Table I. Comparison of f's for impurity diffusion (fcc lattice).

Frequency condition corresponding to different degrees of binding	f (exact) Manning[a]	% Error in f in Le Claire Lidiard[b] approximation	% Error using present recipe $f=1+2\xi\{1+[\xi\sin(-\frac{1}{2}\pi\xi)/(1-\xi)]\}$
$\nu_1=\nu_2=\nu_3$	0.781	5	6
$\nu_1=10\,\nu_2=10\,\nu_3$	0.263	18	1
$\nu_1=100\,\nu_2=100\,\nu_3$	0.035	25	21
$\nu_1=\nu_2=10\,\nu_3$	0.557	3	19
$\nu_1=5\nu_2=25\,\nu_3$	0.233	9	9
$5\nu_1=5\nu_2=\nu_3$	0.933	2	2

[a] See reference 3.
[b] See reference 4.

correlation functions for the hcp and bct lattices can be represented in closed form to about 1% accuracy by a relation of the form $f(\nu_A/\nu_B)=A+B/(C+\nu_A/\nu_B)^n$, where A, B, C, and n are parameters determined by requiring that $f(0)$, $f(1)$, $f(\infty)$, and $f'(1)$ agree with the numerical calculation.[1] These calculated parameters are as follows: For f_{Ax}(hcp), $A=0.560$, $B=0.323$, $C=0.823$, $n=0.616$; for f_{Bx}(hcp) and f_{Bz}(hcp), $A=1.000$, $B=-0.328$, $C=0.894$, $n=0.638$; for f_{Ax}(bct), $A=0.468$, $B=0.495$, $C=1.188$, $n=0.573$; for f_{Bx}(bct) and f_{Bz}(hct), $A=1.000$, $B=-0.563$, $C=2.75$, $n=0.717$. From this empirical representation we see that for $\nu_A/\nu_B\rightarrow 0$, $f_{Bz}(\text{hcp})=0.647$. Using Eq. (2) $(\xi_1{}^A=-\nu_{A1}/\sum A_n\nu_{An},\ \xi_1{}^B=\omega_1{}^B=-\nu_{B1}/\sum B_n\nu_{Bn})$ and Eq. (5), the present procedure gives $f_{Bz}=0.669$, while using the Huntington-Ghate relation, we obtain $f_{Bz}=0.714$, i.e., we have a 3% error by the present technique and a 10% error by the Huntington-Ghate recipe. Also for $\nu_A/\nu_B\rightarrow 0$, $f_{Bz}(\text{bct})=0.755$, compared to the computer value of 0.727. When $\nu_A/\nu_B\rightarrow\infty$ and $\nu_A/\nu_B\rightarrow 1$, we again obtain satisfactory f's in the self-diffusion limits. Similar agreement is found for f_{Ax} in the self-diffusion limits.

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[1] J. G. Mullen, Phys. Rev. 124, 1723 (1961).

[2] H. B. Huntington and P. B. Ghate, Phys. Rev. Letters, 8, 421 (1962).

[3] J. R. Manning, Phys. Rev. 116, 819 (1959).

[4] A. D. Le Claire and A. B. Lidiard, Phil. Mag. 1, 518 (1956).

PHOTOEMISSIVE STUDIES OF THE BAND STRUCTURE OF SILICON*

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As was previously suggested,[1] photoemissive studies of semiconductors may give information on the initial and final states involved in optical transitions.[2-6] As was discussed in more detail, peaks will appear in the spectral distribution of the photoemissive quantum yield (see, for example, Fig. 1) corresponding to the optical absorption peaks, if the final state lies above the vacuum level.[7] Conversely, if the final states lie below the vacuum level, minima may appear in the photoemissive yield curves. Because of this latter characteristic, relatively weak peaks, which cannot be resolved in optical absorption because of the masking effect of a nearby strong peak, may sometimes be resolved in photoemissive curves. In addition, data may be obtained on the absolute energy of the final state of the transition through measurement of the energy of the emitted electrons. From this and the optical absorption data, estimates of the absolute energy of the initial state

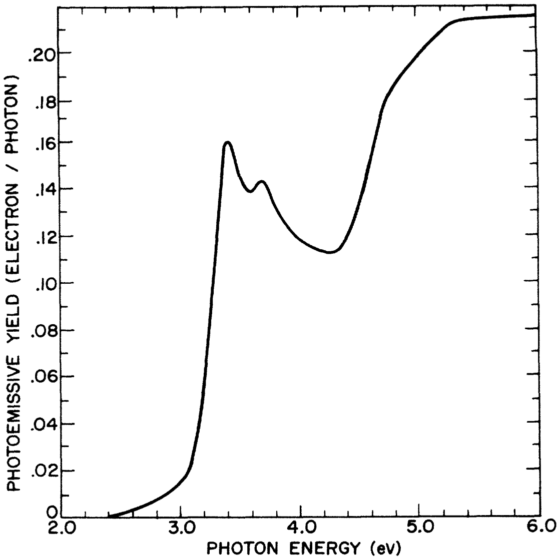

FIG. 1. The spectral distribution of the quantum yield [corrected for reflectivity (reference 3)]. Note the maxima at 3.4, 3.7, and 5.3 eV and the minimum at 4.4 eV. These correspond to well-established optical transitions. The peak at 3.7 eV is resolved for the first time.

can be made.

As has been pointed out previously, the lowest surface barriers[8-10] and thus the highest photoemissive yields will be obtained from semiconductors which have *n*-type surfaces and *p*-type bulk. Since the object of this work has been to reduce the surface barrier of silicon as much as possible in order to study the widest possible range of band structure, the surface of the silicon single crystal studied here was cleaned in a borosilicate-glass vacuum system by heating at 1600°K before cesium was placed on the surface. As Allen, Buck, and Law have shown, such a procedure not only produces an atomically clean surface, but produces a heavy *p*-type doping (up to $10^{20}/\text{cm}^3$) through a depth from the surface which is large compared to the depth (about 100 Å) of optical absorption[3] (and thus of photoemission) in the spectral range of interest. As was previously pointed out,[1] band bending can distort the energy distributions of the emitted electrons. However, this distortion will be reduced if the distance over which band bending takes place is made small compared to the depth of emission. For a *p*-type doping of $10^{20}/\text{cm}^3$, significant band bending should be restricted to a distance (about 20 Å) which is appreciably less than the depth of emission. No direct method existed for measuring the junction depth in the present study; however, estimates may be obtained by comparison of the yield data obtained here (see Fig. 1) with that obtained by van Laar and Scheer[10] in their systematic study of the effect of band bending on photoemission from this system. They have presented similar curves for silicon samples with *p*-type doping as high as $10^{19}/\text{cm}^3$ which gave the highest yield they observed. The fact that the maximum quantum yields for their $10^{19}/\text{cm}^3$ *p*-type samples were a factor of five or more below those reported here strongly suggests that the sample studied here had a *p*-type doping approaching closely the $10^{20}/\text{cm}^3$ which can be produced by the 1600°K heat treatment.[11] As a result, the optimum situation (band bending restricted to a distance appreciably less than emission depth[10]) should be realized. Since the electron affinity at the surface is 1.5 eV[10,12] and, due to the high dopings, the magnitude of the band bending will equal the band gap, the top of the valence band should be only 1.5 eV from the vacuum level over most of the depth of emission.

The spectral distribution of the quantum yield is given in Fig. 1. The maxima at 3.4 eV ($\Gamma_{25'}$ to Γ_{15}) and 5.4 eV ($L_{3'}$ to L_3) and the minimum at 4.4 eV (X_4 to X_1) discussed previously[1] are present. In addition, the absorption peak at 3.7 eV predicted by Tauc and Abraham[4,13] from their studies of the germanium-silicon alloy system is clearly resolved for the first time. The complete resolution of the peak here, but not in the data of van Laar and Scheer,[10] strongly supports the assumption that the significant band bending here was restricted to within about 20 Å of the surface.

Representative energy distribution curves are given in Figs. 2 and 3.[14] These curves have several striking features. For photons with energies less than about 3.0 eV, the curves are roughly Gaussian in form and move to higher energy as $h\nu$ increases, i.e., the distribution to the low-energy side of the peak as well as that on the high-energy side moves to higher energy as $h\nu$ increases. However, for photon energies greater than that (about 3.0 eV) at which the first strong optical absorption starts to appear (see Fig. 4 in reference 3), the distribution on the low-energy side of the maximum changes very little as $h\nu$ increases. This suggests that the lowest energy states for the optical transitions involved are fixed for $h\nu > 3.0$ eV and do not change appreciably as $h\nu$ increases. For energies between 3.0 and 3.4 eV, the distribution is still roughly Gaussian, but the number of higher energy electrons increases with

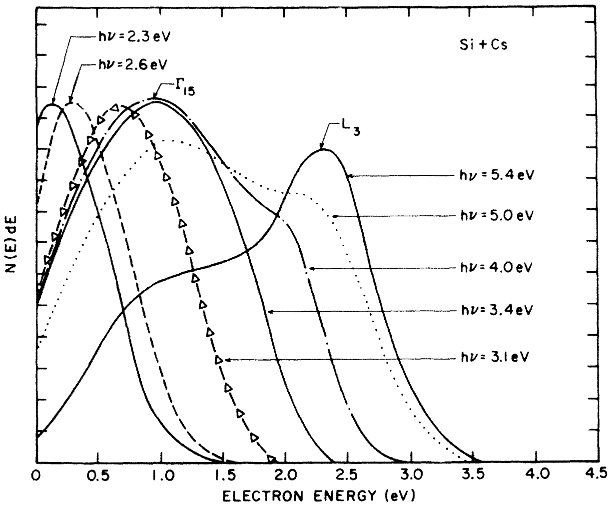

FIG. 2. Energy distribution curves. The energy of the exciting photons is indicated on each curve. The curves have been normalized to give equal peak $N(E)dE$.

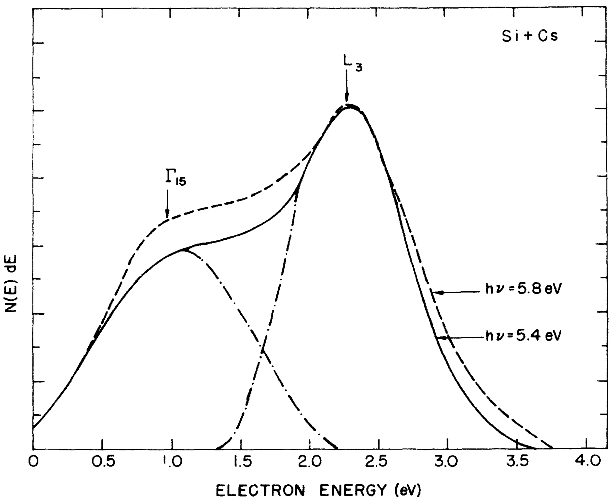

FIG. 3. Energy distribution curves. For $h\nu = 5.4$ eV, the curve has been divided into the two characteristic curves. One is centered at 1.0 eV and the other at 2.3 eV. The symbols Γ_{15} and L_3 indicate the final state assigned (see reference 2) to the optical transition associated with these transitions.

increasing $h\nu$. For $h\nu > 3.4$ eV, the distribution seems to be made up of two components; one is the Gaussian which was obtained for $h\nu = 3.4$ eV (centered at 1.0 eV) and the second is a Gaussian at higher energy. The second distribution[15] attains its final form (centered at 2.3 eV) for a photon energy of 5.4 eV. These are the characteristics to be expected if the dominant optical transitions giving rise to the photoemission are those into two groups of conduction band states.[1] The fact that each characteristic distribution attains its final shape at the photon energy corresponding to a strong absorption peak[3] (see Fig. 1) makes possible the unambiguous assignment of each distribution to an optical transition: the distribution centered at 1.0 eV to the 3.4-eV transition and the distribution centered at 2.3 eV to the 5.4-eV transition.

As was discussed previously,[1] values may be obtained from such data for the absolute energies of the states involved; however, there are several factors which may serve to introduce some uncertainty in such assignments. Experimentally, band-bending and energy-loss processes will tend to "smear out" the distributions. However, for a peak such as that at 2.3 eV which lies near the highest energy of the distribution, these effects will be minimized, since the electrons which have reduced energy due to these effects will lie at energies lower than 2.3 eV and will not tend to mask that peak.

Since the optical transitions are between bands and not discrete stages and since lifetime broadening may prevent an absorption edge from being completely sharp, there is a second possible source of error in associating an absorption maximum with the separation between the extrema of two states.[1,16] However, the flatter and less complicated the bands are at the transition point, the more likely it is that the peak in optical absorption will coincide with the extrema of the bands and also that a peak in the energy distribution curve will coincide with a band extrema. For the $L_{3'}$ to L_3 transition, the bands for both the final and initial states are relatively flat and are well separated from other bands[17]; thus the best data on the absolute value of the final state should be obtained for the 5.4-eV ($L_{3'}$ to L_3) transition.

In Table I, values are presented for the absolute energy (referred to the top of the valence band) of the energy levels obtained experimentally. For comparison, the theoretical values of Phillips[17] are also given. Only the values for the $L_{3'}$ to L_3 and $\Gamma_{25'}$ to Γ_{15} transitions are obtained solely from the energy distribution data. A possible error of ±0.2 eV is estimated for these values based on the uncertainty of the zero of energy in the velocity distribution curves and of the electron affinity.

As is to be expected, the agreement between experiment and theory is very good for the L_3 to $L_{3'}$ states. The apparent disagreement for the $\Gamma_{25'}$ to

Table I. Comparison of the experimentally determined values for the energy levels with the theoretical values (see references 17 and 18).

Transition	Optical transition (eV)	Peak in energy distribution (eV)	Energy[a] of final state[b] Experiment (eV)	Energy[a] of final state[b] Theory[c] (eV)	Energy[a] of initial state[b] Experiment (eV)	Energy[a] of initial state[b] Theory[c] (eV)
$L_{3'} \rightarrow L_3$	5.4	2.3 ± 0.2	3.8 ± 0.2	4.0	-1.5 ± 0.2	-1.4
$\Gamma_{25'} \rightarrow \Gamma_{15}$	3.4	1.0 ± 0.2	2.5 ± 0.2	3.4	-0.9 ± 0.2	0.0
$X_4 \rightarrow X_1$	4.4	⋯	$1.1 \leq E \leq 1.5$	1.3	$-3.3 \leq E \leq -2.9$	-3.1
$\Lambda_3 \rightarrow \Lambda_1$				2.55[d]		1.15[d]
	3.7	0.5 ± 0.4	2.0 ± 0.4		1.7 ± 0.4	
$L_{3'} \rightarrow L_1$				(2.3)		(-1.4)

[a] With respect to highest valence band maximum.
[b] For an effective electron affinity of 0.4 eV.
[c] See reference 17.
[d] Assuming that the energy difference between Λ_3 and $L_{3'}$ is the same for Si and Ge (see reference 16).

Γ_{15} transition is much larger than that due to the uncertainty in the electron affinity and zero of energy for the energy distribution or to other experimental difficulties. The major reason for the apparent disagreement becomes clear, if the E versus k diagrams for silicon[17,18] are examined. Near the Γ point both the lowest conduction band and the highest valence band are practically parallel and slope downward. Thus, for $h\nu = 3.4$ eV, transitions will be made to the lower lying conduction-band states as well as to those at the Γ_{15} point. This will shift the maximum of the energy distribution curve to a lower energy as is observed experimentally.

Based on the measurements reported here, limits may also be placed on the energies of the states involved in 3.7- and 4.4-eV transitions. Since the 4.4-eV transition gives an extremely strong minimum in the spectral distribution curve (Fig. 1), the final state must lie below the vacuum level, putting an upper limit of 0.4 eV on the energy of the final state. This is in good agreement with the assignment of this peak to the $X_4 - X_1$ transition.[2] The experimental data are not in agreement with the suggestion[19] that this transition is due to transitions between states near the middle of both the initial and the final bands, since if such were the case, the energy in the final state should be about 0.9 eV or larger.

Basing their argument on the shape of the absorption curve, Phillips, Brust, and Bassani[16] have recently suggested that the 3.7-eV optical transition is not due to an $L_{3'}$ to L_1 transition,[2,4] but to a Λ_3 to Λ_1 transition. The appearance of a well-defined peak in Fig. 1 corresponding to this transition is in agreement with the new assignment of this transition.[16] Estimates of the energies of the states involved in this transition were obtained by analyzing fine structure in the energy distribution curves[20] and by taking cognizance of the fact that, as can be seen by comparing the data here with that of van Laar and Scheer,[10] the photoemission due to this transition is drastically affected by relatively small variations in band bending. These results are given in Table I and are compared to the calculated energies for both the Λ_3 to Λ_1 and $L_{3'}$ to L_1 transitions. Comparing the experimental energies for this and the $L_{3'}$ state, and remembering that $L_{3'}$ and Λ_3 should be separated by only about 0.25 eV,[16] it is clear that the experimental values of the energy levels are not precise enough to distinguish between the two possible transitions. However, the experimental data do place the initial state for the 3.7-eV optical transition close (in energy) to the $L_{3'}$ state in agreement with either assignment.

More detailed analysis of the energy distribution curves for photon energies which do not correspond to critical points should give information on the band structure away from such points. Appropriate analysis of the energy distribution curves should also give information on the production of secondary pairs by electrons with kinetic energies in excess of the band gap energy.

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[1] W. E. Spicer and R. E. Simon, J. Phys. Chem. Solids (to be published).

[2] H. Ehrenreich, H. R. Philipp, and J. C. Phillips, Phys. Rev. Letters 8, 59 (1962); J. C. Phillips, Phys. Rev. 125, 1931 (1962).

[3] H. R. Philipp and E. A. Taft, Phys. Rev. 120, 37 (1960).

[4] J. Tauc and A. Abraham, Proceedings of the International Conference on Semiconductor Physics, Prague, 1960 (Czechoslovakian Academy of Sciences, Prague, 1961), p. 375.

[5] M. Cardona, Suppl. J. Appl. Phys. 32, 2151S (1961).

[6] M. Aven, D. T. E. Marple, and B. Segall, Suppl. J. Appl. Phys. 32, 2261S (1961).

[7] W. E. Spicer, J. Appl. Phys. 31, 2077 (1960).

[8] W. E. Spicer, RCA Rev. 19, 555 (1958).

[9] J. J. Scheer, Philips Research Repts. 15, 584 (1960).

[10] J. van Laar and J. J. Scheer, Philips Research Repts. 17, 101 (1962); G. W. Gobeli and F. G. Allen, Phys. Rev. 127, 141 (1962).

[11] F. G. Allen, T. M. Buck, and J. T. Law, J. Appl. Phys. 31, 979 (1960).

[12] R. E. Simon and W. E. Spicer, Phys. Rev. 119, 621 (1960).

[13] J. Tauc and A. Abraham, J. Phys. Chem. Solids 20, 190 (1961).

[14] For experimental details, see W. E. Spicer, J. Phys. Chem. Solids 22, 365 (1961); or Phys. Rev. 125, 1297 (1962).

[15] The inability to resolve these two peaks previously (see reference 1) can be attributed to the effect of band bending.

[16] J. C. Phillips, D. Brust, and F. Bassani, Phys. Rev. Letters 9, 94 (1962).

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

[18] D. Brust, M. Cohen, and J. C. Phillips, following Letter [Phys. Rev. Letters 9, 389 (1962)].

[19] M. Cardona and H. S. Sommers, Phys. Rev. 122, 1382 (1961).

[20] W. E. Spicer and R. E. Simon (to be published).

REFLECTANCE AND PHOTOEMISSION FROM Si[†]

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We have used the pseudopotential method[1,2] to calculate the energy bands of Si at about 50 000 points throughout the Brillouin zone in a manner similar to that previously reported for Ge.[3] The pseudopotential parameters in rydbergs were chosen to reproduce the energy levels at Γ, X, and L deduced[4] from cyclotron resonance and reflectance data:

$$V_{111} = -0.21, \quad V_{220} = 0.04, \quad V_{311} = 0.08. \tag{1}$$

The resulting energy bands are shown along the principal symmetry axes in Fig. 1. Neglecting lifetime broadening, the contribution of direct transitions to ϵ_2, the imaginary part of the dielectric constant, is given in terms of the oscillator strength f by

$$\epsilon_2(E_{ij}/h) = \sum_{i,j} f_{ij} N(E_{ij}), \tag{2}$$

where j labels valence bands, i conduction bands, $E_{ij} = E_i - E_j$, and $N(E)$ is the density of states having energy difference E. We have evaluated ϵ_2 as in reference 3, with the result shown in Fig. 2. (The experimental curve is due to Philipp.[5]) The experimental and theoretical energies at the points of interest shown in Fig. 1 are compared in Ta-