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Piezoreflectance in Ge†*

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Observation of the change in position of identified reflectance peaks caused by the application of uniaxial stress along various directions can yield information concerning the shift of band edges under hydrostatic pressure and, in principle, of deformation potential constants. The reflectance peaks of Ge and Si below 5 eV have been studied in crystals subjected to four-point bending. A measurable effect was observed only in the 2-eV peaks associated with the $L_3' \rightarrow L_1$ transitions in Ge. The shift for principal stress along the [111] direction was somewhat larger than that for stress along the [100] direction. Values are obtained for the pressure shift of the $L_3' \rightarrow L_1$ gap, the pressure shift of individual band edges, Γ_{25}', L_3', and L_1, and for the deformation potentials associated with the L_3' minima.

I. INTRODUCTION

Reflectance measurements yield information about band edges at energies greater than the minimum band gap.[1] In particular, in Ge transitions corresponding to $L_{3'}\rightarrow L_1$ near 2.1 eV, $X_4\rightarrow X_1$ near 4.5 eV as well as other transitions have been identified. It has been shown possible[2] to produce large elastic strains in bulk Si; similar techniques have been used here with bulk Ge. Therefore, further information about pressure dependence and deformation potentials of these band edges can be obtained by studying the shift of reflectance peaks in strained crystals. The effect of similar uniaxial stresses on certain band edges has been previously studied by piezoresistance measurements which have yielded information about deformation potentials and pressure coefficients.[3] The present experiments yield related information about other band edges.

II. EXPERIMENTAL

Large elastic strain can be introduced into Ge and Si crystals at room temperature if proper care is taken to remove all surface damage. Bars of these crystals approximately 1.5 mm×6 mm×6 cm were lapped to a smooth finish with 600-mesh carborundum and No. 304 emery. They were then etched in 1 part HF and 3 parts HNO_3 for several minutes to remove residual surface damage. This procedure results in a reproducible reflecting surface.

Bars were mounted for four-point loading as shown in Fig. 1. The ends of the bars were coated with fused polyethylene to protect them from surface damage in the bending jig. The points, which were actually ball bearings, permitted the application of a uniform circular bend over more than 1 cm at the center of the bar and allowed free longitudinal extension and compression of the bar. The longitudinal strain u is determined from the radius of curvature R and the sample thickness by the relationship $u=t/2R$. The curvature was determined optically by observing the focal point of a beam of parallel light reflected from the concave surface.

This strain in the surface layers is approximately equivalent to that produced by the application of a uniform uniaxial stress.[4] It is surface layers of the crystal which are important in reflectance measurements. The advantage of the four-point loading is that an equivalent dilatation and compression is produced on opposite sides of the sample at the same time. This permits measurement of the same sample in both situations. Any observable effect is thus enhanced twofold.

Reflectance data were obtained at nearly normal incidence, using a grating monochromator. The reflected and incident intensities were recorded as the output of a photomultiplier tube. By suppressing a large part of the detector current, small changes in the signal could be observed with greatly increased sensitivity. In this manner, reflectance data could be ob-

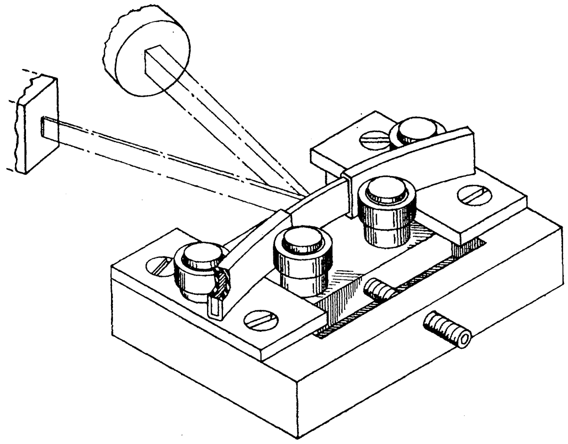

Fig. 1. Four-point bending apparatus used in measuring piezoreflectance. The path of the light beam from the exit slit to the photomultiplier detector is sketched.

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† A preliminary account of this work is given in Bull. Am. Phys. Soc. **7**, 78 (1962).

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[1] H. Ehrenreich, H. R. Philipp, and J. C. Phillips, Phys. Rev. Letters **8**, 59 (1962), and cited references.

[2] W. C. Dash, *Growth and Perfection of Crystals*, edited by Doremus, Roberts, and Turnbull (John Wiley & Sons, Inc., New York, 1958), p. 189.

[3] R. W. Keyes, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Vol. 11 and cited references.

[4] S. Timoshenko, *Strength of Materials* (D. van Nostrand Company, Inc., Princeton, New Jersey, 1955), 3rd ed., Part I, Chap. 4.

tained with considerable precision provided the range of wavelength scanned in the experiment was small, say 200 Å or less. If the data are taken over a larger wavelength interval, errors associated with electrical drifts in the measuring system and inhomogenities in the photomultiplier cathode surface may become appreciable. In the present experiments, the most extensive measurements were made in the vicinity of a sharp reflectance peak where these errors were not important.

For germanium more than 15 samples were measured. The sample curvature was preset for a strain of 0.4 or 0.5%. The measured shift of the reflectance peak near 2.1 eV for these specimens under compression and extension and for a given strain were generally the same to within the resolution of the spectrometer, ±0.003 eV. No attempts were made to measure the shift for smaller strains.

III. RESULTS AND DISCUSSION

Observable shifts were detected for the $L_{3'}\to L_1$ transitions in Ge at 0.4% strain in compression and extension. This corresponds to a uniaxial stress in either direction of 4100 atm. The $X_4\to X_1$ transition at about 4.5 eV in both Ge and Si, and the $\Gamma_{25'}\to\Gamma_{15}$ transition at about 3.4 eV in Si were also examined under the same conditions and up to 1.5% strain in Si. Preliminary measurements showed no detectable strain dependence of these peaks. In view of this preliminary survey, detailed studies were limited to the sharper lower energy peak of the $L_{3'}\to L_1$ structure, which is split by the spin-orbit interaction[1], using unpolarized light. Figure 2 shows the reflectance at the peak of the previously observed reflectance maximum in an unstrained crystal and exhibits clearly the spin-orbit splitting as originally reported by Tauc and Antončík.[5] Typical data showing the displacement of the sharper of the two peaks for stresses along [100] and [111] directions under extension and compression are shown in Fig. 3. It is seen that a strain of 0.4% in either direction produces a shift of 0.013±0.003 eV and 0.016±0.003 eV for stresses along [100] and [111] directions, respectively. The observed maximum reflectance in all cases was the same within 1%.

These results may be interpreted in terms of deformation potential theory.[6,7] The energy shift $\delta\epsilon^i$ of a valley i in band L situated along a direction characterized by unit vector $\hat{n}$ and associated with the strain tensor $\mathbf{u}$ is given by[7]

$$\delta\epsilon_i^{(L)}=\hat{n}_i\cdot\left[E_1^{(L)}\mathbf{1}\mathrm{Tr}\mathbf{u}+E_2^{(L)}(\mathbf{u}-\tfrac{1}{3}\mathbf{1}\mathrm{Tr}\mathbf{u})\right]\cdot\hat{n}_i, \qquad (1)$$

where $E_1^{(L)}$ and $E_2^{(L)}$ are related to the deformation potentials of band L defined by Herring[6] as $E_1^{(L)}=\Xi_d^{(L)}+\frac{1}{3}\Xi_u^{(L)}$ and $E_2^{(L)}=\Xi_u^{(L)}$. The $L_{3'}$ and L_1 band edges both lie along [111] directions on the face of the Brillouin zone. The surfaces of constant energy for both band edges are simple ellipsoids of revolution to first approximation. The displacement of all ellipsoids belonging to a single band edge is identical under [100] stress and given by

$$\delta\epsilon_{\langle 111\rangle}^{(L)}=E^{(L)}(s_{11}+s_{12})X=E_1^{(L)}(1-2\sigma)u. \qquad (2)$$

Here X and $u=X/E_{100}$ are, respectively, the stress and strain along [100] directions, E_{100} is the appropriate Young's modulus, and σ is Poisson's ratio. Since the four-point bending is equivalent to the uniaxial stress X in the present case, u corresponds to the longitudinal strain of 0.4%. On the other hand, for stresses along [111] directions, the shift of [111] ellipsoids is given by

$$\delta\epsilon_{\langle 111\rangle}^{(L)}=E_1^{(L)}(s_{11}+2s_{12})X+\tfrac{1}{3}E_2^{(L)}s_{44}X, \qquad (3)$$

while for [1, −1, 1] and equivalent ellipsoids,

$$\delta\epsilon_{\langle 1\,-1\,1\rangle}^{(L)}=E_1^{(L)}(s_{11}+2s_{12})X-(1/9)E_2^{(L)}s_{44}X. \qquad (4)$$

Here the longitudinal strain $u=X/E_{111}$ in terms of Young's modulus along [111] directions.

Because of the uniform displacement of all [111] valleys belonging to the same band edge under [100] stresses, Eq. (2) may be immediately related to a hydrostatic pressure shift. It is easily shown that a

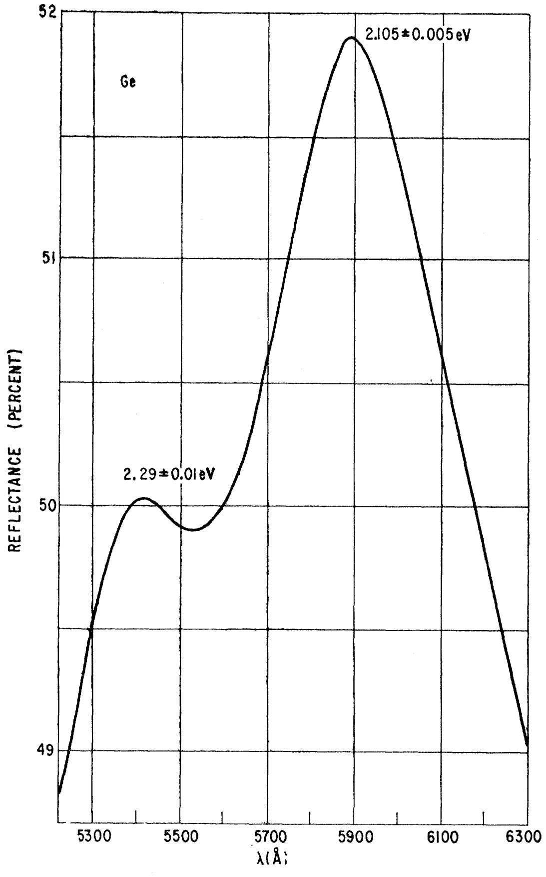

FIG. 2. Reflectance of Ge vs wavelength in the region of 2 eV.

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[5] J. Tauc and E. Antončík, Phys. Rev. Letters **5**, 253 (1960).

[6] C. Herring and E. Vogt, Phys. Rev. **101**, 944 (1956).

[7] H. Brooks, *Advances in Electronics and Electron Physics* edited by L. Marton (Academic Press Inc., New York, 1956), Vol. 7.

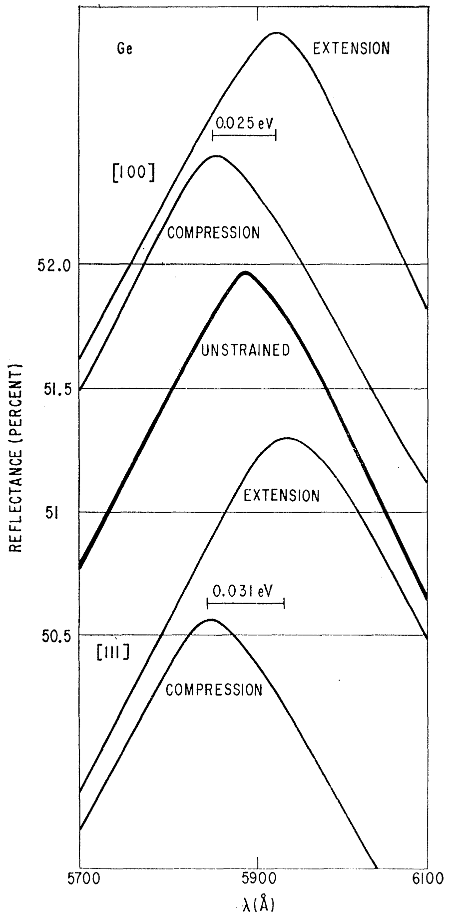

FIG. 3. Reflectance of Ge near the 2.105-eV peak for samples subjected to 0.4% principal extension and compression along [111] and [100] directions. The reflectance scale refers to the unstrained sample. The observed maximum reflectance is the same, to within 1%, in all cases.

uniaxial [100] stress X and a hydrostatic pressure P produce the same shift $\delta\epsilon_{\langle 111\rangle}{}^{(L)}$ for $P=-\frac{1}{3}X$. Thus

$$\partial\epsilon^{(L)}/\partial P=-3E_1{}^{(L)}(s_{11}+2s_{12}). \tag{5}$$

The data show that for Ge, $\delta\epsilon_{\langle 111\rangle}{}^{(L_1)}-\delta\epsilon_{\langle 111\rangle}{}^{(L_{3'})}=0.013$ eV for $u=0.004$. Using Eq. (2) and the known compliance coefficients at room temperature[8] one finds $E_1{}^{(L_{3'})}-E_1{}^{(L_1)}=7$ eV. The pressure coefficient $\partial\epsilon^{(L_1)}/\partial P-\partial\epsilon^{(L_{3'})}/\partial P=(9\pm 2)\times 10^{-6}$ eV/atm associated with the $L_{3'}\rightarrow L_1$ gap is then obtained from Eq. (5). This value agrees within the quoted experimental error with the more precise result of 7.5×10^{-6} eV/atm obtained from hydrostatic pressure measurements by Zallen, Paul, and Tauc.[9]

The pressure coefficient associated with the relative motion of the $\Gamma_{25'}$ valence band edge and the point $L_{3'}$ is also of interest. The experiments of Paul and collaborators[10] yield $\partial\epsilon^{(L_1)}/\partial P-\partial\epsilon^{(\Gamma_{25'})}/\partial P=5\times 10^{-6}$ eV/atm. Thus $\partial\epsilon^{(\Gamma_{25'})}/\partial P-\partial\epsilon^{(L_{3'})}/\partial P=4\times 10^{-6}$ eV/atm and the separation increases with increasing pressure.

Since the deformation potentials associated with the L_1 minima are known from Herring's analysis of transport data for n-type germanium,[6,11] the absolute pressure shift for L_1 may be computed from Eq. (5) to be $\partial\epsilon^{(L_1)}/\partial P=+1.4\times 10^{-6}$ eV/atm.[3] The absolute pressure coefficients associated with the $\Gamma_{25'}$ and $L_{3'}$ edges may therefore be deduced to be $\partial\epsilon^{(\Gamma_{25'})}/\partial P=-4\times 10^{-6}$ eV/atm and $\partial\epsilon^{(L_{3'})}/\partial P=-8\times 10^{-6}$ eV/atm.

It is interesting that the pressure shift of both $L_{3'}$ and $\Gamma_{25'}$ is considerably greater than that associated with L_1 in view of Herman's calculations of the motion of these levels as a function of the core shift. These predict just the opposite behavior. It therefore appears as though pressure effects are not directly related to the core shift. On the other hand, the absence of a shift of the 3.5-eV reflectivity peak in silicon, which has been ascribed[1,12] to $\Gamma_{25'}\rightarrow\Gamma_{15}$ transitions is consistent with Herman's picture since these levels remain parallel to each other under core shift .The absence of a shift in the 4.5-eV reflectivity peak in Ge and Si may be reasonable. This peak remains practically stationary in passing from Ge to Si through all intermediate alloys with a corresponding change in lattice constant of about 4%.

The small and inaccurately determined difference $\Delta=0.003\pm 0.003$ eV between the shifts associated with [111] and [100] stresses may be used to obtain estimates of the deformation potentials $\Xi_d{}^{L_{3'}}$ and $\Xi_u{}^{L_{3'}}$. In principle each of the peaks corresponding to $L_{3'}\rightarrow L_1$ transitions should split under [111] stress since, according to Eqs. (3) and (4), ellipsoids along the direction of stress should shift differently from the others. However, one can show that for the present experiment (direction of stress in the plane of the photon polarization vectors) the optical absorption associated with [111] ellipsoids is only 23% of that due to the remaining three. This results from the fact that there are three times as many ellipsoids along [1 −1 1] and related directions as along [111] and also that the average matrix element for optical absorption for each of these ellipsoids is somewhat larger. Since the index of refraction is rather greater than the extinction coefficient k in this energy range,[13] the reflectance is insensitive to small changes in k and hence in absorption coefficient $\alpha=4\pi k/\lambda$. It can be shown, in fact, that the maximum change in reflectance that could possibly be expected is about 4%. We shall therefore suppose that the shifted peak for [111] stresses is due to optical transitions between ellipsoids along [1 −1 1] and related directions. Accordingly, with the aid of Eqs. (2) and (4) we put $\Delta=-(1/9)(E_2{}^{(L_1)}-E_2{}^{(L_{3'})})s_{44}X$. Upon numerical

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[8] M. E. Fine, J. Appl. Phys. **24**, 338 (1953).

[9] R. Zallen, W. Paul, and J. Tauc, Bull. Am. Phys. Soc. **7**, 185 (1962).

[10] W. Paul, Suppl. J. Appl. Phys. **32**, 2082 (1961).

[11] C. Herring, T. H. Geballe, and J. E. Kunzler, Bell System Tech. J. **38**, 657 (1959).

[12] J. C. Phillips, Phys. Rev. **125**, 1931 (1962).

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

substitution in this equation, the result $E_2^{(L_1)}-E_2^{(L_{3'})}=\Xi_u^{(L_1)}-\Xi_u^{(L_{3'})}=3.5\pm3.5$ eV is obtained. The known deformation potentials associated with the L_1 minima[3,5,11] may then be used in conjunction with the previously determined value of $E_1^{(L_{3'})}-E_1^{(L_1)}$ to deduce the highly approximate values of the deformation potentials of the $L_{3'}$ minima, $\Xi_u^{(L_{3'})}=14\pm3.5$ eV and $\Xi_d^{(L_{3'})}=1.5\pm3$ eV.

Since pressure coefficients associated with band gaps involving the same points in the Brillouin zone in many of the group 4 and 3–5 semiconductors are nearly the same,[10] it would be of interest to perform similar experiments on the 3–5 compounds. Because of this similarity, piezoreflectance experiments would aid in the identification of observed reflectance structure.

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Energy Dependence of Indirect Optical Absorption in Semiconductors

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Formulas are obtained for the indirect absorption coefficient as a function of photon energy, for both degenerate and nondegenerate semiconductors, taking into account the dependence of the energy denominator on the energy of the intermediate states. The light-hole and heavy-hole contributions and the total absorption were computed for germanium. The results are displayed as a function of photon energy, in graphs, for the nondegenerate case and for several Fermi energies. The results show that, for degenerate material, absorption edges obtained by extrapolation of the experimental absorption spectrum are liable to be too low.

IN a semiconductor, indirect optical absorption[1] connects an initial state in the valence band, through the optical matrix element M_R, to an intermediate state in the conduction band near the zone center, and then by the scattering matrix element M_S to a final state near the conduction band edge[2,3] (see Fig. 1). The states are designated, respectively, *i*, *a*, and *f*. The probability of this transition determines dN/dt, the number of quanta of incident radiation absorbed per unit time per unit volume. The indirect optical absorption coefficient is $\alpha=(n/Nc)dN/dt$, where n is the index of refraction.

The interaction represented by M_S may be due to phonon scattering or to impurity scattering. In either case $|M_S|$ will be taken here as independent of the state, in the range of states contributing. When M_S is due to phonon scattering, a term $\pm E_p$ (energy of the phonon) appears in the formulas for dN/dt, on account of conservation of energy.[3] This will have the effect of shifting the absorption spectrum's edge by an amount $\pm E_p$, and can be taken into account by replacing ΔE_g (see Fig. 1) by $E_{g\text{ phonon}}=\Delta E_g\mp E_p$ in the results [Eq. (7), etc.] below. The energy variation of M_R may be neglected compared to the variation of the denominator in Eq. (2) below, since M_R is proportional to $(E_a+\Delta E_g+E_g)$ whereas the denominator is proportional to $(E_a+\Delta E_g-E_f)$, so that a change in E_a affects the energy denominator much more than it does M_R. Furthermore, $|M_R|^2$ is independent of the direction of $\mathbf{k}$ for unpolarized incident radiation.[4] By assuming a spherical energy surface for each hole band we can write α as an integral over the energies only, as in (2)

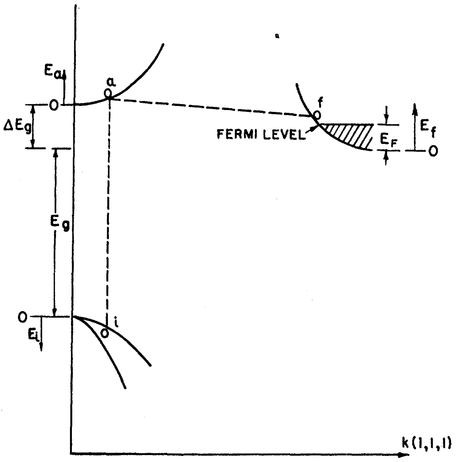

FIG. 1. The conduction and valence bands illustrating the transition discussed in this paper. This figure defines the various energies used in this paper and their zeros.

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[1] J. Bardeen, F. J. Blatt, and L. H. Hall, in *Proceedings of the Conference on Photoconductivity, Atlantic City, 1954* (J. Wiley & Sons, Inc., New York, 1956), p. 146.

[2] The other process given in reference 1, scattering of a hole from a valence band edge, involves a larger energy denominator than the transition considered here and therefore is considered a negligibly smaller contribution to α. Processes in which an exciton is created, also not considered here, are thought to contribute to α in the immediate neighborhood of the indirect absorption edge for pure material, reference 3, and presumably have their analog for degenerately doped material.

[3] G. G. MacFarlane, T. P. McLean, J. E. Quarrington, and V. Roberts, Phys. Rev. **108**, 1377 (1957).

[4] M. Tiersten (private communication).