from the expression given by Born and Huang[14] in terms of the dielectric constants and the fundamental crystal frequency. This value is in agreement with the one reported earlier by Picus *et al.*,[15] although the input data which they used for their calculation were significantly different than the ones reported in this paper.

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Theory of Photoelectric Emission from Semiconductors

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The yield vs energy relation is determined for a number of possible photoelectric production and escape mechanisms involving volume and surface states in semiconductors. Calculations are based on density-of-states considerations and involve energy-band expansions to lowest nonvanishing order about the threshold point. The "direct" and "indirect" processes involving volume states have yields proportional to $E-E_T$ and $(E-E_T)^{\frac{5}{2}}$, respectively. Both processes appear to have been identified experimentally by Gobeli and Allen. The linear yield also requires, in addition to production by "direct" optical excitation, that the observed photoelectrons escape without scattering in the volume or at the surface. Energy and angle distribution functions of the emitted carriers are also determined.

I. INTRODUCTION AND CONCLUSIONS

THE early theoretical work on the photoelectric effect generally made the free-electron approximation for the energy band structure. Fan[1] has given a general quantum mechanical treatment of the volume production of photoelectrons. In his more detailed work he also made the free-electron approximation.

Huntington and Apker[2] have generalized Makinson's[3] work on the surface production of photoelectrons by taking the band structure into account where Makinson assumed "free" electrons with a surface barrier.

The present paper deals primarily with the form of the yield vs energy curve near threshold for a general band structure and for a variety of photoelectron production and scattering mechanisms. These results should be useful in inferring the production mechanism from the yield curve. The principal results are summarized in Table I. The discussion follows the ordering in the table.

In Sec. II the volume production of photoelectrons by "direct" optical transitions is studied. In the absence of volume or surface scattering the yield should be linear with energy, $E-E_d$, above threshold E_d. There is good evidence that this mechanism has been observed by Gobeli and Allen[4] in silicon and by Scheer[5] in CdTe and CdS. This mechanism should produce the highest quantum yields near threshold but it also has the highest threshold energy. The threshold energy will consist of the energy to free the electron, the energy of the hole

TABLE I. Dependence of photoelectric yield, Y, on photon energy, E, near threshold, E_T, for a variety of production and scattering mechanisms. $\mathcal{E}_F$ is the Fermi level measured from the vacuum.

VOLUME PROCESSES	DIRECT OPTICAL EXCITATION	UNSCATTERED		$Y\sim(E-E_T)$
		ELASTICALLY SCATTERED		$Y\sim(E-E_T)^2$
	INDIRECT OPTICAL EXCITATION	UNSCATTERED; ELASTICALLY SCATTERED		$Y\sim(E-E_T)^{5/2}$
SURFACE PROCESSES	VOLUME STATES; SURFACE AS MOMENTUM ABSORBER	"ROUGH" SURFACE		$Y\sim(E-E_T)^{5/2}$
		PERFECT SURFACE		$Y\sim(E-E_T)^{3/2}$
	SURFACE BAND STATES	DIRECT OPTICAL EXCITATION	THRESHOLD $E_T>\lvert\mathcal{E}_F\rvert$	$Y\sim(E-E_T)$
			THRESHOLD $E_T=\lvert\mathcal{E}_F\rvert$	$Y\sim(E-E_T)^{3/2}$
		INDIRECT OPTICAL EXCITATION	$E_T>\lvert\mathcal{E}_F\rvert$	$Y\sim(E-E_T)^2$
			$E_T=\lvert\mathcal{E}_F\rvert$	$Y\sim(E-E_T)^{5/2}$
	SURFACE IMPERFECTION STATES	DISTRIBUTED IN ENERGY; $E_T=\lvert\mathcal{E}_F\rvert$		$Y\sim(E-E_T)^2$
		LOCALIZED IN ENERGY BELOW $\mathcal{E}_F$		$Y\sim(E-E_T)$

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[1] H. Y. Fan, Phys. Rev. **68**, 43 (1945).

[2] H. B. Huntington and L. Apker, Phys. Rev. **89**, 352 (1953); H. B. Huntington, *ibid.* **89**, 357 (1953).

[3] R. E. B. Makinson, Phys. Rev. **75**, 1908 (1949).

[4] G. W. Gobeli and F. G. Allen, following paper [Phys. Rev. **127**, 141 (1962)].

[5] J. J. Scheer and J. van Laar, Philips Research Repts. **16**, 323 (1961).

which is usually not at the valence band maximum, and the kinetic energy of the emitted electron tangential to the emitting surface which is required by conservation of tangential momentum. Since the surface will usually be normal to a symmetry direction, the threshold may often occur at a point on the symmetry axis so that no tangential energy would be required. In fact, tangential momentum will often be a strong factor in forcing the threshold to occur on the symmetry axis normal to the surface. However, for the [111] direction in silicon studied by Gobeli and Allen, the upper valence band is known to be degenerate in the absence of spin-orbit interaction. Normal to the [111] direction, the degenerate bands separate with terms linear in k. Unless the relatively small spin-orbit interaction negates the importance of the linear terms, the direct threshold should occur at three equivalent points off the [111] axis and tangential kinetic energy should be required at threshold.

In Sec. III the effect of surface or volume scattering on the yield due to direct transitions in the volume is considered. The yield is found to rise quadratically, $(E-E_{ds})^2$, above the threshold, E_{ds}. E_{ds} will often be lower than E_d because there is no transverse momentum conservation requirement.

In Sec. IV indirect transitions in the volume are considered. The yield is found to increase as $(E-E_i)^{\frac{5}{2}}$ above the indirect threshold, E_i. In this process the hole is left at the maximum in the valence band and there is no tangential energy of the emitted electron at threshold.

In Sec. V the yield vs energy is calculated for a number of processes which may occur at the surface. These processes are divided into two categories. The first category, treated in Sec. V A, consists of processes in which the hole is left in a "volume" state. In Sec. V B we treat processes where the hole is left in a surface state.

In category A, an imperfect surface may be the momentum absorber for an "indirect" process whose yield would vary as $(E-E_i)^{\frac{5}{2}}$ just as for the volume indirect process. A perfect surface can only absorb "normal" momentum. For processes of type "A" with a perfect surface, the yield is proportional to $(E-E_i)^{\frac{3}{2}}$ assuming that the valence maximum lies along the surface normal. This need not be true in general, but is true for Si, Ge, and all III-V's as far as is known, since their maxima lie at $k=0$.

Huntington and Apker[2] have demonstrated that for a valence band possessing a nondegenerate maximum at $k=0$, the $k=0$ wave function possesses a node at the surface. All transition probabilities at the surface are then proportional to $E-E_i$ which would introduce an extra power of $E-E_i$ into all yield-energy dependences quoted above for surface mechanisms. We find that the Huntington-Apker node is not present for degenerate bands or for bands, where k_n, $-k_n \neq 0$ are the k-coordinate projections normal to the emitting surface of equivalent maxima. In particular, for Si, Ge, and the III-V's whose maxima are degenerate, the Huntington-Apker extra power of $E-E_i$ should not be included.

In Sec. V A we also consider the effect of the attenuation of the light intensity, $|A_0|^2 e^{-\alpha x}$, which may not always be negligible, since α has a value of 2×10^6 cm^{-1} for Si at 4.5 eV according to Philipp and Taft.[6] The effect is to relax the selection rule, $\Delta k_n=0$, on momentum normal to the surface for "direct" transitions.

In Sec. V B a number of processes involving surface states are discussed briefly. Four cases involve the perfect surface with band states. The cases depend on whether momentum tangential to the surface is or is not conserved ("direct" or "indirect" processes) and whether the threshold occurs at or away from the Fermi level. The yield energy dependences may be listed:

1. Direct; threshold $E_{dS} \neq |\mathcal{E}_F|$; $Y \sim E-E_{dS}$.
2. Direct; threshold $|\mathcal{E}_F|$; $Y \sim (E-|\mathcal{E}_F|)^{\frac{3}{2}}$.
3. Indirect; threshold $E_{iS} \neq |\mathcal{E}_F|$; $Y \sim (E-E_{iS})^2$.
4. Indirect; threshold $|\mathcal{E}_F|$; $Y \sim (E-|\mathcal{E}_F|)^{\frac{5}{2}}$.

Two cases involve states due to imperfections. If the states are distributed in energy with constant density at the Fermi level, the yield is proportional to $(E-|\mathcal{E}_F|)^2$. If they are lumped at a discrete value, $-E_L$, the yield goes as $E-E_L$.

A. Assumptions and Conventions

The yield vs energy dependences quoted are based entirely on "density of state" considerations assuming that matrix elements do not vary rapidly near threshold. The only exception is Sec. V, where we discuss the Huntington-Apker node. Symmetry "forbidden" matrix elements may be important in practice but we do not discuss them further in this paper. The general effect would be to add an extra power of E to the relevant yield vs energy relationships. When quantum yields are written down, it is assumed that optical absorption varies slowly near threshold. In general, if a quantity is not zero at threshold it is assumed to be slowly varying.

Strict energy conservation is always assumed. In fact, "lifetime broadening" effects due to strong scattering mechanisms, particularly where "pair production" is possible, will act to smear out predicted thresholds.

Energy loss is treated on an "all or nothing" basis, see Sec. III B. This assumption is certainly not always adequate.

Taylor expansions to lowest nonvanishing order for functions of the energy bands are always made about the threshold point. This approximation may go bad quickly when bands are close together in energy at the relevant k point. The simple results, in general, apply only for energies small compared to appropriate band separations.

We assume a complete set of states which are Bloch states inside the crystal and join smoothly through the

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

image barrier to free electron states of equal energy and equal tangential k vector. These states are indexed by their Bloch k vector. All "transitions" and "scatterings" are between such states, either in the volume or at the surface.

Transitions are considered between a valence band, indexed 2, and a conduction band indexed 1. Sums over different band pairs may be important, as in Eq. (1), but will be suppressed, when possible, to avoid proliferation of symbols. Similarly, sums over phonon modes will not be explicitly indicated.

The symbol E refers to photon energies while $\mathcal{E}$ is used to denote electronic energy levels with the vacuum chosen as the zero of energy.

All calculations are made for a filled valence band, empty conduction band at $T=0$ with no "band bending" at the surface.

II. DIRECT TRANSITIONS IN THE VOLUME

The rate of photon absorption in a semiconductor in the one-electron approximation is given by the "golden rule"

$$w_{12}=\frac{2\pi}{\hbar}\frac{e^2}{m^2c^2}\frac{2V}{(2\pi)^3}\times\int_{\text{B.Z.}}|\mathbf{A}\cdot\mathbf{p}_{12}(\mathbf{k})|^2\delta(\mathcal{E}_1(\mathbf{k})-\mathcal{E}_2(\mathbf{k})-E)d\mathbf{k},\quad(1)$$

$$w_{\text{total}}=\sum_{1,2}w_{12}.$$

$\mathbf{A}$ is the vector potential of the light, V is the volume. A factor of 2 for spin is included, the integration goes over one Brillouin zone (B.Z.) and transitions are considered between pairs of bands with energy $\mathcal{E}_i(\mathbf{k})$. The index 1 runs over all empty bands, 2 runs over all filled bands. E is the photon energy.

If scattering and energy loss in the volume and at the surface are neglected, the condition for escape may be written

$$\begin{gathered}\partial\mathcal{E}_1/\partial k_n>0,\\ \mathcal{E}_1(\mathbf{k})=\hbar^2(k_t^2+k_n'^2)/2m.\end{gathered}\quad(2)$$

The energy zero is taken to be the vacuum. The k vector tangential to the surface, k_t, is conserved but the normal k vector, k_n, k_n' in solid and vacuum, respectively, is not. The positive group velocity condition assumes the vacuum is on the right of the solid. We neglect the reflection by the image field barrier which MacColl has shown to be small.[7]

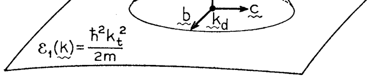

FIG. 1. The intersection of the "optical energy" surface with the "escape" surface. As E is decreased the circle of intersection shrinks to the point $\mathbf{k}_d$. $\mathbf{a}$ is normal to the escape surface at $\mathbf{k}_d$.

The quantum yield, electrons per photon, denoted by Y, is then given by

$$Y=\int'\sum_{1,2}|\mathbf{A}\cdot\mathbf{p}_{12}(\mathbf{k})|^2\delta(\mathcal{E}_1(\mathbf{k})-\mathcal{E}_2(\mathbf{k})-E)d\mathbf{k}\div\int_{\text{B.Z.}}\sum_{1,2}|\mathbf{A}\cdot\mathbf{p}_{12}(\mathbf{k})|^2\delta(\mathcal{E}_1(\mathbf{k})-\mathcal{E}_2(\mathbf{k})-E)d\mathbf{k},\quad(3)$$

where the prime denotes integration over those values of $\mathbf{k}$ satisfying condition (2). The factor by which the yield is reduced due to scattering is treated in Sec. III F.

Equation (1) assumes "direct" transitions with the customary neglect of the k vector of the light. We treat "indirect" transitions in Sec. IV.

A. Energy Dependence of Yield

We are interested in the energy dependence near threshold of the yield, Y, in Eq. (3). At threshold, E_d, we assume that the range of integration in $\int'$ collapses to a single point, or set of points equivalent by symmetry, $\mathbf{k}_d$.

The energy conservation relation,

$$E=\mathcal{E}_1(\mathbf{k})-\mathcal{E}_2(\mathbf{k}),\quad(4)$$

defines an "optical energy" surface. The critical escape condition,

$$\mathcal{E}_1(\mathbf{k})=\hbar^2k_t^2/2m,$$

defines an "escape" surface. At threshold these two surfaces are tangent at the point $\mathbf{k}_d$ for an optical energy E_d. Let $\mathbf{a}$ be the common normal at $\mathbf{k}_d$ directed toward increasing optical energy. These surfaces are depicted in Fig. 1. Let a, b, c be an orthonormal coordinate system in k space with origin $\mathbf{k}_d$. We may make the following expansions which will be valid for small k_a, k_b, k_c:

$$\mathcal{E}_1-\mathcal{E}_2=E_d+|\nabla_{\mathbf{k}}(\mathcal{E}_1-\mathcal{E}_2)|_{\mathbf{k}_d}k_a+\text{quad}(k_b,k_c),\quad(5)$$

$$\mathcal{E}_1-\left(\frac{\hbar^2k_t^2}{2m}\right)=\alpha_1k_a+\text{quad}'(k_b,k_c).\quad(6)$$

The absence of terms linear in k_b, k_c in Eqs. (5) and (6) is implied by the quadratic functions quad, quad′. Positive α_1 corresponds to a "lower" threshold which is the customary situation with the yield increasing for energies above E_d. For negative α_1 we have an "upper" threshold with yield increasing below E_d. A different type of "upper" threshold would be caused by a maximum in $\mathcal{E}_1-\mathcal{E}_2$. Since $\nabla_{\mathbf{k}}(\mathcal{E}_1-\mathcal{E}_2)=0$ in this case, a different expansion than that of Eqs. (5) and (6) is required.

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[7] L. A. MacColl, Bell System Tech. J. **30**, 588 (1951).

If we substitute Eq. (5) in the integral in Eq. (3) we can integrate over the variable k_a. This integration removes the δ function and installs the energy conservation relation, $E=\mathcal{E}_1-\mathcal{E}_2$. If we eliminate k_a between Eqs. (5) and (6) using Eq. (2), energy conservation may be written

$$E-E_d=\beta' k_n'^2+\beta_b k_b^2+\beta_c k_c^2,$$

$$\beta'\equiv\left(\frac{\hbar^2}{2m\alpha_1}\right)|\nabla_{\mathbf{k}}(\mathcal{E}_1-\mathcal{E}_2)|_{\mathbf{k}_d}. \tag{7}$$

β_b and β_c must have the same sign, which is positive or negative for a "lower" or "upper" threshold, respectively. The orientation of axes b and c has been chosen to simplify the quadratic form in k_b, k_c in Eq. (7).

The integral in Eq. (3) is then over those values of k_b, k_c which satisfy Eq. (7). The "differential yield" is proportional to the area $dk_b dk_c$. When the surface is normal to a symmetry direction, the threshold point $\mathbf{k}_d$ and $\nabla_{\mathbf{k}}(\mathcal{E}_1-\mathcal{E}_2)$ will often also be normal to the surface. In this case k_n', k_b, k_c are the k-vector components of the emitted electrons. They must lie on the *ellipsoidal yield surface* given by Eq. (7). The surface character of the yield clearly means that in a given direction the emitted electron has a unique energy. This is to be contrasted with the case of scattering or "indirect" transitions discussed later where the yield relation has a volume character and a range of energies will correspond to a single direction. This fact may prove useful in differentiating between different processes.

When $\mathbf{k}_d$ is not normal to the surface, k_b and k_c refer only to the internal electron. Let $\delta\mathbf{k}=(0,k_b,k_c)$. [We may neglect k_a compared to k_b, k_c in the region where Eqs. (5) and (6) are valid expansions.] Then k_n', $(\mathbf{k}_d+\delta\mathbf{k})_t$ are coordinates of the emitted electron, where the subscript, t, refers to the projection on the plane of the surface. The electrons are nearly tangential to the surface in the direction k_{dt}.

The integration over k_b, k_c in Eq. (3) is just the total area for which Eq. (7) can be satisfied. We find[8]

$$Y=\gamma(E-E_d),$$

$$\gamma=\frac{\pi g|\mathbf{A}\cdot\mathbf{p}_{12}(\mathbf{k}_d)|^2}{|\nabla_{\mathbf{k}}\mathcal{E}_1-\mathcal{E}_2|_{\mathbf{k}_d}(\beta_b\beta_c)^{\frac{1}{2}}\int_{\text{B.Z.}}|\mathbf{A}\cdot\mathbf{p}_{12}(\mathbf{k})|^2\delta(\mathcal{E}_1(\mathbf{k})-\mathcal{E}_2(\mathbf{k})-E)d\mathbf{k}}. \tag{8}$$

g is the number of points, $\mathbf{k}_d$, equivalent by symmetry. We have assumed that $p_{12}(\mathbf{k})$ is slowly varying in the vicinity of $\mathbf{k}_d$. If the total absorption is also slowly varying, γ will be nearly constant and the yield will rise linearly with energy. Linear dependences of this sort have been observed by Gobeli and Allen[4] and Scheer.[5]

B. Nondegenerate Symmetric Bands

When the emitting surface is normal to a symmetry direction of twofold or higher symmetry, the threshold point, $\mathbf{k}_d$, and the gradient $\nabla_{\mathbf{k}}(\mathcal{E}_1-\mathcal{E}_2)$ will often occur along this direction. This is because energy terms linear in k normal to the axis are required to vanish by symmetry. As noted earlier, k_n', k_b, and k_c in Eq. (3) are then the k-vector components of the emitted electron. The band parameters β', β_b, β_c are probably most easily determined from the energy of the emitted electron as a function of direction, as given by Eq. (7). These parameters also enter into the differential yield, dY, which may be described with the following choice of polar coördinates:

$$k_n'=k\cos\theta, \tag{9}$$

$$k_b=k\sin\theta\cos\varphi, \tag{10}$$

$$k_c=k\sin\theta\sin\varphi,$$

$$d\Omega\equiv\sin\theta d\theta d\varphi,$$

$$dY=\frac{(\beta_b\beta_c)^{\frac{1}{2}}\gamma d\Omega\, k^2}{\pi\{\cos\theta\cos^2\varphi[1+(\beta_b/\beta')\tan^2\theta]+\cos\theta\sin^2\varphi[1+(\beta_c/\beta')\tan^2\theta]\}}, \tag{11}$$

$$k^2=\frac{(E-E_d)}{\{\beta'\cos^2\theta+\beta_b\sin^2\theta\cos^2\varphi+\beta_c\sin^2\theta\sin^2\varphi\}}. \tag{12}$$

$d\Omega$ is the differential element of solid angle defined by Eq. (10). θ is measured from the surface normal. γ is defined in Eq. (8). Equation (12) is obtained by substituting Eq. (9) in Eq. (7). The energy of the emitted electron is $\hbar^2k^2/2m$, which is a unique function of direction for a given photon energy, E.

If the symmetry axis has only twofold rotation sym-

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[8] Equation (44) gives the reduction in yield due to scattering.

metry, energy is quadratic in k normal to the axes but the principal axes are not specified. The axis will in general be different for conduction and valence bands and for the relevant axes in Eq. (7). For "two-mirror plane" symmetry the axes are specified. In this case we may write

$$\begin{aligned}\mathcal{E}_1&=\alpha_1k_a+\beta_{1b}k_b^2+\beta_{1c}k_c^2,\\ \mathcal{E}_2&=\alpha_2k_a+\beta_{2b}k_b^2+\beta_{2c}k_c^2-E_d.\end{aligned}\tag{13}$$

k_a is normal to the emitting surface; energy zero is the vacuum. The quantities β_b, β_c, β' in Eq. (7) are easily found to be

$$\begin{aligned}\beta_b&=\frac{(\alpha_1-\alpha_2)(\hbar^2/2m)+\alpha_2\beta_{1b}-\alpha_1\beta_{2b}}{\alpha_1},\\ \beta_c&=\frac{(\alpha_1-\alpha_2)(\hbar^2/2m)+\alpha_2\beta_{1c}-\alpha_1\beta_{2c}}{\alpha_1},\\ \beta'&=|\alpha_1-\alpha_2|(\hbar^2/2m\alpha_1).\end{aligned}\tag{14}$$

The number of equivalent threshold points, $\mathbf{k}_d$, will be unity in the case where $\mathbf{k}_d$ is normal to the emitting surface.

C. Degenerate Symmetric Bands

In cubic materials the [111] and [100] directions are symmetry directions of special interest. They both possess doubly degenerate bands which split under spin-orbit interaction. Group theoretical considerations show that the forms of E vs k in the vicinity of the symmetry axes are

[100] direction

$$E(\mathbf{k})=\alpha k_z+\beta(k_x^2+k_y^2)\pm[B_1(k_x^2+k_y^2)^2+B_2k_x^2k_y^2+(\Delta/2)^2]^{\frac{1}{2}}\tag{15}$$

[111] direction

$$E(\mathbf{k})=\alpha k_a+\beta(k_b^2+k_c^2)\pm[A(k_b^2+k_c^2)+B(k_b^2+k_c^2)^2+C(k_c^3-3k_ck_b^2)+(\Delta/2)^2]^{\frac{1}{2}},\tag{16}$$

$$\begin{aligned}\mathbf{k}_a&=k_a(1/\sqrt{3},1/\sqrt{3},1/\sqrt{3}),\\ \mathbf{k}_b&=k_b(1/\sqrt{2},-1/\sqrt{2},0),\\ \mathbf{k}_c&=k_c(1/\sqrt{6},1/\sqrt{6},-2/\sqrt{6}).\end{aligned}\tag{17}$$

Equations (17) define the vectors $\mathbf{k}_a$, $\mathbf{k}_b$, $\mathbf{k}_c$ in terms of their x, y, z components. Δ is the spin-orbit splitting. A linear k dependence along the symmetry axis is assumed.

In what follows, we assume the surface is normal to the symmetry direction in question. If the computation leading to Eq. (8) is carried out using Eq. (15) and ignoring Δ, the same linear dependence of yield on photon energy is found. This is due to the quadratic character of the energy dependence on transverse momentum. The angular dependence of the square root in Eq. (15) enters into the constant γ. Two regions of different linear slope might be found for $E-E_d\ll\Delta$ and for $E-E_d\gg\Delta$ in favorable circumstances.

In the [111] direction a new feature appears. The quadratic terms associated with A under the square root which were not present for the [111] direction will have the effect of displacing the threshold point away from the [111] axis if Δ is small. The emitted electrons will then have a finite transverse kinetic energy at threshold.

If Δ is small and if the constant C in Eq. (16) were negligible (there is no reason it should be), the energy bands would be cylindrically symmetric and the threshold would occur on a circle rather than at three equivalent points. In this case, the yield goes as $(E-E_d)^{\frac{1}{2}}$ and then abruptly changes to linear, $E-E_d$, when the emitted electrons are finally able to appear with zero transverse energy. To illustrate these points we consider a less general case, namely,

$$\mathcal{E}_1(\mathbf{k})=\alpha_1k_a+\beta_1(k_b^2+k_c^2),\tag{18}$$

$$\mathcal{E}_1-\mathcal{E}_2=\alpha k_a+\beta(k_b^2+k_c^2)\pm_1[A(k_b^2+k_c^2)]^{\frac{1}{2}}+E_0,\tag{19}$$

$$E=\mathcal{E}_1-\mathcal{E}_2.\tag{20}$$

With the use of Eq. (19) the integral in Eq. (3) is easily performed. The integral of dk_a over the δ function gives a factor $1/\alpha$ and requires energy conservation, [Eq. (20)]. The integral is then proportional to the area in k_b, k_c space which satisfies Eqs. (2), (18), (19), and (20). Eliminating k_a between these equations, we have

$$(k_b^2+k_c^2)^{\frac{1}{2}}=\frac{\pm_1A^{\frac{1}{2}}\pm_2\{A+b[E-(\alpha/\alpha_1)(\hbar^2/2m)k_n'^2]\}^{\frac{1}{2}}}{(b/2)},\tag{21}$$

$$b\equiv4\left[\beta-\left(\beta_1-\frac{\hbar^2}{2m}\right)\frac{\alpha}{\alpha_1}\right].\tag{22}$$

The two ± signs are independent, the first refers to Eq. (19). The coefficient $b\alpha/\alpha_1$ must be positive in order that unbounded values of $k_n'^2$ and $(k_b^2+k_c^2)^{\frac{1}{2}}$ do not occur. We also assume b positive so that we get the normal case of a "lower" threshold. The threshold is easily seen to be given by

$$E_d=-(A/b)+E_0,\tag{23}$$

$$(k_b^2+k_c^2)_d^{\frac{1}{2}}=2A^{\frac{1}{2}}/b,\tag{24}$$

$$k_{ad}=\left(\frac{\hbar^2}{2m}-\beta_1\right)\frac{4A}{\alpha_1b^2}.\tag{25}$$

The solution clearly involves transitions corresponding to the (−) case in Eq. (19). For $E<E_0$, only the (−) case is involved and the permissible area is given by

$$Y\sim\text{area}=16\pi[Ab(E-E_d)]^{\frac{1}{2}}/b^2,\quad E-E_0<0.\tag{26}$$

For $E>0$, both ± bands contribute and the total permissible area summed over both + and − transitions is

$$Y\sim\text{area}=8\pi[A+b(E-E_d)]/b^2,\quad E-E_0>0.\tag{27}$$

Hence, the yield abruptly switches from square root to linear (but with continuous value and slope) as the permissible area touches the symmetry axis.

As remarked earlier, this solution may not have much significance since there is no good reason for ignoring the cubic terms in Eq. (16). With the inclusion of cubic terms the threshold would reduce to a set of three equivalent points off the [111] axis which would give a linear yield as shown earlier. However, one would expect a small range for this linear dependence because of the proximity of the other band.

III. DIRECT VOLUME TRANSITIONS WITH SCATTERING

In the event that the threshold energy for direct transitions, E_d, corresponds to a k vector, $\mathbf{k}_d$, which is not normal to the emitting surface, there will be a lower energy threshold, E_{ds}, resulting from surface or volume scattering which allows the electron to escape with very little momentum tangential to the surface. The yield near threshold will be much lower in this case and will rise like $(E-E_{ds})^2$ as compared to $(E-E_d)$ since only a small fraction of the scattered electrons will lie within the solid angle permitting emission.

The total yield, Y_{ds}, in the scattering case depends on the product of four factors which we shall consider in turn.

$$Y_{ds}=p_e p_s f_i f_s (E-E_{ds})^2. \tag{28}$$

$f_i(E-E_{ds})$ is that fraction of the internally excited electrons which have sufficient kinetic energy to escape. p_s is the probability that the electron is scattered without substantial loss of energy. $f_s(E-E_{ds})$ is the fraction of the scattered electrons which lie within the escape cone determined by the external tangential kinetic energy. p_e is the probability that the scattered electron can escape without substantial loss of energy.

A. Internal Kinetic Energy

The threshold, E_{ds}, is defined as the minimum photon energy for which the conduction electron is energetically able to escape. We make our energy-band expansions about the point, $\mathbf{k}_{ds}$, defined by

$$\begin{aligned} \mathcal{E}_1(\mathbf{k}_{ds})&=\pm\hbar\omega, \\ E_{ds}&=\mathcal{E}_1(\mathbf{k}_{ds})-\mathcal{E}_2(\mathbf{k}_{ds}). \end{aligned} \tag{29}$$

Energy zero is still the vacuum and $\mathcal{E}_1(\mathbf{k})$ is the conduction band. $+$, $-$ is for phonon emission and absorption, respectively; $\hbar\omega=0$ for elastic scattering. We expand E about $\mathbf{k}_{ds}$ in the same way as in Eq. (5):

$$\mathcal{E}_1-\mathcal{E}_2=E_{ds}+|\nabla_{\mathrm{k}}\mathcal{E}_1-\mathcal{E}_2|_{\mathrm{k}_{ds}}k_a+\mathrm{quad}(k_b,k_c). \tag{30}$$

We also expand $\mathcal{E}_1(\mathbf{k})$,

$$\begin{aligned} \mathcal{E}_1(\mathbf{k})&=\alpha_1 k_a+\mathrm{quad}'(k_b,k_c)\pm\hbar\omega, \\ \epsilon&\equiv\mathcal{E}_1(\mathbf{k})\mp\hbar\omega. \end{aligned} \tag{31}$$

ϵ is the energy of the emitted electrons. The absence of linear terms in k_b, k_c is a necessary consequence of the assumption that $\mathbf{k}_{ds}$ is a threshold. The procedure is entirely analogous to that used for Eqs. (5) and (6). Substituting Eq. (30) in the integral in Eq. (3), we integrate over k_a to remove the δ function. Then k_a can be eliminated between Eqs. (30) and (31), giving

$$E-E_{ds}=[\nabla_{\mathrm{k}}(\mathcal{E}_1-\mathcal{E}_2)_{\mathrm{k}_{ds}}/\alpha_1]\epsilon+\beta_b k_b^2+\beta_c k_c^2. \tag{32}$$

Axes have been chosen for b and c to simplify the quadratic form in Eq. (32). β_b, β_c, and $\nabla_{\mathrm{k}}(\mathcal{E}_1-\mathcal{E}_2)/\alpha_1$ must be positive for a "normal" threshold. We use Eq. (32) to define an "internal" differential yield, dY_i, for electrons of energy ϵ in an energy range $d\epsilon$. Using Eq. (3), we calculate

$$dY_i=f_i(|\nabla_{\mathrm{k}}(\mathcal{E}_1-\mathcal{E}_2)|_{k_{ds}}/\alpha_1)d\epsilon, \tag{33}$$

$$f_i=\frac{\pi g|\mathbf{A}\cdot\mathbf{p}_{12}(\mathbf{k}_{ds})|^2(\alpha_1/|\nabla_{\mathrm{k}}(\mathcal{E}_1-\mathcal{E}_2)|_{\mathrm{k}_{ds}})}{(\beta_b\beta_c)^{\frac{1}{2}}\int_{\mathrm{B.Z.}}|\mathbf{A}\cdot\mathbf{p}_{12}(\mathbf{k})|^2\delta(E-\mathcal{E}_1(\mathbf{k})+\mathcal{E}_2(\mathbf{k}))d\mathbf{k}}, \tag{34}$$

$$0\leq\epsilon\leq(\alpha_1/|\nabla_{\mathrm{k}}(\mathcal{E}_1-\mathcal{E}_2)|_{\mathrm{k}_{ds}})(E-E_{ds}). \tag{35}$$

The total fraction of electrons having sufficient kinetic energy to escape is $f_i(E-E_{ds})$ as contained in Eq. (28). g is the number of distinct points $\mathbf{k}_{ds}$ which are equivalent by symmetry.

B. Probability of Scattering

We should first mention and then dismiss the possibility of "surface umklapp" scattering. By "surface umklapp" we mean scattering by a principal vector of the two-dimensional surface lattice. For high-index surfaces these vectors may be much smaller than the principal vectors of the solid. For low-index planes such as [111] and [100] in the face-centered cubic lattices, the principal vectors of the surface are just the principal vectors of the volume projected on the surface plane; hence, no new scattering is obtained. Since the usual surfaces are low index, it seems unlikely that "surface umklapp" will be important.

Note added in proof. In the case of "surface superlattice" structures such as those found in germanium, "surface umklapp" could be more important.

We divide scattering mechanisms into two types:

(a) Phonons, impurities, or imperfections in the volume or the surface. (b) Electron-electron collisions resulting in pair production. Within one band gap of threshold, category b necessarily leads to loss of the excited electron. w_a and w_b represent the total scattering rate of mechanisms a and b, respectively. We assume that energy losses can be ignored for processes of type a (obviously not always true for phonons), and that type b scattering always removes the electron from consideration. Then the probability, p_s, that one or more scatterings of type a precede a scattering of type b may easily be shown to be

$$p_s = w_a/(w_a + w_b). \tag{36}$$

C. "Escape" Cone

We now calculate the fraction of scattered electrons which are able to escape. Their tangential momentum, k_t', must satisfy the energy conservation relation

$$\epsilon = \hbar^2(k_t'^2 + k_n''^2)/2m, \tag{37}$$

where ϵ is the total kinetic energy of the emitted electrons. A detailed treatment of the scattering seems uncalled for; hence, we assume that the scattered particles are distributed uniformly over the energy shell $\delta(\mathcal{E}_1(k) \mp \hbar\omega - \epsilon)$. This is equivalent to assuming a momentum independent scattering matrix element. For the case $w_a \gg w_b$, so that many quasi-elastic scatterings occur, the assumption should be quite accurate.

The fractional "volume" of the energy shell satisfying Eq. (37) is easily seen to be $2f_s[|\nabla_{\mathbf{k}}(\mathcal{E}_1 - \mathcal{E}_2)_{\mathbf{k}_{ds}}|/\alpha_1]\epsilon$, where

$$f_s = \frac{\pi m[\alpha_1/|\nabla_{\mathbf{k}}(\mathcal{E}_1 - \mathcal{E}_2)_{\mathbf{k}_{ds}}|]}{\hbar^2|\nabla\mathcal{E}_1|_{\mathbf{k}_n}\int_{\mathrm{B.Z.}} \delta(\mathcal{E}_1(\mathbf{k}))d\mathbf{k}}. \tag{38}$$

$\mathbf{k}_n$ is the point on the energy shell $\delta(\mathcal{E}_1)$ normal to the emitting surface and assumed to be normal to the energy shell also. f_s is assumed not to vary rapidly with energy near threshold. The total yield factor introduced by the escape momentum condition, Eq. (37), is

$$f_s(E - E_{ds}),$$

where an average has been taken over all ϵ for which escape is energetically possible, i.e., values of ϵ satisfying Eq. (35).

The differential yield is easily computed to be

$$dY \sim \cos\theta d\Omega\, \epsilon d\epsilon, \tag{39}$$

where θ is measured from the normal and ϵ is the emitted electron's kinetic energy. $d\Omega$ is given by Eq. (10). For a given direction, a range of energies from $\epsilon = 0$ to $\epsilon = \{\alpha_1/|\nabla_{\mathbf{k}}(\mathcal{E}_1 - \mathcal{E}_2)|_{\mathbf{k}_{ds}}\}(E - E_{ds})$ may be found in contrast to the unscattered case where a single energy occurred. The fact that $\epsilon_{\max} \neq E - E_{ds}$ still attests to the initial production by direct transitions, but most of the band structure information contained in the unscattered case has been washed out by scattering.

D. "Escape" Probability

The final factor to be considered is the probability that the electron travels from the point of origin to the surface without suffering an energy losing collision. This we call the escape probability, p_e.

The escape probability may be written

$$p_e = e^{-w_b t}, \tag{40}$$

where t is the time required to reach the surface. If the electron moves without scattering, this time is

$$t = \frac{\hbar x}{|\partial\mathcal{E}_1/\partial k_n|}, \tag{41}$$

where x is the distance from the surface of the point of origin. If many quasi-elastic scatterings occur, the electron will diffuse to the surface and the escape probability will be lowered.

The absorption probability per unit length is proportional to $\exp(-x/l_\alpha)$. If we crudely ignore the electrons motion prior to the first scattering and average over x for t given by Eq. (41), we find

$$p_e = l_e/(l_e + l_\alpha), \tag{42}$$

$$l_e = (\partial\mathcal{E}_1/\partial k_n)1/\hbar w_b. \tag{43}$$

E. General

The yield in the scattering cases rises like $(E - E_{ds})^2$ as compared to the linear rise $(E - E_{ds})$ of the momentum-conserving case. The two processes will become comparable within a few volts of threshold as $f_s(E - E_{ds})$ approaches unity. Of course, the approximations leading to the linear and quadratic energy dependences will not generally be applicable for more than a volt above threshold.

F. Escape for Unscattered Electrons

In computing the yield for direct transitions without scattering we should include an escape factor, $1 - p_s'$, so that Eq. (8) becomes

$$\eta = (1 - p_s')\gamma(E - E_d). \tag{44}$$

p_s' is the probability of any type of scattering. Replacing w_b by $w_a + w_b$ in Eq. (43) and using Eq. (42), we find

$$1 - p_s' = l_e'/(l_e' + l_\alpha),$$

$$l_e' = \left(\frac{\partial\mathcal{E}_1}{\partial k_n}\right)\frac{1}{\hbar(w_a + w_b)}. \tag{45}$$

IV. INDIRECT TRANSITIONS IN THE VOLUME

We have so far considered processes where the excited electron is produced by a direct optical transition.

The threshold energy then contains the energy necessary to excite the electron above the vacuum zero plus the energy of the hole. Since the threshold will seldom correspond to a hole located at the valence band maximum, a lower threshold is generally possible for processes where the initial excitation is "indirect."

The rate of "indirect" excitations is given by the second-order "golden rule"

$$w_{13}=\frac{2\pi}{\hbar}\sum_3\left|\sum_2\frac{h_{12}h_{23}}{E_1-E_2}\right|^2\delta(E_1-E_3). \tag{46}$$

1, 2, 3 index the initial, intermediate, and final states, respectively. The initial state is the unexcited crystal plus a photon; the final state is the electron at $\mathbf{k}_1$, the hole at $\mathbf{k}_2$, and no photon. The intermediate state is formed by optical excitation producing a virtual electron-hole pair both at either $\mathbf{k}_1$ or $\mathbf{k}_2$ (ignoring the k vector of the light). A phonon or imperfection then scatters either the electron or the hole to the final configuration.

Assuming that matrix elements and energy denominators are approximately constant for all possible transitions near threshold, we write Eq. (46) as

$$w_{13}=\frac{2\pi}{\hbar}\frac{2V^2}{(2\pi)^6}\left|\sum_2\frac{h_{12}h_{23}}{E_1-E_2}\right|^2 \times\int\delta(\mathcal{E}_1(\mathbf{k}_1)-\mathcal{E}_2(\mathbf{k}_2)-E)d\mathbf{k}_1d\mathbf{k}_2. \tag{47}$$

The symbols are the same as in Eq. (1). The quantum yield is given by the ratio of w_{13} from Eq. (47) to w of Eq. (1).

The "escape" condition is

$$\mathcal{E}_1(\mathbf{k})=\{\hbar^2(k_t^2+k_n'^2)/2m\}\pm\hbar\omega. \tag{48}$$

k_t is the momentum tangential to the surface, + is for phonon emission, − for absorption, $\hbar\omega=0$ for elastic processes. Energy zero is the vacuum. We eliminate the δ function in Eq. (47) by integrating over k_n, the component of $\mathbf{k}_1$ normal to the surface. This installs the energy conservation relation which we use, together with Eq. (48), to integrate over k_t, the tangential component of $\mathbf{k}_1$.

$$\rho_i(E)\equiv\frac{2V^2}{(2\pi)^6}\int\delta(\mathcal{E}_1(\mathbf{k}_1)-\mathcal{E}_2(\mathbf{k}_2)-E)d\mathbf{k}_1d\mathbf{k}_2, \tag{49}$$

$$\rho_i(E)=\frac{mV^2\int[\mathcal{E}_2(\mathbf{k}_2)+E\mp\hbar\omega]d\mathbf{k}_2}{16\pi^5\hbar^2(\partial\mathcal{E}_1/\partial k_n)}. \tag{50}$$

In the neighborhood of an extremum, k_m, we write

$$\mathcal{E}_2(\mathbf{k}_2)=e_2+\hbar^2(k-k_m)^2s(\theta,\varphi)/2m_2^*. \tag{51}$$

s denotes a possible angular dependence of effective mass. The "indirect" threshold energy, E_i is then given by

$$E_i=-e_2\pm\hbar\omega \tag{52}$$

with + for phonon emission, − for absorption. The density of states may then be written

$$\rho_i(E)=c(E-E_i)^{\frac{5}{2}},$$
$$c=\frac{\sqrt{2}m(m_2^*)^{\frac{3}{2}}V^2}{15\pi^4\hbar^5(\partial\mathcal{E}_1/\partial k_n)}. \tag{53}$$

m_2^* is a density of states mass which has the well-known value

$$m_2^{*\frac{3}{2}}=g(m_am_bm_c)^{\frac{1}{2}} \tag{54}$$

for g equivalent ellipsoids. The value of m_2^* in Eq. (51) is chosen, so that

$$\int s(\theta,\varphi)d\Omega/4\pi=1. \tag{55}$$

Equation (55) is applicable for degenerate bands. The density of states for degenerate bands should also be summed over bands, although this has not been explicitly indicated. The yield, Y, will be proportional to the density of states as given in Eq. (53).

The differential yield may be written

$$d\eta\sim\cos\theta\, d\Omega\, \epsilon(E-E_i-\epsilon)^{\frac{1}{2}}d\epsilon,\quad 0\leq\epsilon\leq E-E_i. \tag{56}$$

ϵ is the energy of the emitted electron. The yield does not depend on any band structure parameters except in the factor of proportionality.

V. TRANSITIONS AT THE SURFACE

We distinguish two main categories of optical transitions occurring near the surface. The first category is that where the hole left behind is in a "volume" state and the second category where the hole is in a surface state. In both cases we assume the electron is in a "volume" type state characterized by asymptotic momenta k_n, $\mathbf{k}_t$ in the solid or k_n', $\mathbf{k}_t$ in the vacuum. Near the surface the normal momentum, k_n, is not constant. For convenience we use the volume state density appropriate to the k_n degree of freedom. Alternatively, one could use the apparently different vacuum state density appropriate to k_n' but the volume amplitudes would have to be renormalized. We take the state density for k_n as a constant near threshold and always integrate out this variable to remove the δ function on energy. The remaining degrees of freedom are then integrated over subject to strict energy conservation.

A. Transitions from "Volume" States

1. *Diffuse Surface Transitions*

Equation (53) should apply for any form of indirect scattering mechanism including diffuse scattering at surface imperfections, provided the final state involves a hole free in the volume.

2. *Specular Surface Transitions*

Transitions made at a perfect surface must conserve momentum tangential to the surface (ignoring "surface" umklapp). The energy threshold will be the same as for indirect transitions for those cases where the valence band maximum lies along the k vector normal to the surface. In this case, we write

$$\begin{aligned}\mathcal{E}_1(k)&=\hbar^2(k_t^2+k_n''^2)/2m,\\ \mathcal{E}_2(k)&=-E_i+\hbar^2(k_t^2+k_n^2)/2m_2^*.\end{aligned}\tag{57}$$

The yield integral is

$$\eta\sim\int d\mathbf{k}_t dk_n,\tag{58}$$

subject to the energy conservation relation

$$E-E_i=\frac{\hbar^2}{2}\left\{k_t^2\left(\frac{1}{m}-\frac{1}{m_2^*}\right)+\frac{k_n''^2}{m}-\frac{k_n^2}{m_2^*}\right\}.\tag{59}$$

The electron momentum k_n' has been integrated over, as described above, with the constant state density factor being absorbed in the proportionality sign. In Eq. (59), m_2^* has its (negative) algebraic sign. The emitted electron has its maximum kinetic energy when $k_n=0$. The parameter m_2^* can be determined from Eq. (59) by measuring this maximum energy at any angle not normal to the surface. The total and differential yields are easily found by integrating over $d\mathbf{k}_t$, dk_n in Eq. (58) using Eq. (59) and Eq. (10)

$$\begin{aligned}Y&\sim(E-E_i)^{\frac{3}{2}},\\ dY&\sim\epsilon\cos\theta d\Omega d\epsilon/(E-E_i-\tilde{\epsilon})^{\frac{1}{2}},\\ \tilde{\epsilon}&\equiv\epsilon[1-(m/m_2^*)\sin^2\theta],\\ \tilde{\epsilon}_{\max}&=E-E_i.\end{aligned}\tag{60}$$

ϵ is the kinetic energy of the emitted electron.

3. *Huntington-Apker Node*

Huntington and Apker[2] have demonstrated that for a nondegenerate valence band with maximum at $k=0$ the electrons close to $k=0$ will have a node at the surface. They show this by calculating the ratio of incident and reflected amplitudes using matching conditions at the surface. The incident Bloch wave is $u_{\mathbf{k}}(r)e^{i\mathbf{k}\cdot\mathbf{r}}$ and the reflected wave is $au_{\mathbf{k}'}(r)e^{i\mathbf{k}'\cdot\mathbf{r}}$, where $k_n'=-k_n$, $\mathbf{k}_t'=\mathbf{k}_t$ which results from the requirements of transverse momentum and energy conservation. They find that they are unable to match at the surface (except for an unusual special case) unless $a\rightarrow -1$ as $\mathbf{k}\rightarrow 0$, which gives a node at the surface. The reason this occurs is that $u_{\mathbf{k}}(r)e^{i\mathbf{k}\cdot\mathbf{r}}\rightarrow u_{\mathbf{k}'}(r)e^{i\mathbf{k}'\cdot\mathbf{r}}$ as $\mathbf{k}\rightarrow 0$ so that one is attempting to satisfy two matching conditions with a single function which can only be done by making the combined amplitude zero.

In the case of a degenerate maximum, $\mathbf{k}$ and $\mathbf{k}'$ may lie in different bands; for a group of equivalent extrema $\mathbf{k}$ and $\mathbf{k}'$ may lie in different minima (if the minima have the same transverse momentum). In either of the above situations $\psi_{\mathbf{k}}$ and $\psi_{\mathbf{k}'}$ do not become identical as $\mathbf{k}$ tends to the extremum so there appears to be no reason to expect a node at the surface in these cases. Si, Ge, and all known III-V's come in this category since their valence extrema are degenerate at $k=0$.

As Huntington and Apker have pointed out, in those materials where a node is required, the transition probability vanishes proportional to $E-E_i$ at the threshold for processes where the hole is left at the valence maximum. The "diffuse" and "specular" yields calculated in Secs. I and II would then vary as $(E-E_i)^{7/2}$ and $(E-E_i)^{\frac{5}{2}}$, respectively.

4. *Effect of Light Attenuation*

In all calculations so far we have ignored the k vector of the light. Even if this were not done, no qualitative change would result. When we consider the effect of the attenuation of the light, however, the situation is qualitatively different because of the "fuzzing out" of momentum conservation.

We assume the light attenuates according to

$$A_0e^{-\alpha x/2},\tag{61}$$

where x is normal to the surface. The matrix elements for optical transitions are then easily seen to be proportional to

$$|H_{ij}|^2\sim\delta(\mathbf{k}_t)/4(\Delta k_n)^2+\alpha^2,\tag{62}$$

instead of being proportional to a δ function of the total momentum change.

If Eq. (62) could be trusted a long way in the "wings," the calculation would be quite analogous to the case of "specular" surface transitions as treated in Sec. II. This conclusion is almost certainly wrong. Equation (61) is of classical origin. It may be derived semiclassically by considering a wave packet moving with the group velocity and decaying with a Weisskopf-Wigner factor e^{-wt} where w is the rate of making absorptive transitions. This formulation suggests the "energy broadening" approach which yields the energy nonconservation factor

$$1/4(\Delta E/\hbar)^2+w^2.\tag{63}$$

Equations (63) and (62) are very similar. Equation (63) is known from more accurate considerations to give far too much amplitude in the "wings," hence it appears that Eq. (62) should likewise be mistrusted. The true effect is no doubt to give a slight fuzzing of the "direct" yield characteristic. One might hope to study the "fuzzing" effect with the use of expansions similar to Eq. (13). The results are seen to diverge which could be corrected by more accurate expressions for $\mathcal{E}(k)$ but more likely necessitates the use of an improvement on Eq. (62).

B. Transitions from Surface States

We now consider rather briefly a variety of processes in which the hole is left behind in a surface state. The first four processes assume a perfect surface so that the surface states possess well defined bands and tangential momenta, k_b, k_c. The normal momentum of the excited electron has been integrated out, leaving strict energy conservation.

1. *Direct Transitions; Threshold*$>|\mathcal{E}_F|$

We assume for this case that the threshold point lies below the Fermi level and that tangential momentum is conserved. The appropriate energy band expansions are

$$\epsilon_1=\hbar^2(k_n^2+k_b^2+k_c^2)/2m, \tag{64}$$

$$E=\epsilon_1-\epsilon_2=\left(\frac{\hbar^2k_n^2}{2m}\right)+\beta_b(k_b-k_{bdS})^2+\beta_c(k_c-k_{cdS})^2+E_{dS}. \tag{65}$$

ϵ_1 is the energy of the electron in vacuum, ϵ_2 is the energy of the hole. Equation (65) is energy conservation. Threshold occurs at $\mathbf{k}_{dS}$, E_{dS}. The absence of linear terms in k_b-k_{bdS}, k_c-k_{cdS} is a requirement for $\mathbf{k}_{dS}$ to be a threshold. The yield Y, is proportional to

$$\begin{aligned}Y&\sim\int dk_bdk_c\\ &\sim E-E_{dS}.\end{aligned} \tag{66}$$

This case is quite analogous to the case of direct volume transitions. One difference is that the maximum normal energy, $(\hbar^2k_n^2/2m)$ is equal to $E-E_{dS}$ rather than differing from it by a constant factor.

2. *Direct Transitions; Threshold*$=|\mathcal{E}_F|$

In this case the threshold point lies at the Fermi level. We use the expansion

$$\epsilon_2=-|\mathcal{E}_F|+\alpha_2(k_b-k_{bdF})+\beta_2k_c^2, \tag{67}$$

$$\begin{aligned}\epsilon_1&=\left(\frac{\hbar^2}{2m}\right)(k_n^2+k_b^2+k_c^2)\\ &\simeq\left(\frac{\hbar^2}{2m}\right)(k_n^2+2k_{bdF}(k_b-k_{bdF})+k_c^2).\end{aligned} \tag{68}$$

We have chosen the axis k_b normal to the constant energy contour of the hole. Linear terms in k_c-k_{cdF} are absent for ϵ_2 by this construction. Linear terms in (k_c-k_{cdF}) must be absent from $\epsilon_1-\epsilon_2$, hence from ϵ_1, by the condition that $\mathbf{k}_{dF}$ is a threshold. This then requires $k_{cdF}=0$. Linear terms in $\alpha_2(k_b-k_{bdF})$ are allowed since this quantity has only negative values for states which are initially occupied.

The yield integral is

$$Y\sim\int dk_bdk_c \tag{69}$$

subject to energy conservation

$$E-|\mathcal{E}_F|=\frac{\hbar^2k_n^2}{2m}+\left(\frac{\hbar^2k_{bdF}}{m}-\alpha_2\right)\times(k_b-k_{bdF})+\left(\frac{\hbar^2}{2m}-\beta_2\right)k_c^2, \tag{70}$$

which integrates to

$$Y\sim(E-|\mathcal{E}_F|)^{\frac{3}{2}}. \tag{71}$$

3. *Indirect Transitions; Threshold*$>|\mathcal{E}_F|$

In this case the surface band maximum, $-E_{iS}$, located at k_{bm}, k_{cm} must lie below the Fermi level. The appropriate expansions are

$$\begin{aligned}\epsilon_1&=\left(\frac{\hbar^2}{2m}\right)(k_n^2+k_b^2+k_c^2),\\ \epsilon_2&=-E_{iS}+\beta_b(k_b'-k_{bm})^2+\beta_c(k_c'-k_{cm})^2.\end{aligned} \tag{72}$$

The yield integral is

$$\begin{aligned}Y&\sim\int dk_bdk_cdk_b'dk_c',\\ Y&\sim(E-E_{iS})^2.\end{aligned} \tag{73}$$

4. *Indirect Transitions; Threshold*$=|\mathcal{E}_F|$

In this case, the energy band expansions are very similar to those of Sec. II.

$$\epsilon_1=\left(\frac{\hbar^2}{2m}\right)(k_n^2+k_b^2+k_c^2), \tag{74}$$

$$\epsilon_2=-|\mathcal{E}_F|+\alpha_2(k_b'-k_{bdF})+\beta_2(k_c'-k_{cdF})^2. \tag{75}$$

The yield integral is

$$\begin{aligned}Y&\sim\int dk_bdk_cdk_b'dk_c',\\ Y&\sim(E-|\mathcal{E}_F|)^{\frac{5}{2}}.\end{aligned} \tag{76}$$

5. *Distributed Imperfection States*

We consider here the case where a variety of imperfections gives rise to a distribution of localized states with a constant density per unit energy in the vicinity of the Fermi level. We write

$$\epsilon_1=\left(\frac{\hbar^2}{2m}\right)(k_n^2+k_b^2+k_c^2), \tag{77}$$

$$Y\sim\int dk_b dk_c\, \rho(\epsilon_2)d\epsilon_2$$

$$\sim(E-E_F)^2. \tag{78}$$

6. *Discrete Imperfection States*

If the imperfection states are localized in energy at the value $-E_L$ below the Fermi level, the yield will be

$$\eta\sim(E-E_L).$$

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Direct and Indirect Excitation Processes in Photoelectric Emission from Silicon

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The spectral dependence of saturation photoelectric emission has been studied for atomically-clean (111) silicon surfaces which were prepared by cleavage in high vacuum. The observed spectra, and their dependence on sample doping, are interpreted as being due to a volume excitation process which is modified by space charge band bending effects. Both direct and indirect optical excitation thresholds are observed, at 5.45 eV and 5.15 eV, respectively, with the latter being equal to the electron affinity, χ, plus the energy gap, E_G. The spectral dependence of the direct excitation process is in agreement with the theoretical model developed by Kane, in which there is a complete absence of scattering either in the bulk or at the surface for those excited electrons which are emitted. The indirect process is also in agreement with Kane's theory. The dependence of the yield on sample doping, in conjunction with the theoretical model, may be used to determine a direct-flight escape depth for excited electrons of 25 Å±5 Å for electron energies about 5.5 eV above the valence-band maximum.

I. INTRODUCTION

PHOTOELECTRIC emission from metals has been studied extensively, and it is usually assumed that light absorption leading to photoelectric emission takes place only at the surface of the metal where the electrons are subject to the surface effect. Some recent work on alkali metals,[1–3] however, has indicated that photoelectrons can originate at depths below the surface of several hundreds of angstroms. Such observations indicate rather that a volume effect dominates the emission.

The theory that photoelectric emission from semiconductors is a volume effect is generally accepted. The effect of band bending at the surface[4–6] and the energy distribution of valence-band density of states[5–7] have been discussed theoretically. Recently, some work on cesium-coated silicon surfaces[8] has substantiated the theoretical expectation that *p*-type samples should exhibit a higher photoelectric quantum efficiency than *n*-type samples. Work on alkali antimonides also indicates that photoelectrons can originate at depths well beneath the surface.[9] These results again indicate that the volume effect must be considered.

Optical excitation leading to photoelectron emission in a volume effect would be subject to the optical absorption selection rules of the lattice and would therefore consist, in general, of an indirect or phonon-assisted transition and a direct transition in which the initial and final electron states differ in **k** vector only by the photon **k** vector.

This paper discusses experimental measurements of photoelectric emission from atomically clean silicon surfaces prepared by cleavage in high vacuum, as a function of the sample doping. The results confirm the dominance of the volume photoelectric effect. As expected, *p*-type samples have a higher yield than *n*-types samples. In addition, the spectral yields from certain resistivity ranges show distinct structure, which is interpreted as the onset of an efficient direct excitation mechanism about 0.3 eV above the lower-energy indirect excitation threshold. The spectral dependence of these two components is determined and the influence of the profile of the space-charge region and the mean free path of the excited photoelectrons is examined.

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