Electron-Hole-Pair Creation Energies in Semiconductors

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The rule that the electron-hole-pair creation energy is 3 times the semiconductor band gap is extended to include a large group of insulators. It is used, together with the free-particle approximation, to describe cathodoluminescent phosphor efficiencies and the escape probabilities of secondary electrons.

When a semiconductor is bombarded with high-energy radiation, electron-hole pairs are created. The average energy required to create a single pair, called the radiation ionization energy or pair-creation energy, ϵ, is empirically[1] about 3 times the band gap energy E_g of the semiconductor. The measured values of ϵ for several semiconductors are plotted versus E_g in Fig. 1. Many of these data points lie close to a straight line and the slope of this line is consistent with that predicted using a free-particle approximation.

We have used this linear relation between ϵ and E_g to describe the efficiency of cathodoluminescent phosphors and to describe the probability that a secondary electron escapes from an insulator. The efficiency of a cathodoluminescent phosphor is expected to be inversely proportional to ϵ; thus it should be inversely proportional to E_g. We find this to be true for a number of different phosphor hosts containing the same activator impurity. The probability that an internally excited secondary electron escapes the solid upon reaching the surface is related linearly to ϵ through the experimental secondary-emission data. These probabilities lie between zero and unity and are consistent with predictions obtained using a free-particle approximation. These examples confirm the existence of a linear relation between ϵ and E_g for a large group of insulators and they support the use of the free-particle approximation to describe electrons and holes with kinetic energies in excess of an eV.

Shockley,[2] Klein,[3] and others have explained the empirical relation between ϵ and E_g illustrated in Fig. 1 using the free-particle approximation and conservation of energy[2] and momentum.[3] It is assumed that the energy of the ionizing radiation goes to create excited electrons and holes. When one of these particles reaches a final state where it can no longer excite another electron-hole pair, i.e., its energy is below a threshold energy E_M needed to create another pair, it thermalizes by phonon emission. Each available state is assumed[2] equally likely to be a final state. In terms of the particle kinetic energy E above the band edge, the density of these states is proportional to $\sqrt{E}$. Thus, since ϵ must be the sum of the band gap and the average kinetic energies of the final electron and hole,

$$\epsilon = E_g + 2\int_0^{E_M} E\sqrt{E}\,dE \Big/ \int_0^{E_M} \sqrt{E}\,dE$$
$$= E_g + 6E_M/5.$$

By momentum conservation, the momentum P of the ionizing particle before creating a pair must equal the sum of its momentum afterwards plus the momenta of the newly created electron and hole. If the ionizing particle initially has energy

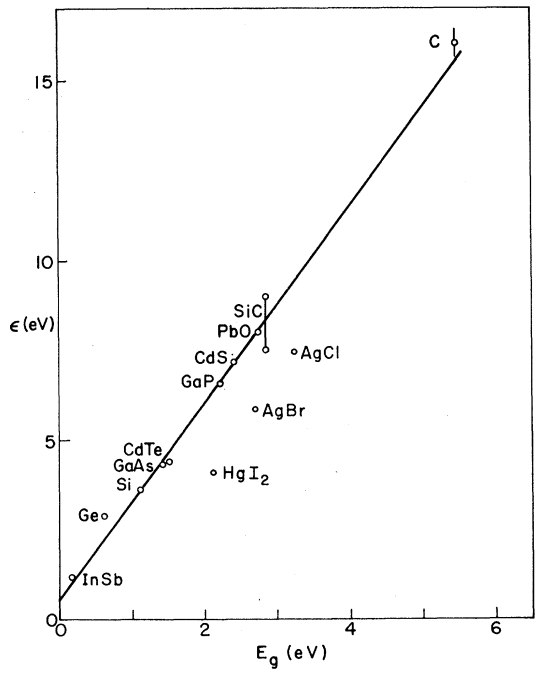

FIG. 1. The measured pair-creation energies ϵ of several semiconductors, versus the fundamental semiconductor band gap E_g. A straight line has been fitted to selected points on this plot.

E_M, then in the free-particle approximation, the momenta of the final particles must be collinear and of magnitude $\frac{1}{3}P$ to be consistent with the definition of E_M. Then, energy conservation requires $3(E_M/9)+E_g=E_M$ or $E_M=3E_g/2$; thus $\epsilon=2.8E_g$. This agrees well with the line

$$\epsilon=2.73E_g+0.55 \text{ eV}, \quad (1)$$

drawn through the data[4,5] points of Fig. 1; the constant energy represents the energy lost to the lattice by particles with energies greater than E_M.

A cathodoluminescent phosphor is a host semiconductor containing impurities or defects called activators. When the phosphor is bombarded by high-energy electrons, electron-hole pairs are created and these pairs recombine at activators to yield optical photons of energy E_{ph}. Thus the energy efficiency η of the phosphor should be $\eta=SE_{ph}/\epsilon$ where S may depend on the host and activator.[6] Hence, we expect $\eta\approx SE_{ph}/2.8E_g$ for phosphors with $E_g\gtrsim 1$ eV. In Fig. 2 the efficiency η is plotted[7] versus E_g^{-1} of the phosphor host for many of the efficient phosphors. For a given activator the photon energy E_{ph} is nearly independent of the host and so a linear relation between η and E_g^{-1} extrapolating to the origin is expected. This relation, heretofore unnoted, is seen from Fig. 2 to be roughly obeyed by many phosphors.

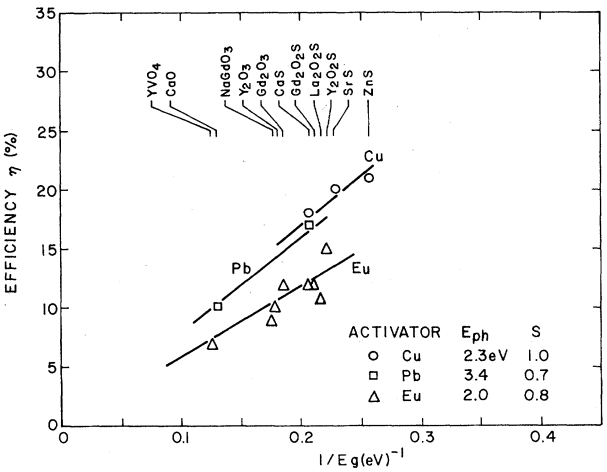

FIG. 2. The measured cathodoluminescent energy efficiencies η of several phosphors, versus the reciprocal of the fundamental band gap E_g of the phosphor host. The phosphor hosts are indicated at the top of the figure and the activators are indicated by the symbols shown at the right of the figure. Straight lines of slope parameter S, calculated using photon energy E_{ph}, have been fitted to selected points associated with the same activator.

This supports the existence of a linear relation between ϵ and E_g for these phosphor hosts. Also S, which can be extracted from the slope of these lines, should be less than unity since it represents a probability. The slopes of the lines shown in Fig. 2 yield values of S between 0.5 and 1.0 in accord with this expectation. This observation is therefore consistent with the empirical rule that $\epsilon\approx 3E_g$.

When a solid is bombarded by high-energy primary electrons, secondary electrons[8] are emitted. Phenomenologically, the probability that an excited electron becomes a secondary can be separated into two factors, the probability that an electron created a distance x below the surface reaches the surface, and the probability that an electron reaching the surface escapes. The former probability is frequently written $e^{-\alpha x}$, where α is a constant, and the latter by the constant B. It is shown below that B/ϵ, where ϵ is the average energy needed to excite an electron internally, can be extracted from measurements of the secondary-electron emission with the aid of this phenomenological theory and Eq. (1).

The secondary-emission yield δ is the number of secondary electrons emitted per incident primary electron. This yield will, of course, be a function of the primary electron energy E_0. The yield is the product of the number of electrons excited internally, E_0/ϵ, the probability $e^{-\alpha x}$ that these electrons reach the surface, and the probability B that they escape from the surface.[8] The distance x below the surface that the electrons are excited should be given by the range R of the incident primaries. We expect R to be related to the primary energy, i.e., $R=E_0/A$. Then $\delta=Be^{-\alpha R}E_0/\epsilon=(BA/\alpha\epsilon)\alpha Re^{-\alpha R}$. Since $\delta=0$ when $E_0=0$ because no secondaries are generated, and $\delta=0$ when E_0 approaches infinity because no secondaries reach the surface, at some primary energy E_{0m} the yield is a maximum δ_m. Since $BA/\alpha\epsilon$ is a constant of the material, E_{0m} is defined by the value of αR for which $\alpha Re^{-\alpha R}$ is a maximum, i.e., $\alpha R=1$. Hence $\delta_m=BA/\alpha\epsilon e=e^{-1}BE_{0m}/\epsilon$ and $\delta/\delta_m=e(E_0/E_{0m})\exp(-E_0/E_{0m})$. This last equation is called a reduced, or universal, yield curve. The use of better range-energy relations and more realistic descriptions of δ gives[8] values near 0.4 for $\delta_m\epsilon/E_{0m}B$ instead of e^{-1}, so we have taken

$$B=2.5\delta_m\epsilon/E_{0m}. \quad (2)$$

From Eq. (1) and data for δ_m, E_{0m}, and E_g from the literature,[4,9] the values of B shown in Fig. 3

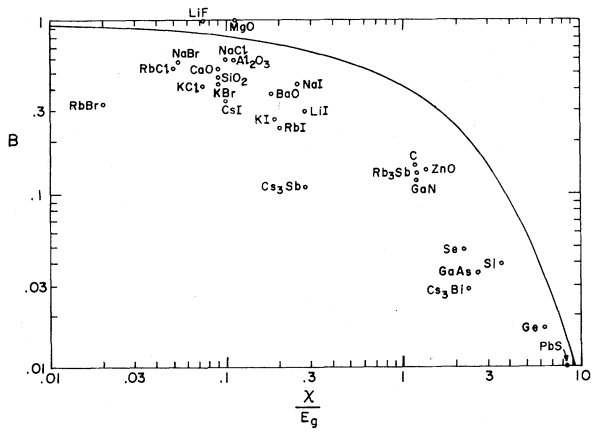

FIG. 3. The escape probabilities B for secondary electrons extracted from the measured secondary-electron-emission data, versus the measured ratio of the electron affinity χ and the fundamental band gap E_g for several insulators. The solid curve was calculated using the theory discussed in the text.

were calculated for 28 insulators. The values range between zero and unity, consistent with the concept of B as a probability.

It is also possible to develop a simple theory to calculate B *a priori* if it is assumed that the excited electrons lose energy solely by electron-hole-pair creation, i.e., if losses to the lattice are ignored. Since these electrons must surmount the energy barrier defined by the electron affinity χ to escape the solid, and since ϵ is related to E_g by Eq. (1), the escape probability B is expected to be a function of χ/E_g. By definition the escape probability B is the probability that an electron inside the solid escapes into the vacuum upon reaching the surface of the solid, that is

$$B = \int_0^\infty P(E)f(E)g(E)\,dE \Big/ \int_0^\infty f(E)g(E)\,dE, \qquad (3)$$

where $P(E)$ is the probability that an electron of energy E reaching the surface escapes from the solid, $f(E)$ is the distribution of electrons in states of energy E, and $g(E)$ is the density of electronic states. Classically[10] $P(E) = 0$ for $E \leq \chi$ and $P(E) = 1 - (\chi/E)^{1/2}$ for $E > \chi$. In the free-particle approximation, $g(E)$ is proportional to $\sqrt{E}$.

To define the electron distribution function, we shall assume that the only energy-loss mechanism available to the electrons is electron-hole-pair creation. Since electrons with energy $E < E_M = 3E_g/2$ above the conduction-band edge cannot create an electron-hole pair, all energy-loss mechanisms for these electrons are ignored and $f(E) = 1$ for $0 \leq E < 3E_g/2$. Since electrons with $E \geq 3E_g/2$ lose energy in units of ϵ, the probability that an electron is scattered to a lower energy is unity over an energy range ϵ, i.e., $\partial f/\partial E = -f/\epsilon$, or $f = f_0 e^{-E/\epsilon}$. If $f(E)$ is continuous, then $f_0 = e^{\gamma}$ where $\gamma \approx 1.5/2.8$, assuming E_g is 0.5 eV or more.

With these definitions of $P(E)$, $f(E)$, and $g(E)$ and Eq. (1), the dependence of B on χ/E_g can be calculated from Eq. (3); this dependence is illustrated by the solid curve in Fig. 3. The values of B obtained from Eq. (2) are also plotted versus χ/E_g in Fig. 3; the values of χ and E_g were taken from the literature.[4,11] Although, as expected, these values of B lie below the calculated curve, they exhibit a dependence on χ/E_g similar to that calculated.

In addition to the understanding of the cathodoluminescent efficiency and of secondary-electron emission provided by these examples, they also provide support for the extension of the empirical rule relating ϵ to $3E_g$ to a group of insulators larger than that on which direct measurements of ϵ have been made. These examples also provide support for the use of the free-particle approximation to describe electrons and holes with kinetic energies of an eV or more. The applicability of this approximation may be a consequence of the de Broglie wavelengths of these particles (10 Å or less) being commensurate with the lattice spacing.

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Nonradiative Recombination at Deep Levels in GaAs and GaP by Lattice-Relaxation Multiphonon Emission

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Measurements of the temperature dependence of the carrier capture cross sections for ten deep levels in GaAs and GaP give strong evidence for nonradiative capture by lattice-relaxation multiphonon emission. A simple one-coordinate theory which takes into account the breakdown of the adiabatic approximation gives a good quantitative fit to the data.

The understanding of deep levels in semiconductors is a problem of both great fundamental and technical importance. One of the principal ways in which such deep levels affect semiconductor properties is as an efficient path for nonradiative recombination of nonequilibrium minority carriers. There is to date, however, almost a complete lack of understanding as to how large amounts of energy (over 1 eV) can be efficiently dissipated in a rapid nonradiative capture process (capture cross sections as large as $\sigma \sim 10^{-14}$ cm^2). The only possible known nonradiative mechanisms are the Auger effect[1] and lattice-relaxation multiphonon emission (MPE).[2-4] A third mechanism, cascade capture,[5] is applicable only to relatively shallow centers with closely spaced excited states between which single phonons can be emitted in a "cascade" of electronic transitions. Only Sinyavskii and Kovarskii[3] have attributed large capture cross sections observed at deep levels in Si and Ge to MPE. The commonly held view in recent reviews of the subject[1,6-9] is that MPE recombination is of little importance. This Letter describes experimental and theoretical work which shows that lattice-relaxation MPE is a mechanism which can account for the large capture cross sections observed for some very deep levels and is in fact a frequently occurring mechanism in GaAs and GaP.

We have used various techniques of capacitance spectroscopy[10-12] to measure directly the carrier capture cross sections of a variety of deep levels in GaAs and GaP as a function of temperature and, in two cases, carrier concentration. Many of these cross sections can be described by the theory of MPE capture to be presented here; others are due, perhaps, to a different mechanism. The data supporting MPE are shown in Figs. 1 and 2. Figure 1 shows the capture cross sections in GaP of holes at O-state 1 and O-state 2, and of electrons at Zn-O; in GaAs the cross sections shown are for electrons at O, the $E3$ radiation-