R and T by methods discussed previously.[1] When experimental and calculational difficulties peculiar to the film method are accounted for, the results correspond closely to those of Kramers-Kronig analyses of bulk reflectivity data.

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[1] Paul M. Grant, Bull. Am. Phys. Soc. 10, 546 (1965).

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axis of the specimen nearly parallel to the incident beam. The results are interpreted in terms of nonvertical transitions across a forbidden-energy gap having a value of approximately 3.3 eV at room temperature for light with the E vector $\perp$ to the c axis. Several luminescent peaks in the visible portion of the spectrum have been observed over a range of temperatures.

* Work supported by the U. S. Air Force.

F2. Optical Constants of Barium and Silver in the Vacuum Ultraviolet.* E. I. FISHER, L. R. WHALLEY, AND I. FUJITA, *University of Southern California.*—The complex index of refraction, consisting of the real part n and the imaginary part, the extinction coefficient k, were determined for barium and silver, using data taken on the reflected intensities at two angles of incidence, 17.5° and 72.5°. The values of n and k were then obtained from the graphical solution of the Fresnel equations. The films were prepared in an ultrahigh-vacuum reflectometer at 5×10^{-10} Torr, and reflected intensities were measured immediately after evaporation.[1] The plasmon energy, corresponding to a peak in the value $\mathrm{Im}(1/\epsilon)=2nk/(n^2+k^2)^2$ was now found to be $h\nu=7.6$ eV in barium, differing from an electron-loss value[2] of 6.25 eV. However, data taken on the reflected intensities of silver agree very well with other work.[3]

* Work supported by the National Aeronautics and Space Administration.
[1] E. I. Fisher, I. Fujita, and G. L. Weissler, Bull. Am. Phys. Soc. 10, 375 (1965).
[2] J. L. Robins and P. E. Best, Proc. Phys. Soc. (London) 79, 110 (1962).
[3] E. A. Taft and H. R. Philipp, Phys. Rev. 121, 1100 (1961).

F3. Electrical and Optical Properties of Co Impurities in GaP.* D. H. LOESCHER (introduced by G. L. Pearson), J. W. ALLEN, AND G. L. PEARSON, *Stanford University.*—Electrical measurements have shown that Co is an acceptor in GaP. The site symmetry and the electronic configuration of the cobalt impurities have been determined. Optical-transmission measurements were made on sulfur-doped, epitaxially grown GaP single crystals, into which Co had been diffused. A crystal-field analysis of the data has shown that the cobalt had substituted for gallium in the crystals. The analysis also showed that the cobalt retained the $3d^7$ electronic configuration. That is to say, the accepted electron went into an s–p bonding orbital, not into the cobalt d shell. These results are in agreement with theory of transition-metal impurities proposed by Allen.[1]

* Work supported by National Aeronautics and Space Administration.
[1] J. W. Allen, Proc. Intern. Conf. Semiconductors, Paris, p. 781 (1964).

F4. Optical Properties of Thin Germanium Films in the Wavelength Range 2000–6000 Å.* PAUL M. GRANT, *Harvard University* and *IBM Research Laboratory, San Jose.*—Measurements have been made of the normal-incidence reflectivity and transmissivity coefficients R and T of thin germanium films. Films were deposited *in vacuo* on fused-quartz substrates where the crystalline perfectiveness of the film was controlled by varying the substrate temperature so that the effect of crystalline order or reflectivity could be observed. In addition, epitaxial films were grown on cleaved CaF_2 substrates to thicknesses in the range 100–3000 Å. Structure in the reflectivity and transmission spectra showed these films to possess bulk band properties. However, the amplitudes of R and T were affected by the presence of film-surface roughness believed to originate from nucleation and growth phenomena. Also, compressive strain induced by the difference in thermal expansion coefficients between Ge and CaF_2 shifted interband transition structure to slightly higher energies. Values of the optical constants were deduced from R and T by methods discussed previously.[1] When experimental and calculational difficulties peculiar to the film method are accounted for, the results correspond closely to those of Kramers–Kronig analyses of bulk-reflectivity data.

* Research supported by the U. S. Office of Naval Research and the IBM Corporation.
[1] P. M. Grant, Bull. Am. Phys. Soc. 10, 546 (1965).

F5. Spatial Distribution of Photoluminescence in Diffused GaAs p–n Junctions. L. A. D'ASARO, P. R. FOURNIER, AND H. J. QUEISSER, *Bell Telephone Laboratories.*—The spatial distribution of photoluminescence was measured across an Zn-diffused p–n junction in GaAs. A focused 6328-Å gas laser excited luminescence on an etch-beveled sample with a 1000:1 taper. The luminescence spectra across this bevel are similar to those observed in bulk samples of equivalent doping, but quantum efficiency varies with position. Samples with junction depths $x_j=1.2$ μ and average diffused concentrations $p=1\times10^{20}$ cm^{-3} from a Zn_3As_2 source in a Sn-doped crystal with $n=10^{18}$ cm^{-3} showed an intensity minimum at the junction, as expected from charge separation by the junction field. Other samples with identical x_j and n but $p=2.5\times10^{18}$ cm^{-3} diffused from a Zn–Ga source showed, in addition to the minimum, a relative maximum located 0.3 μ from the junction on the n side. This maximum was observed at 77° and 300°K. The maximum intensity was enhanced by heating above the diffusion temperature and then quenching. The diffusions from the Zn–Ga source were found to affect the quantum efficiency in the n–GaAs down to three times the junction depth.

F6. Photoemission Studies and Band Structure of Palladium.* A. YU (introduced by W. E. Spicer) AND W. E. SPICER, *Stanford University.*—Photoemission measurements have been made on evaporated Pd film in a continuously pumping vacuum chamber with pressure less than 10^{-9} Torr. Nondirect transitions are dominant in this material, although there is also evidence of direct transitions. Using photoemission data alone, density-of-states maxima are located at 0.1 and 1.1 eV below the Fermi energy E_F. Using photoemission and optical data,[1] a third density-of-states maximum is tentatively located 3.6 eV above E_F. For $E>E_F-2$ eV, the density-of-states curve appears strikingly similar to that of Ag (Ref. 2) when the Fermi-level shift of 4 eV is taken into account. The occurrence of a high density-of-states peak just below the Fermi level is in agreement with specific-heat data[3] and deHaas–van Alphen measurements.[4]

* Work supported by the National Science Foundation and by the Advanced Research Projects Agency.
[1] D. Beaglehole, private communication.
[2] (a) C. N. Berglund and W. E. Spicer, Phys. Rev. A136, 1044 (1964). (b) Earlier results [Ref. 2(c)] of these studies indicated that the band structure of Pd was more like that of Ni than of Ag; however, the complete studies reported here establish that this is not the case. (c) A. J. Blodgett and W. E. Spicer, Phys. Rev. Letters 15, 29 (1965).
[3] N. K. Hindley and P. Rhodes, Proc. Phys. Soc. 81, 717 (1963).
[4] J. J. Vuillemin and M. G. Priestley, Phys. Rev. Letters 14, 307 (1965).

F7. Photoemission Investigation of the CdSe Band Structure.* J. L. SHAY† AND W. E. SPICER, *Stanford University.*—Using energy distributions normalized to the quantum yield, the photoemission data[1] from single crystals of CsSe, cleaved in vacuum ranging from 10^{-4} to 10^{-9} Torr, have been analyzed in detail in order to separate the contributions arising from direct and nondirect transitions. The strongest direct transitions occur at $h\nu=7.4$ and 8.8 eV (corresponding to peaks in the reflectivity spectra[2]). Both direct transitions are found to originate from states approximately 1.7 eV below the valence-band maximum. If the transition for $h\nu=8.8$ eV originates from states near Γ_6 in the valence band,[3] one concludes that the $h\nu=7.4$ eV transition also originates from these states and that the final states for the $h\nu=7.4$-eV transition are near Γ_8 in the conduction band. Hence, the matrix element $\langle\Gamma_8|p|\Gamma_8\rangle$ is not as small as previously suggested. From the nondirect transitions, the valence-band density o

Introduction

This talk will describe an attempt to determine the optical constants of germanium through measurements of the normal incidence reflectivity and transmissivity coefficients of thin films. The wavelength range considered was 6000-2000 Å where the skin depth is of the order of only a few hundred Å. The reflectivity of bulk single crystal germanium has been accurately measured by Donovan, Ashley and Bennett and the optical constants have been derived from these data by Philipp using Kramers-Kronig procedures. The results will be used as a standard against which to compare our thin film data.

Slides 1 and 2. Previous Thin Film Optical Constant Results

Let me review briefly previous attempts to determine germanium optical constants from thin film data.

SHOW SLIDE 1.

This slide shows the film optical constants of Sebbie (taken in 1962, shown by the broken line) displayed against those calculated by Philipp from bulk reflectivity. Sebbie used films deposited on amorphous substrates at or near room temperatures with subsequent annealing at higher temperatures. The agreement with bulk results is not very good, and we believe the large oscillations in n to be due to the calculational method used and does not represent an intrinsic effect.

SHOW SLIDE 2.

The broken line in this slide gives the results of Tudeš published in 1961. Here we see the qualitative agreement has improved; however, we still have depressingly little correspondence quantitatively and also in structural details.

slide 3. Epitaxial Reflection Election Diffraction Patterns

We felt that the poor results of previous workers [redacted] was due to the uncertain crystalline properties of their films. In an effort to improve crystallinity, we vacuum deposited [redacted] a large number of epitaxial germanium films on cleaved CaF2 substrates. It is well known to thin film workers that film surface roughness increases with increasing substrate temperatures. Hence, [redacted] deposition parameters were chosen to produce epitaxy, yet keep surface roughness at a minimum

SHOW SLIDE 3.

This slide shows the RED patterns and important deposition parameters for three typical films. We see that these films possess the usual Laue patterns for <111> growth directions with the election beam incident in a <110> type direction. Note the presence of satellite spots indicating some twin or stacking fault formation. We show here three different thicknesses (1850Å, 250Å and 135Å) deposited under nearly identical conditions of substrate temperature (600°C) and deposition rate (~820Å/min

Slide 4. Reflectivity of 1850 Å Film

SHOW SLIDE 4

This slide shows the reflectivity of the 1850 Å epitaxial film with reflectivity of an etched single crystal as background. Note the decreased reflectivity amplitude of the film. This is caused by surface roughness scattering which becomes more severe the shorter the wavelength. In addition, there was a small optical misalignment which gave an overall systematic error. However, the film features all of the interband transitional structure typical of the bulk material. We have examined the effect of crystalline order on the E_1, X peak by depositing films on fused quartz at various substrate temperatures. One notices a very nice correlation between the width of the DSH rings and the shape of the E_1, X peak. For amorphous films deposited at room temperature, the peak completely disappears.

Note that the reflectivity peaks of the films are shifted to slightly higher energies. Detailed study shows that this shift almost certainly arises from compressive strain induced in the film when cooled from its formation temperature by the difference in thermal expansion coefficient between germanium and CaF_2.

Slides 5 and 6 Reflectivity and Transmissivity of a 250 Å Epitaxial Film

[redacted]

SHOW SLIDE [redacted] 5

This slide gives the reflectivity of the 250 Å epitaxial film shown by the solid dots. The crosses are values computed using appropriate theoretical equations and the bulk optical constants of Philipp. Note again that interband transitional structure is present but that amplitudes are depressed by surface roughness scattering.

SHOW SLIDE [redacted] 6

Here we have the transmission spectrum of the same film, with the dots and crosses having the same meaning. The agreement between theory and experiment appears to be quite close; however, these curves are plotted on a logarithmic scale and the actual relative error is the same as or greater than the reflectivity. Note again the good agreement in interband transitional structure with the bulk in a film whose mean thickness is only about [redacted] 50 atoms.

Slide 7 Optical Constants of 250 Å Epitaxial Film

SHOW SLIDE 7

This slide shows the optical constants n and k deduced from the R and T of the 250 Å epitaxial film.* The mathematical analysis employed was discussed in a previous talk. [redacted] The line indicates bulk Ge and the dots film data. We note that there is a region in which no optical constants were obtained. This is due to the existence of a branch point in the expressions relating n and k to R and T near which small errors in R and T can lead to large errors in n and k as has been pointed out previously by the speaker. The error bars denote the error range possible for combined uncertainties of ± 2.5% absolute in R, ± 10% relative in T and ± 10 Å absolute in the thickness. We see that everywhere roots were obtained, the error analysis overlaps the difference between the two values of the optical constants.

* Before proceeding with the actual derivation, R was corrected for surface roughness scattering.

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Conclusion

From the results of the last slide, I think it is safe to conclude that once experimental and calculational difficulties peculiar to the film method are accounted for, the films seem to possess the features of bulk band structure. Roughness scattering rather than crystalline perfection now seems to be the principle factor preventing replication of bulk germanium optical properties in the film state, and future work on the production of epitaxial [redacted] semiconductor films for optical studies should concentrate on reducing the surface roughness problem. Nevertheless, I think we are now at the stage where we can perform on epitaxial films those experiments most conveniently done by transmission and interpret the results as indicative of bulk behavior.