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PHOTOELECTRON EMISSION FROM SEMICONDUCTORS WITH LOW VALENCE BAND DISPERSION

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In application to the group of compounds under consideration, a simple analytical expression is obtained for the quantum yield. Electron scattering processes of both elastic and inelastic nature are taken into account. The influence of such scattering processes on the structure of the spectral dependence of the quantum yield is discussed. It is shown that they can be responsible for the appearance of a number of features in this spectral dependence.

The band spectrum and associated properties of antimony-alkali compounds were studied in [1-3]. It is shown that the characteristic property of these crystals is the plane nature of their valence bands. Fundamental relationships for the computation of the photoemission characteristics of such semiconductors are obtained in this paper. The influence of scattering parameters on the spectral dependence of the quantum yield $Y(\omega)$ is studied when using the simple model of the electron energetic spectrum while taking account of the low valence band dispersion and the graphic representation of the electron scattering mechanisms. Underlying the description of the photoemission process is a multistage theory.

1. Absorption of electromagnetic radiation of sufficiently high frequency ω results in the excitation of part of the valence electrons in the conduction band, whose three-dimensional distribution over the specimen bulk is determined by the nature of light wave attenuation, while their energy distribution is described by the function $N_0(E, \omega)$. This initial distribution $N_0(E, \omega)$ is distorted by photoelectron scattering processes as well as by their interaction with the surface. The following can be extracted as the most important scattering mechanisms: 1) scattering with the formation of electron-hole pairs, which are substantially inelastic processes; and 2) interaction with lattice vibrations. The probability of the first process ($e-e$ scattering) depends strongly on the electron energy. It is zero for $E < 2E_g$ (E_g is the forbidden bandwidth) and grows rapidly as the energy increases for $E > 2E_g$. Energy losses in one $e-e$ scattering act exceed E_g . Scattering by phonons also results in a reduction in the energy of the excited electrons since the processes of phonon emission by electrons predominate over absorption processes, i.e., on the average an electron loses a certain energy E_p in the $e-p$ interaction act. Ordinarily E_p is 10^{-2} eV in order of magnitude so that even those electrons that underwent a noticeable number of $e-p$ scatterings can have sufficient energy for emergence into a vacuum. It is characteristic that the direction of electron velocity in each $e-p$ interaction act can change substantially. Consequently, those electrons which moved initially from the surface, as well as the electrons reflected from the surface, can change the direction of their propagation and induce a contribution to the photoemission current because of scattering by phonons. This means that the presence of such scattering processes can contribute to the emergence of a large number of excited electrons in a vacuum. The mechanism mentioned also results in an effective increase in the path traversed by the photoelectron up to the emitting surface, i.e., in an increase in the probability of $e-e$ scattering.

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2. Only electrons undergoing not more than one e⁻e scattering yield a substantial contribution to the photocurrent in a calculation of the photoemission characteristics in a sufficiently broad energy range. The electrons can here experience multiple e⁻p scattering both before and after e⁻e interaction. The following expression

$$N(E, \omega) = \sum_n N_0(E + nE_p, \omega) P_n(\alpha; E) + \sum_{k,n} \int dE_0 N_0(E_0, \omega) S(E_0 - \kappa E_p, E + nE_p) P_{k,n}(\alpha; E_0; E) \quad (1)$$

can be written for the energy distribution function of the emitted electrons. The first component describes electrons that emerge into the vacuum without generating secondary excitations. The second term in (1) takes account of both the electrons which were excited by light and underwent scattering with the formation of an electron-hole pair prior to emerging into the vacuum, and the electrons excited because of this scattering process. Here $P_n(\alpha; E)$ is the probability averaged with respect to the degree of light absorption, for the process in which an electron excited in a state with energy $E + nE_p$ emerged into the vacuum after n acts of e⁻p interaction without e⁻e scattering, $P_{k,n}(\alpha; E_0, E)$ is the probability of an electron emerging into a vacuum after k e⁻p, one e⁻e, and n acts of e⁻p interaction in the sequence mentioned, and $S(E, E')$ is the probability of electron scattering from a state with energy E into a state with energy E' in the e⁻e interaction act.

In that electron energy domain in which scattering with the formation of electron-hole pairs is energetically possible, the probability of some significant number of e⁻p interactions prior to e⁻e scattering is small. Therefore, the electron energy directly ahead of e⁻e scattering should not differ substantially from its energy E_0 after optical excitation. Hence, the quantity κE_p in (1) can be neglected in comparison with those E_0 for which the probability S is different from zero. This permits summation over k in (1) and subsequent utilization of the total probabilities

$$Q_n = \sum_k P_{k,n} \quad (2)$$

in place of $P_{k,n}$.

It is expedient to take account of the combined influence of the e⁻e and e⁻p processes in a sufficiently simple model. The Kane model [4] can be such a basis. In this model one-dimensional random walks of primary electrons are considered with the e⁻e and e⁻p interactions and partial electron reflection from the surface taken into account. The fundamental parameters characterizing the probability of electron emergence into a vacuum are the mean free paths l_e and l_p with respect to the e⁻e and e⁻p processes, respectively, the coefficient R_e of electron reflection from the surface, and the coefficient of optical absorption α . The dependence of these parameters on the initial electron energy is taken into account, but their changes during the acts of e⁻p interaction are neglected. Under the assumption of normal light incidence and its exponential attenuation in the substance, a simple analytical expression is obtained in [4] for the probability $P_n(\alpha; E)$:

$$P_n(\alpha; E) = \left(\frac{l}{l_p}\right)^n \frac{1}{n!} r \alpha l \sum_{s=2}^{n+1} \frac{(2n-s)!(s-1)}{(n-s+1)! 2^{2n-s+1}} \left[\frac{(1+r)^{-s} - (1+\alpha l)^{-s}}{\alpha l - r} \right], \quad (3)$$

where $r = (1 - R_e(E))/(1 + R_e(E))$, $l^{-1} = l_p^{-1} + l_e^{-1}$.

It is shown in [5-7] that the Kane model allows of generalization. Thus, this model is generalized to the three-dimensional case in [5, 6]. A simple method is proposed in [7] which would permit including secondary electrons in the analysis and would take into account in a single manner the e⁻e and e⁻p interactions of both the primary and secondary electrons. The expressions

$$Q_n(\alpha, E_0, E) = l_e^{-1} l_0^{-1} (\mu_0^2 - \alpha^2)^{-1} [P_n(\alpha; E) - P_n(\mu_0; E) (r_0 + \alpha l_0) \alpha / (r_0 + \mu_0 l_0) \mu_0], \quad (4)$$

where $r_0 = r(E_0)$, $l_0 = l(E_0)$, $l_{e0} = l_e(E_0)$, $\mu = l^{-1} \sqrt{1 - l/l_p}$, $\mu_0 = \mu(E_0)$, are obtained for the probabilities Q_n .

The function $N_0(E, \omega)$ in (1) is related to the band spectrum structure and is expressed in the indirect transition model in terms of the state densities ρ_v and ρ_c (in the valence and conduction bands, respectively):

$$N_0(E, \omega) = \rho_c(E) \rho_v(E - \hbar\omega) / \int dE_1 \rho_c(E_1) \rho_v(E_1 - \hbar\omega). \quad (5)$$

(The energetic dependence of the matrix elements of the optical transitions is neglected in this expression.)

The scattering probability $S(E, E')$ is also expressed in terms of the state density in the "random wave vectors" approximation [8]:

$$S(E, E') = \frac{2\rho_c(E') \int dE_0 \rho_v(E_0) \rho_c(E_0 + E - E')}{\int dE_1 \int dE_0 \rho_c(E_1) \rho_v(E_0) \rho_c(E_0 + E - E_1)} \quad (6)$$

(the energy is measured from the apex of the valence band). Let us note that the denominator of the last expression is the reciprocal lifetime $\tau(E)$ of the electron state with energy E with respect to e^-e scattering to the accuracy of a constant.

The approximations used in deriving (5) and (6) are of the same nature, neglect of the selection rule in the quasimomentum. For compounds with small valence band dispersion, whose states density $\rho_V(E)$ can be represented approximately in the form

$$\rho_V(E) = \text{const} \sum_i \delta(E - E_i), \quad (7)$$

such a selection rule is not important since ignoring it does not result in a substantial increase in the number of states between which transitions are allowed. Therefore, there is a foundation to expect [9] that the "random wave vectors" approximation should work well for the class of compounds under consideration, especially for the calculation of quantities whose structure is similar to (5) and (6).

Taking account of (5) and (7) and integrating (1) with respect to E , we obtain the following simple expression for the quantum yield:

$$Y(\omega) = \eta(\omega) \sum_i \rho_c(\hbar\omega + E_i) \sum_n \{P_n(x; \hbar\omega + E_i - nE_p) + \int dES(\hbar\omega + E_i, E + nE_p) Q_n(x; \hbar\omega + E_i, E)\}, \quad (8)$$

where $\eta^{-1}(\omega) = \sum_i \rho_c(\hbar\omega + E_i)$, and the subscript i enumerates the valence subbands.

Equation (8) can be simplified by replacing nE_p in the arguments for P_n and S by a certain mean value $\bar{n}E_p$. It is possible to identify \bar{n} approximately with the mean number of e^-p collisions. It should be kept in mind that in deriving (3) and (4) the quantities l_e, l_p, r were assumed invariant after an arbitrary number of e^-p interactions. Consequently, for electron energies less than the threshold for electron-hole pair formation, the probabilities P_n are different from zero even for arbitrarily large n because there is no mechanism for the excited electrons leaving the emission process in the model itself in this case. There is such a mechanism in the real process, viz., electron roll-up in energy because of phonon emission. The electron departure can be taken into account phenomenologically if the effective free path \tilde{l} is introduced by replacing l^{-1} in (3) and (4) by $\tilde{l}^{-1} = l^{-1} + L^{-1}$, where $L = (\bar{n} + 1)l_p$. This is equivalent to the fact that an additional factor enters into the expression for P_n which is almost one for $n < \bar{n}$ and decreases rapidly as n grows for $n > \bar{n}$. Therefore, actually only those P_n which have physical meaning will enter the sum $G = \sum_{n=0}^{\infty} P_n$. The summation over n

can now be executed in (8)

$$Y(\omega) = \eta(\omega) \sum_i \rho_c(\hbar\omega + E_i) [G(x; \hbar\omega + E_i - \bar{n}E_p) + \int dES(\hbar\omega + E_i, E + \bar{n}E_p) H(x; \hbar\omega + E_i, E)], \quad (9)$$

where according to [4, 7]

$$G(x; E) = rx\tilde{l} \left(x\tilde{l} + \sqrt{1 - \tilde{l}/l_p} \right)^{-1} \left(r + \sqrt{1 - \tilde{l}/l_p} \right)^{-1}, \quad (10)$$

$$H(x; E_0, E) \equiv \sum_{n=0}^{\infty} Q_n = G(x; E) (x + \mu_0 + \tilde{\mu} + r_0/l_0) [l_{e0}l_0(x + \mu_0)(\mu_0 + r_0/l_0)(\mu_0 + \tilde{\mu})]^{-1}. \quad (11)$$

Thus, for the spectral dependence of the quantum yield of the compounds under consideration we obtain a simple expression that takes account of electron scattering with electron-hole pair formation and their multiple scattering by phonons.

3. Let us analyze qualitatively the effects resulting from e^-p scattering processes. To do this we compare the spectral dependences of the quantum yield computed with and without taking account of these processes. The exclusion of the e^-p interaction is achieved by the passage to the limit $l_p \rightarrow \infty, \bar{n} \rightarrow 0$. Here just the expression in the square brackets changes in (9), while the relationships (10) and (11) take the form

$$G_e(x; E) = (1 - R_e) \alpha l_e / 2 (1 + \alpha l_e), \quad (12)$$

$$H_e(x; E_0, E) = G_e(x; E) (1 + r_0 + \alpha l_{0e} + l_{0e}/l_e) [(1 + r_0)(1 + \alpha l_{0e})(1 + l_{0e}/l_e)]^{-1}. \quad (13)$$

As $\hbar\omega + E_i$ changes from the vacuum level E_V to the threshold of electron-hole pair formation, $G_e(\alpha; \hbar\omega + E_i)$ grows as $(1 - R_e)/2$. As the photon energy rises further, the e^-e scattering processes start to play a governing role in the behavior of G_e .

Now, let us examine the probability $G(\alpha; \hbar\omega + E_i - \bar{n}E_p)$ in (9). Near the photoemission threshold, $e-p$ interaction results in part of the excited electrons leaving the emission process (as is depicted in (9)) by the shift of the energetic argument for \hat{G} by $\bar{n}E_p$. As the electron energy rises above the vacuum level, their energy losses in the $e-p$ scattering acts become less substantial, and the chaotization effects of the directions of electron motion acquire importance. This is easily seen if $\sqrt{1 - \tilde{l}/l_p}$ is represented in the form

$$\sqrt{1 - \tilde{l}/l_p} = \sqrt{\frac{l_p(\bar{n} + 1) + l_e}{l_p(\bar{n} + 1) + l_e(\bar{n} + 2)}}. \quad (14)$$

In the domain of "pure $e-p$ interaction" $\sqrt{1 - \tilde{l}/l_p} = (\bar{n} + 2)^{-1/2}$, so that for large \bar{n} the probability G can be close to one. If the path length l_e is of the same order as l_p , then $G(\alpha; E - \bar{n}E_p) \approx G_e(\alpha, E)$, i.e., the $e-p$ interaction exerts no noticeable influence on photoelectron transport.

Since a change in ω is accompanied by a significant change in the spectral composition of the excited electrons, then under favorable conditions the appearance of singularities due to the effect of $e-e$ and multiple $e-p$ scattering processes can be expected in the dependence $Y(\omega)$. This means that in principle it is possible to obtain certain information about the processes of excited electron scattering in a solid on the basis of the integral characteristics, for instance, the spectral dependence of the quantum yield.

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