

scattering of the emitted electrons by the random array of Cs ions on the surface.

The polarization effect from a cleaved Ge surface was observed both before and after annealing. The effect increased in amplitude upon annealing but did not change in phase. We emphasize this point because a polarization effect not requiring momentum conservation could be generated by a surface having domains of low symmetry such as the ladderlike structure given by cleavage.⁴ The presence of the enhanced effect, after annealing has produced a surface of threefold rotational symmetry, proves that such a surface domain structure is not the cause of the present effect.

In conclusion, it is believed that the polarization effect has proven the existence of unscat-

tered electrons in photoelectric emission, and has itself provided a highly sensitive new technique to study the perfection of a surface.

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IMPLICATIONS OF CRYSTAL MOMENTUM CONSERVATION IN PHOTOELECTRIC EMISSION FOR BAND-STRUCTURE MEASUREMENTS

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Compelling evidence¹ has been obtained that a sizable component of the photoelectric yield from silicon and germanium consists of electrons produced optically which have undergone no scattering events in escaping from the solid. In this case momentum tangential to the surface is conserved while normal momentum is altered by interaction with the crystal as a whole. Good evidence exists² that this is also true in GaAs and it may be quite generally true whenever clean, cleaved surfaces of high perfection can be produced.

Subject to several important limitations, the existence of crystal-momentum conservation implies that energy vs \vec{k} for the solid may be inferred directly from measurements of the energy and momentum of the emitted electrons. The first and most obvious limitation is that the lifetime of the electron in the solid be sufficiently long. Energy vs \vec{k} is, of course, always limited as a physical concept by the lifetime broadening uncertainty. The second important limitation is that the optical absorption must be assumed to occur sufficiently deep within the volume that no significant exchange of momentum normal to the surface takes place during the act of absorption. In this case we may write

$$h\nu = E_c(\vec{k}) - E_v(\vec{k}), \quad (1)$$

assuming direct transitions and ignoring the \vec{k} vector of the light. The photon energy is $h\nu$, E_c and E_v are conduction and valence-band energies, respectively. Equation (1) defines an optical energy surface in \vec{k} space. If normal momentum is not conserved during excitation, transitions occur over a volume in \vec{k} space rather than a surface. Evidence supporting normal momentum conservation is found in the work of Gobeli and Allen,³ and Kane,³ since the explanation of the linear yield vs $h\nu$ characteristics observed in silicon are based on this assumption. In what follows we assume the validity of Eq. (1).

Let k_1, k_2 be the components of momentum tangential to the surface. Since k_1, k_2 are conserved during emission they can be measured directly. For a given value of k_1, k_2 a set of two or more discrete values of the energy $E_c(k_1, k_2, k_3')$ is determined by the intersection of the line $k_1 = \text{const}$, $k_2 = \text{const}$ with the optical energy surface of Eq. (1). Although there are generally at least two points of intersection, half of the intersections will correspond to group velocities directed into the crystal for which escape without scattering is impossible. k_3' is the momentum normal

to the crystal surface inside the crystal. Since normal momentum is not conserved during escape from the crystal, k_3' cannot be measured directly. However, since k_3' is not an independent variable when k_1 , k_2 , and $\hbar\nu$ are fixed, we find that k_3' can be inferred by an "energy-coincidence" method if measurements of energy and tangential momentum are made on two different surfaces. In the presence of symmetry, measurements from a single surface are sufficient. The "energy-coincidence" scheme assumes that $E_C(\vec{k}) = E_C(\vec{k}')$ implies either that $\vec{k} = \vec{k}'$ or that \vec{k} and \vec{k}' are related by a symmetry operation.

Let any symmetry operation exist transforming k_1, k_2, k_3' into k_1'', k_2'', k_3'' , where

$$\begin{aligned} k_1'' &= a_{11}k_1 + a_{12}k_2 + a_{13}k_3', \\ k_2'' &= a_{21}k_1 + a_{22}k_2 + a_{23}k_3'. \end{aligned} \quad (2)$$

Symmetry then implies

$$E_C(k_1, k_2) = E_C(k_1'', k_2''). \quad (3)$$

If we may assume that any energy coincidence between measurements with different momenta implies a symmetry relation, then either of Eqs. (2) may be used to determine k_3' from a measurement of k_1, k_2, k_1'', k_2'' .

The analysis is greatly simplified when a direction, k_1 , in the surface can be found which is invariant under the transformation. Important examples are

diamond-type $\{111\}$ surfaces:

$$\begin{aligned} k_1'' &= k_1, \\ k_2'' &= \frac{2}{3}\sqrt{2}k_3' - \frac{1}{3}k_2, \end{aligned} \quad (4)$$

where k_1 and k_2 are $\langle 1\bar{1}0 \rangle$ and $\langle 11\bar{2} \rangle$ directions, respectively;

zincblende-type $\{110\}$ surfaces:

$$\begin{aligned} k_1'' &= k_1, \\ k_2'' &= k_3', \end{aligned} \quad (5)$$

where k_1 and k_2 are $\langle 001 \rangle$ and $\langle 1\bar{1}0 \rangle$ directions, respectively. In the case of Eqs. (4) and (5), k_1 can be held fixed and energy vs k_2 can be scanned

for coincidences. In fact, one must survey energy vs k_2 for both k_1 and $-k_1$ to include the cases where the group velocity normal to the crystal surface is opposite for \vec{k}'' and \vec{k} . By time reversal $E(\vec{k}'')$ and $E(-\vec{k}'')$ are always degenerate and their group velocities are antiparallel.

If, for a given energy with $k_1, -k_1$ fixed, there is only one pair of values k_2, k_2'' , the identification is, of course, unique. If there is any value of the energy for which only one "coincidence pair" of k_2 values occurs, the proper pairing may be followed into energy regions of multiple pairs by continuity. The correctness of a given assignment can also be tested for values of \vec{k} having special symmetry by studying the response to optical polarization.

Aside from the approximations implied in Eq. (1), the determination of E_C vs \vec{k} may be complicated by the fact that one or both members of an "energy-coincidence" pair may be energetically unable to escape while conserving tangential momentum. (For clean silicon the energy of an escaping electron relative to the valence band must be at least 5.45 eV.³) Cesium deposition lowers the surface barrier but at the same time causes scattering due to surface disorder. If an ordered monolayer of some low work-function material could be deposited, the available energy range would be increased. The valence-band energies are, of course, immediately determined from Eq. (1) if any conduction-band energies can be found.

It seems reasonable to expect that momentum-conserving emission from perfect surface states will also be observable. In this case $E(k_1, k_2)$ would give complete information about surface band structure for occupied bands.

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