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Photoluminescence determination of minority-carrier kinetics in semiconductors

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A new optical technique has been developed to measure the electronic transport properties of semiconductors. It requires only a semiconductor for which the absorption spectrum is known and for which the luminescence can be observed. On the high-energy side of the band-band luminescence peak, the luminescent intensity is proportional to the logarithm of the quasi-Fermi-level separation μ and independent of any other details of the semiconductor's electronic properties. On the low-energy side of the peak, the intensity is additionally proportional to $\alpha(E)l$, where l is the minority-carrier diffusion length, and $\alpha(E)$ is the material's absorption coefficient. The combination of μ and l with an estimate of the equilibrium carrier density gives the minority-carrier lifetime. The value of μ reflects both surface and bulk recombination rates; manipulation of the experimental parameters allows them to be separated. This technique and its limitations have been demonstrated with measurements on thin polycrystalline films of CdS and on wafers of Zn_3P_2 and CdTe.

I. INTRODUCTION

The characterization of electronic transport in semiconductors is normally accomplished by techniques which require electrical contact (either blocking or Ohmic) to the sample. The nature of a given contact depends on the metal-semiconductor interface chemistry, and producing the apppropriate contact may be a research problem in itself. In addition, the presence of the contact unaviodably alters—by generation of recombination centers, band pinning, etc.—the semiconductor's surface characteristics.

Photons do not interact with semiconductors nearly as strongly as electrons. Their absorption length is $\sim 10^3$ Å even for energies above the band gap. As a result, they can be used to generate and examine carriers some distance below the surface. In this case, the surface affects the measurements only through its interactions with the photoexcited carriers, and both the surface structure and carrier distribution may be freely modified, and even overcoated with a wider band-gap material, to elucidate and separate surface- and bulk-recombination mechanisms.

The analysis and measurements which follow demonstrate the information which can be gotten by an optics-only technique, and the effort which is required to obtain it.

Previously, experiments have gone halfway toward an all optical approach and have carefully analyzed the usefulness of photoconductivity[1] and electroluminescence[2] for the measurement of electronic properties of thick films. Photoluminescence in very thin films has been analyzed and used to measure surface-recombination velocities.[3] It has also been used in relatively simple ways to determine semiconductor band gaps,[4] and carrier-recombination rates.[5]

This approach is based on a principle first introduced by Einstein[6] that the coupling to an external field of a transition between two states is symmetric in time—that is, its spontaneous emission cross section is equal to its absorption cross section.

Einstein discussed this concept with regard to isolated atomic levels. Since then, this principle has been rediscovered many times in different applications;[7,8] it generally goes under the heading "detailed balance." The form which we will follow is due to van Roosbroeck and Shockley.[8] It was derived for two thermalized bands in a solid. Section II will show the derivation of their equations and generalize them to include the effects of a thick sample with surface and bulk recombination. Section III discusses the problems involved in detecting this luminescence. In Sec. IV we will show some results achieved using CdS, Zn_3P_2, and CdTe. Finally, in Sec. V, we will summarize the potential of this technique.

II. ANALYSIS

As mentioned above, this analysis is based on the time reversibility of energy coupling between any system and an external field. That is, the radiative coupling into (absorption) and out of (luminescence) a transition between any two states are equal. The existence of other (nonradiative) transition channels affects the population in the initial and final states (and therefore the observed flux) but not the coupling constant; van Roosbroeck and Shockley began their argument with a semiconductor at equilibrium with a blackbody radiation field. In that case, the rate of optical generation of electron-hole pairs by the ambient photons is equal to their rate of radiative recombination:

$$R(E)dE\,dx = P(E)\rho(E)dE\,dx \; , \tag{1}$$

where $P(E)$ is the probability/time of a photon being absorbed,

$$P(E)dx = 1/\tau(E) = \alpha(E)(c/n)dx \; , \tag{2}$$

and $\rho(E)dE$ is the density of photons,

$$\rho(E)dE = \frac{8\pi E^2 n^3}{h^3 c^3}\left[\exp\left[\frac{E}{kT}\right]-1\right]^{-1} dE \; . \tag{3}$$

In equilibrium then the emission from a thin $[\alpha(E)dx \ll 1]$ volume element is

$$R(E)dE\,dx = 8\pi\alpha(E)dx\left[\frac{En}{hc}\right]^2 \times\left[\exp\left[\frac{E}{kT}\right]-1\right]^{-1}\frac{dE}{h}\,, \tag{4}$$

which for $E > KT$ can be rewritten as

$$\sim 8\pi\alpha(E)dx\left[\frac{En}{hc}\right]^2\exp\left[-\frac{E}{kT}\right]\frac{dE}{h}\,, \tag{5}$$

where I have neglected reflections from the surface of the slab (it is embedded in more of the same material).

This emission intensity is quite low. It is impossible in principle to use a room-temperature detector to see this radiation (because the detector is in thermal equilibrium with the emitter, the radiation cannot do any work—such as generate a current or voltage). In a luminescence experiment, one remedies this by departing from equilibrium. The sample is irradiated with an intense, nonthermal light (or electron) beam. This results in a steady-state excess of electrons and holes in the conduction and valence bands, respectively. If these excess carriers thermalize (by exchanging energy with phonons) very quickly in their bands compared to any loss mechanism (direct recombination, traps) the electrons and holes will have a well-defined temperature;[9] that is, the energy dependence of their steady-state occupation probability $n(E)$ will be the same as that of a population in equilibrium at temperature T where T is the lattice temperature. That is,

$$n(E_1)/n(E_2) = \left[\exp\left[\frac{E_1-E_2}{kT}\right]+1\right]^{-1} \sim \exp\left[-\frac{(E-E_g)}{kT}\right] \quad \text{for } E_g > E\,. \tag{6}$$

The thermalization, however, is not complete. Because we required the losses from two bands to be slow, the absolute density of electrons n_n, and holes n_p, is substantially increased. The effect is as if the Fermi level moved up in energy for the electrons and down for the holes. If we labeled the separation between these "quasi"-Fermi levels as μ, then the increase in the electron-hole density product $n_n n_p$ is just $\exp(\mu/kT)$.[10]

Since the emission from any set of levels is just proportional to the probability that the initial state is occupied, and the final state is empty, $n_n n_p$, the emission from a pumped semiconductor is also increased by the factor $\exp[\mu(x)/kT]$. Equation (5) now becomes

$$R(E,\mu)dE\,dx = 8\pi\alpha(E)dx\left[\frac{En}{hc}\right]^2\exp\left[-\frac{E-\mu(x)}{kT}\right]\frac{dE}{h}\,. \tag{7}$$

Equation (7) is valid for an optically thin film embedded in similar material. Since for a typical semiconductor $\alpha(E)$ is $\sim 10^5\ \text{cm}^{-1}$ above its band edge, this condition is rarely satisfied in bulk samples, and we have to integrate the luminescent emission over the film thickness to account for the absorption of the incident light, the nonuniform distribution of recombination mechanisms, and the reabsorption of luminescent light on the way out of the film. We also have to account for reflections at the film's interface with air.

The interfacial losses, L, can be accounted for readily. Total internal reflection reduces the solid angle for which light can escape by $1/n^2$, and impedance mismatch reduces the amount transmitted through the surface by $(1-r_f)$ where r_f is the front-surface reflectance averaged over the solid angle for light collection. We only collect light from one side of the film, and assume that the film is thick enough so that we never have to worry about light reflected from the back interface. In addition, we assume that the emitted light has a Lambertian distribution (i.e., the surface is rough). Combining these effects gives

$$L = (1-r_f)/(4n^2)\,. \tag{8}$$

The integral is more complicated. It can be simplified a little by assuming, as above, no back reflections. However, there is still the problem that the carriers are not uniformly distributed throughout the film; they are generated near the front surface, and are lost uniformly through the bulk as well as at the front-surface and interior grain boundaries. A one-dimensional diffusion equation incorporating the appropriate carrier sources and surface as well as bulk sinks is worked out in Appendix A. In steady state, the spatial dependence of the photocarrier density is

$$u(x) = \frac{J_0\tau_{\text{eff}}}{l}\left[\left[1+\frac{A}{\alpha_0 l}\right]\exp\left[-\frac{x}{l}\right] - A\exp(-\alpha_0 x)\right]\,, \tag{9}$$

where

$$A = \left[\frac{\alpha_0 l + S\tau/l}{1+S\tau/l} - \frac{1}{\alpha_0 l}\right]^{-1}\,. \tag{10}$$

These equations were derived for a semiconductor absorbing flux J_0 $[J_0 = 1-r_f)I_0$ where I_0 is the incident flux] with an extinction length $1/\alpha_0$ [i.e., $J(x) = J_0\exp(-\alpha_0 x)$]. The surface-recombination velocity is given by S and is normalized to l/τ where l is the minority-carrier diffusion length and τ is its lifetime. Both τ and l are bulk parameters. τ_{eff} is the average lifetime of carriers in this steady-state distribution. It is smaller than τ because of the addition of surface-recombination channels to the bulk-recombination mechanisms. From Eq. (A5)

$$\tau_{\text{eff}} = \tau\frac{1}{\alpha_0 l A}\,. \tag{11}$$

Since the concentration of photocarriers is position dependent, it is clear that $\mu(x)$ is not a state variable but only defines the local increase in population (the product of hole and electron concentration) over the thermal population. We are generating electrons and holes at the same rate. If their lifetimes are equal and their numbers overwhelm the thermal populations in both bands (the high-intensity limit), the electron and hole populations are equal:

$$\exp\left[\frac{\mu(x)}{kT}\right]=\left[\frac{u(x)}{u_{\text{thermal}}}+1\right]^2\sim\left[\frac{u(x)}{u_{\text{thermal}}}\right]^2, \tag{12}$$

where

$$u^2_{\text{thermal}}\sim=(n_0kT)^2\exp\left[\frac{-E_g}{kT}\right]. \tag{13}$$

In this case τ and l in Eqs. (9)–(11) are the ambipolar values. For average excess population,

$$\bar{u}=J_0\tau_{\text{eff}}/l \tag{14}$$

and so we can define an average μ within the luminescing layer of

$$\mu=2kT\ln\left[\frac{J_0\tau_{\text{eff}}}{ln_0kT}\right]+E_g\ . \tag{15}$$

This relationship would be valid for an intrinsic semiconductor. A more typical semiconductor is sufficiently n (p) type that the high density of thermal electrons (holes) is only slightly perturbed by the additional photocarriers (low-intensity limit) and the electron-hole product is

$$n_n n_p=(J_0\tau_{\text{eff}}/l)\left[n_0kT\exp\left[\frac{-E_c}{kT}\right]\right], \tag{16}$$

where E_c is the separation of the majority-carrier band edge from the Fermi energy. In that case, Eq. (12) becomes

$$\exp\left[\frac{\mu}{kT}\right]=\frac{(J_0\tau_{\text{eff}}/l)}{(n_0kT)}\exp\left[\frac{E_g-E_c}{kT}\right] \tag{17}$$

and

$$\mu=kT\ln\left[\frac{J_0\tau_{\text{eff}}/l}{n_0kT}\right]+E_g-E_c\ , \tag{18}$$

so finally the $\exp[\mu(x)/kT]$ in Eq. (7), where $\mu(x)$ is used as a local variable, becomes

$$\exp\left[\frac{\mu(x)}{kT}\right]=\exp\left[\frac{\mu}{kT}\right]\left[\left[1+\frac{A}{\alpha_0l}\right]\exp\left[-\frac{x}{l}\right]-A\exp(-\alpha_0x)\right], \tag{19}$$

where μ is an average value for the luminescing layer.

In most cases we will be dealing with n- or p-type semiconductors, rather than intrinsic, and it will be very hard to get out of the low-intensity limit.[10] Therefore, Eq. (18) will be used to define μ in following text. We can now plug Eqs. (8) and (19) into (7) and get

$$R(E,\mu,x)dE\,dx=\alpha(E)c_1(E)\exp\left[\frac{\mu(x)}{kT}\right]c_2(x)dE\,dx\ , \tag{20}$$

where

$$c_1(E)dE=2\pi\left[\frac{E}{hc}\right]^2\exp\left[-\frac{E}{kT}\right]\frac{dE}{h} \tag{21}$$

and

$$c_2(x)dx=\left[\left[1+\frac{A}{\alpha_0l}\right]\exp\left[-\frac{x}{d}\right]-A\exp(-\alpha_0x)\right]dx\ . \tag{22}$$

Then the spectrum observed from a film of thickness d_f is

$$R_{\text{obs}}(E,\mu)dE=\alpha(E)c_1(E)\exp\left[\frac{\mu}{kT}\right](1-r_f)\int_0^{d_f}\exp[-\alpha(E)x]c_2(x)dx\,dE\ , \tag{23}$$

where $\exp[-\alpha(E)x]$ accounts for the reabsorption of the emitted light and we take the limit of $d_f\rightarrow\infty$. Solving the integral yields

$$R_{\text{obs}}(E,\mu)dE=\left[2\pi\left[\frac{E}{hc}\right]^2\exp\left[-\frac{E}{kT}\right]\right]\left[\exp\left[\frac{\mu}{kT}\right]\right](1-r_f)\left[\frac{1+A/\alpha_0l}{1+1/\alpha(E)l}-\frac{A}{1+\alpha_0/\alpha(E)}\right]\frac{dE}{h}\ . \tag{24}$$

The first term is material independent—it contains the $E^2\exp(-E/kT)$ factor typical of an infinitely thick material containing uniform distribution of carriers thermalized to temperature T within their band. The second factor, $\exp(\mu/kT)$, reflects our success in increasing the minority-carrier population and thus incorporates the effective carrier lifetime. The effects caused by the spatial distribution of the carriers are separated into the third factor.

We want to examine the limiting behavior of Eq. (24) with and without surface recombination, and with and without diffusion. It is assumed that the material will be pumped at an energy such that $\alpha_0>\alpha(E)$.

Case 1. *($\alpha_0l\ll1$, $S=0$):* Without recombination ($S=0$), or diffusion (e.g., with sufficiently rapid recombination that $l\ll1/\alpha_0$) one finds from Eq. (10) that $A=-\alpha_0l$ and hence

$$R_{\text{obs}}(E,\mu)dE=2\pi\left[\frac{E}{hc}\right]^2\exp\left[-\frac{E}{kT}\right]\exp\left[\frac{\mu}{kT}\right](1-r_f)\frac{\alpha_0l}{1+\alpha_0/\alpha(E)}\frac{dE}{h}\ . \tag{25}$$

We can use Eq. (17) to write this in terms of incident intensity and so

$$R_{\mathrm{obs}}(E,I_0,\tau)=2\pi\frac{I_0(E/hc)^2\exp[(E_g-E_c-E)/kT]}{(n_0kT)}\tau(1-r_f)^2\frac{\alpha_0}{1+\alpha_0/\alpha(E)}\frac{dE}{h}\ . \tag{26}$$

The luminescing layer in this case is always optically thin. For a typical band edge, in which $\alpha(E)$ below the band-gap energy E_g varies much faster than $\exp(-E/kT)$, this distribution will peak at the energy at which $\alpha(E)$ saturates. As this energy is close to E_g, it is a convenient technique for measuring the band gap of a semiconductor.[4]

Case 2. *($\alpha_0 l \ll 1$, $S=\infty$):* Surface recombination is never important in case 1 because the diffusion length is much less than the thickness of the carrier distribution—very few of the carriers survive long enough to get to the surface. An infinite recombination velocity causes a luminescence reduction by a factor of $\sim(1-\alpha_0 l)$.

Case 3. *($\alpha_0 l > 1$, $S=0$):* The case of large diffusion and no surface recombination is of course the ideal one for devices. In that case $A=(\alpha_0 l)^{-1}$, and is very small, so

$$R_{\mathrm{obs}}(E,\mu)dE=2\pi\left[\frac{E}{hc}\right]^2\exp\left[\frac{\mu-E}{kT}\right](1-r_f)\left[1+\frac{1}{\alpha(E)l}\right]^{-1}\frac{dE}{h}\ . \tag{27}$$

In terms of incident intensity instead of μ, this becomes

$$R(E,I_0,\tau)dE=\frac{2\pi I_0(E/hc)^2\exp[(E_g-E_c-E)/kT]}{(n_0kT)[1+1/\alpha(E)l]}(1-r_f)^2\tau/l\frac{dE}{h}\ . \tag{28}$$

The major difference between this and case 1 is that the thickness of the diffusion layer is defined by the diffusion length l instead of the laser absorption length $1/\alpha_0$. Of course, the fact that the carriers diffuse implies that τ is larger, and that therefore the luminescence is larger—for low energies $[\alpha(E)l<1]$ it is proportional to τ. For high energies $[\alpha(E)l>1]$ it is proportional to $\tau^{1/2}$. The peak of this spectrum occurs at $\alpha(E)l\cong 1$. Since $l>1/\alpha_0$, that is a noticeably lower energy than the absorption edge saturation energy, and so might cause confusion if the position of the luminescence peak were used to define E_g.

In thin-film devices, this distribution could be substantially modified if $l>df$. The luminescent spectrum would be more as described by Duggan and Scott[3] except that in general, one would have to account for multiple reflections of the luminescence between the front and back interfaces.

Case 4. *($\alpha_0 l > 1$, $S=\infty$):* Adding surface recombination to this case has a substantial effect. In the limit that $s\tau/l \gg 1/\alpha_0 l$, $A=1$. Using this limit in Eq. (24), and substituting for $\exp(\mu/kT)$ using Eq. (17), we find

$$R_{\mathrm{obs}}(E,I_0,\tau)dE=\frac{2\pi I_0(E/hc)^2\exp[(E_g-E_c-E)/kT]}{(n_0kT)}(\tau/\alpha_0)l(1-r_f)^2\left[\frac{1}{1+1/\alpha(E)l}-\frac{1}{1+\alpha_0/\alpha(E)}\right]\frac{dE}{h}\ . \tag{29}$$

The surface recombination has the effect of reducing intensity by a factor of $\sim\alpha_0 l$ for low energies $[\alpha(E)<\alpha_0]$ without changing the shape. The effect is as substantial but more complex at higher energies. If we normalize the luminescent intensity to the case with no surface recombination we find

$$\begin{aligned}\frac{[R_{\mathrm{obs}}(E,J_0,\tau)]_{S=\infty}}{[R_{\mathrm{obs}}(E,J_0,\tau)]_{S=0}}&=\frac{1}{\alpha_0 l}\left[\frac{1+1/\alpha_0 l}{1+1/\alpha(E)l}-\frac{1}{1+\alpha_0/\alpha(E)}\right]\left[1+\frac{1}{\alpha(E)l}\right]\\&\cong\frac{1}{\alpha_0 l}\left[1-\frac{1}{1+\alpha_0/\alpha(E)}\right]\end{aligned} \tag{30}$$

to first order in $\alpha_0 l$. Note that the effectiveness of the surface-recombination states depends on incident-light absorption length. As a result, we can separate out surface effects by measuring the change in intensity with incident wavelength.

Previously, we have dealt with semiconductors in which the excitations were thermalized in two bands. As was noted above, that is generally an adequate description of crystalline semiconductors. It is not, however, necessarily valid for those crystalline semiconductors with broad Uhrbach tails,[5] or for amorphous semiconductors (a-SC). In those materials, the states which would have constituted the band edge, had the material been perfectly ordered, are localized traps. The delocalized states extend down only to a mobility edge at somewhat higher energy. The localized states in the band do not thermalize directly, but rather by interchange with states above the mobility edge. This interchange rate goes down rapidly as one moves away from the mobility edge. One has the possibility then in an a-SC of an interchange, e.g., (thermalization) time constant which gets longer in a more or less continuous manner as one goes from the delocalized band states, past the mobility edge, and into the band tail. Eventually, the thermalization rate would become comparable to the recombination rate. In that region then, the assumption of a thermalized band of excitation breaks down. This breakdown energy, called the demarcation level E_d by Rose,[12] occurs within about kT of the electron (-hole) quasi-Fermi level.

Below the demarcation level, the steady-state population of carriers does not exhibit the Boltzmann-type distribution assumed in Eq. (1). The distribution is determined by the balance between recombination rate and the capture rate between each localized state and the band.[13]

One way of expressing this effect would be to assign a quasi-Fermi level to each localized state; if the states were sufficiently similar, one μ_{loc} might be sufficient to describe the population in all of them. In general, that would not be true, and Eq. (24) has to be generalized to

$$R_{\text{obs}}[E,\mu(E)]dE = 2\pi \left[\frac{E}{hc} \right]^2 \exp\left[\frac{\mu(E)-E}{kT} \right] \left[\frac{1+A/(\alpha_0 l)}{1+1/\alpha(E)l} - \frac{A}{1+\alpha_0/\alpha(E)} \right] \frac{dE}{h} , \tag{31}$$

where $\mu(E)$ is constant for $E > E_d$, and decreases for $E < E_d$. From the variation of $\mu(E)$, one might identify a demarcation level in a given system, and from that something of the states involved in the band tail.[7]

III. DETECTION

The formulas in Sec. II showed how a measurement of the band-band luminescence of a semiconductor could characterize the diffusion length and lifetime of its minority carriers and their surface-recombination velocity. One could even observe effects from the localization of states in the band tail. Appendix B analyzes the requirements for making such measurements. Table I was computed from the formulas in Appendix B. It gives an idea of the difficulty of observing the band-band luminescence which has been discussed. Listed there are the mean free paths, l_{eff}, corresponding to a range of μ's, as well as the peak luminescent count rate, and its intensity relative to the incident-light intensity. Since the incident intensity and diffusion constant are held constant in these calculations, μ is a measure of the semiconductor quality; it is proportional to $\ln\tau$. It is apparent from Table I that it is feasible to detect the band-band luminescence if one can induce a quasi-Fermi-level separation greater than $E_g - 0.8$ eV. At that level, its intensity is adequate for photon counting.

The band competes for recognition with scattered laser light and other luminescent sources, but its unique shape—$R(E)dE \,\alpha \exp(-E/kT)$ on the high-energy side—not only allows one to discriminate the band-band luminescence from background, but also serves as a check that the sample is not overheating.

TABLE I. Required sensitivity, I_{sig}, and selectivity, R, to detect the luminescence from a semiconductor with a band gap E_g, and which has a μ and a minority-carrier diffusion length, l_{eff}, as indicated. The numbers were calculated using Eqs. (B1)—(B3).

μ (eV)	l_{eff} (cm)	R	I_{sig}
	$E_g = 1.5$ eV		
0.5	4.3×10^{-11}	4.1×10^{-15}	8.5×10^{-2}
0.6	2.3×10^{-9}	2.2×10^{-13}	4.5×10^{0}
	Detection limit		
0.7	1.3×10^{-7}	1.2×10^{-11}	2.5×10^{2}
0.8	6.9×10^{-6}	6.7×10^{-10}	1.4×10^{4}
0.9	3.8×10^{-4}	3.7×10^{-8}	7.5×10^{4}
	$E_g = 1.2$ eV		
0.2	2.6×10^{-12}	2.6×10^{-15}	5×10^{-4}
0.3	1.4×15^{-10}	1.4×10^{-13}	3×10^{-2}
0.4	7.7×10^{-9}	7.7×10^{-12}	1.5×10^{0}
	Detection limit		
0.5	4.2×10^{-7}	4.3×10^{-10}	8.5×10^{1}
0.6	2.3×10^{-5}	2.3×10^{-8}	4.7×10^{3}

This shape is not so simple for $\alpha_0 l < 1$. Since typical semiconductors have $\alpha \leq 10^5$ cm^{-1}, it becomes more difficult to interpret the luminescence from semiconductors whose $l < 10^{-5}$ cm; it is necessary to use Eqs. (25) or (26) in which the α dependence is not so simple.

IV. LUMINESCENCE MEASUREMENTS

A. CdS

CdS has been seriously studied as a photovoltaic material since 1954 when Reynolds first reported on the photovoltaic effect in a junction with copper.[14] By now its electronic structure is well characterized, and it can be routinely fabricated into very pure polycrystalline thin films. Its energy gap E_g is 2.42 eV,[15] the mobility is ~350 cm^2/V sec (Ref. 16) for the electrons, and about 16 cm^2/V sec for the holes.[15] The film we used came from the Institute of Energy Conversion at the University of Delaware. It consisted of 3-μm-diameter columnar grains in a film 47 μm thick on a Cu-Zn foil. Its room-temperature resistivity (through the film) is 6 Ω cm. It reportedly has an absorption spectrum typical of the curve published by Dutton for $E \perp C$ (since the grains were all basally oriented).[17]

For our luminescence measurements, the CdS was illuminated with 30 μW of 457 nm light (2.71 eV) on a 2-mm-diameter spot. The luminescence was collected through an Instruments SA $f/5.6$ $\frac{1}{4}$-m single monochromator in series with a Schott glass cutoff filter, and detected with a cooled GaAs photomultiplier tube (PMT). The throughput (including detector efficiency) of the detection system was measured to be 1.5×10^{-5}. The counts were compensated for incident-intensity fluctuations using a reference detector.

Figure 1 shows the luminescent spectrum as a function of temperature. At lower temperatures than used here one can see luminescence from a variety of traps as well as the 510-nm luminescence from band-to-band recombination. This is the regime in which one works if one is studying trapping mechanisms, as the carriers fall into traps before they can reach nonradiative recombination centers. At the temperatures used here, the trap luminescence, and most of the band-band luminescence, has disappeared as the increased mobility of the carriers has enabled them to diffuse to the recombination centers. The peaks reflect the

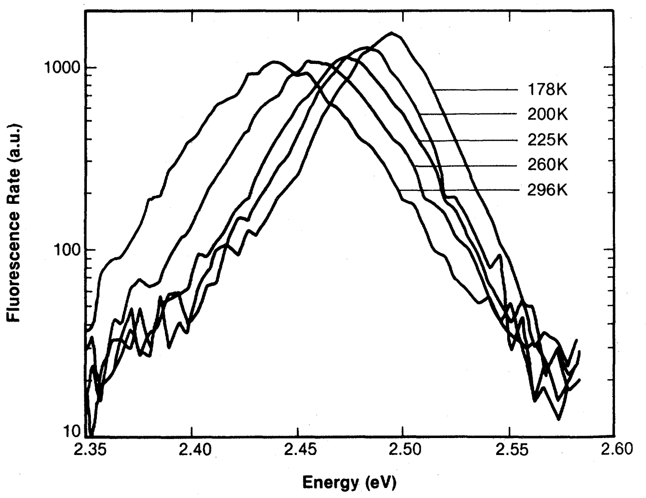

FIG. 1. CdS band-edge luminescence spectrum as a function of temperature. Its shape is temperature dependent as discussed in the text.

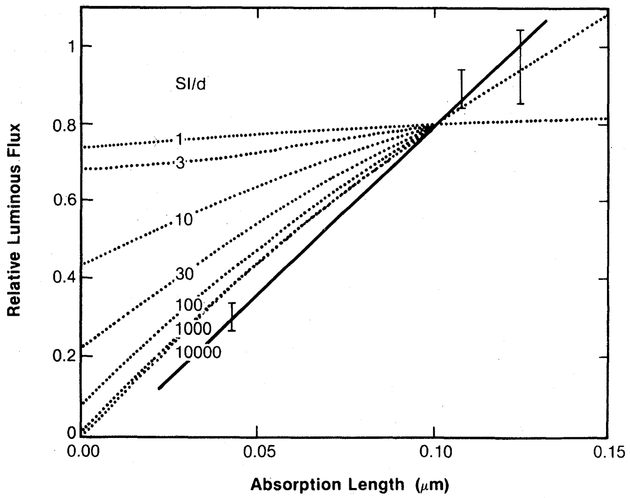

FIG. 2. Integrated CdS luminescence intensity vs incident-light absorption length. The dotted lines are the calculated values for a variety of recombination velocities and are normalized to 0.8 at $1/\alpha_0=0.105$ μm. The solid line connects experimental measurements. This curve was also normalized to 0.8 at $1/\alpha_0=0.105$ μm.

steady-state free-carrier population under the specified illumination intensity. The change in slope with temperature of the high-energy side of the luminescence peak is a characteristic of the thermalized bands. Analysis of the room-temperature spectrum using Dutton's absorption curve, and Eq. (21) yields a minority-carrier (hole) diffusion length of 0.4 μm and a chemical potential of 1.71 eV (under illumination of 0.6 mW/cm^2 of 457 nm light). The light absorption length at the excitation wavelength, $1/\alpha_0$, is ~ 0.1 μm. Since $\alpha_0 l \sim 4$, this sample is (barely) in the large diffusion limit [Eqs. (27)—(29)], and the luminescent intensity is sensitive to the existence of surface states.

In order to measure the surface-recombination velocity, it is necessary to determine the luminescent efficiency as a function of $1/\alpha_0$. The experimental points in Fig. 2 were obtained using Ar$^+$ laser lines ranging from 325 nm ($1/\alpha_0=0.043$ μm) to 488 nm ($1/\alpha_0=0.125$ μm). The plotted points are averages of measurements in which the incident power was varied by a factor of 10.

The dotted lines in Fig. 2 show the expected dependence of luminescence on $1/\alpha_0$ for different surface-recombination velocities, S. The curves are normalized to a value of 0.8 at $1/\alpha_0=1.05$ μm. Note that the calculated curves are indistinguishable from each other for $S\tau/l > 100$. These curves are also indistinguishable from the experimental points. Therefore, $S\tau/l > 100$. $\tau = l^2/\mu_m kT$ and $\mu_m = 16$ cm^2 V^{-1} sec^{-1} from earlier drift mobility measurements,[15] so the bulk lifetime τ is $\sim 4\times 10^{-9}$ sec and $S \gtrsim 10^5$ cm/sec.

As a result of the large S, the average hole lifetime is reduced by a factor of $1/\alpha_0 l$ from the bulk value, or

$$\tau_{\text{eff}} \sim 10^{-9} \text{ sec} .$$

An attempt was made to check this value by a first photon time of arrival technique.[18] The time evolutions of the elastically scattered light and of the luminescence peak are shown in Fig. 3. The luminescence peak shows a very fast decay, estimated at $\tau_1 = 1.3\times 10^{-10}$ sec followed by an indication of a low-intensity, long-lived decay with a lifetime of $\tau_2 \sim 0.7\times 10^{-9}$ sec. τ_2 is reasonably close to τ_{eff}. τ_1 may be the transient associated with the collapse of the initial $\mu(x)=\exp(-\alpha_0 x)$ distribution of carriers into the steady-state distribution. Most $[\sim(1-1/\alpha_0 l)]$ of the carriers diffuse to the surface and recombine on that collapse. It involves diffusing a distance $1/\alpha_0$, and so should take a time

$$\tau_{\text{collapse}} = \frac{(1/\alpha_0)^2}{D} ,$$

$$\tau_{\text{collapse}} = \frac{(1/\alpha_0)^2}{D} = \frac{(1/\alpha_0)^2}{l^2/\tau} = (1/\alpha_0 l)^2 \tau \sim 2\times 10^{-10} \text{ sec} ,$$

in rough agreement with the observed τ_1.

There is the potential for several systematic errors in the above analysis. The chief candidates are (1) errors in $\alpha(E)$, (2) band bending, and (3) thermalization.

The first possibility, an error resulting from measuring $\alpha(E)$ and $R(E)$ on different films, is unlikely to be large as the film was made by people with a lot of experience in reproducibly making high-quality films.

The second possibility is difficult to analyze. Band bending causes internal electric fields which distort the steady-state minority-carrier depth distribution. One might expect surface states to pin the Fermi level near the center of the gap, so any bending would tend to force the minority carriers to the surface. That would tend to enhance the surface-recombination velocity and decrease the measured l. This possibility will be pursued and analyzed further in future reports.

The third possibility, anomalous hot-carrier diffusion during thermalization ought to be small compared to the calculated $l \sim 0.4$ μm. One would expect the carriers to diffuse at most a few hundred angstroms.[19] It can be

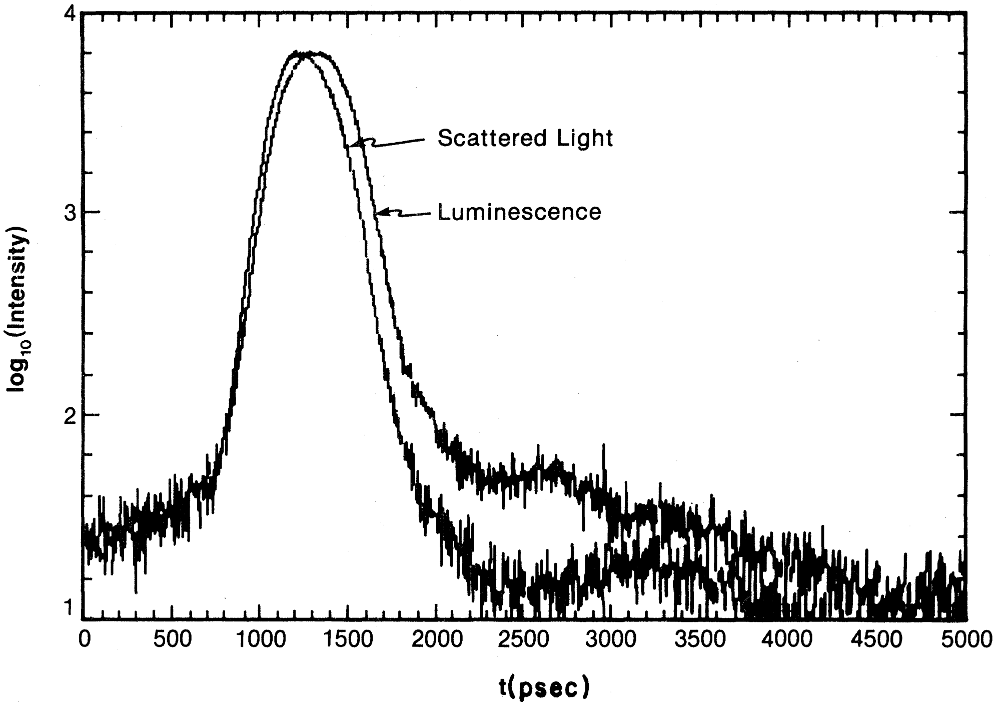

FIG. 3. *n*-type CdS fluorescence decay. Time evolution of (1) scattered ($\lambda=456$ nm) and (2) luminescent ($\lambda=506$ nm) light from a CdS film excited with 132 psec light pulse. The pulse is broadened to ~570 psec by PMT response time. The luminescent pulse is delayed relative to the scattered pulse by a time of 130 psec. There is also an indication of a $\tau_2=700$ psec tail in the luminescent response.

detected in this experiment by looking for changes in l as a function of the incident photon energy. Figure 4 shows that l appears to be about 10% longer for high-energy photons than for low-energy photons. That would impute a hot-carrier diffusion length of ~400 Å which is rather high compared to simple estimates.

B. Zn$_3$P$_2$, CdTe

The Zn$_3$P$_2$ and CdTe measurements are included to illustrate the limitations of this technique. Both have direct band gaps near 1.5 eV, and neither luminesce as intensely as the CdS. Furthermore, neither luminescence spectra are as simple as would be predicted by Eqs. (28) or (29). In both cases, the slope of the high-energy side of the luminescence peak is not proportional to $\exp(-E/kT)$ where T is room temperature.

The Zn$_3$P$_2$ required incident intensity greater than the intensity of the Sun at noon on a clear day (1 sun) to produce a detectable luminescent spectrum. Figure 5 shows the spectrum obtained using 250 mW/cm^2 (approximately 2.5 sun) of 647 nm light. As one might expect from such high intensities, the slope of the high-energy side of the luminescence band indicates a substantially heated sample—380 K. Measurements using 380 mW/cm^2 incident energy yielded a sample temperature of 440 K. Clearly, the sample is being overheated, and as a result $\alpha(E)$ does not have its room-temperature value. One can calculate μ from this, but not l without the correct $\alpha(E)$.

The CdTe measurement shown in Fig. 6 did not require such a high intensity (68 mW/cm^2) for an observable luminescence but still presented difficulties as the high-energy side of the peak not only had a lower than expected slope, but was not even straight. In this case, the luminescent peak energy corresponded to the beginning of the absorption edge in CdTe.[20] That implies that diffusion in CdTe is so small that we are in the $\alpha_0 l < 1$ regime[21] and the curve is described by Eq. (26). In that case, $R_{\text{obs}} \cong \alpha(E)\exp(-E/kT)$ where $\alpha(E)$ is slowly varying for high energies and very rapidly varying for lower energies. It is possible to obtain information on μ in this case, but only an upper limit for the diffusion length. In addition,

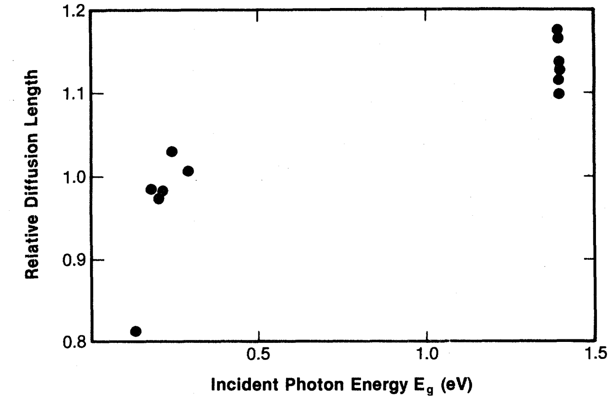

FIG. 4. Relative diffusion length in CdS vs incident photon energy.

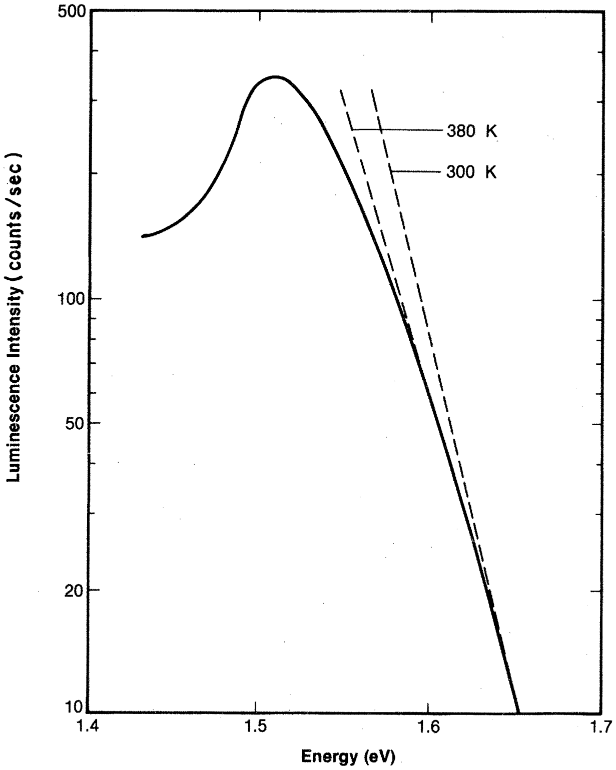

FIG. 5. Zn_3P_2 luminescence intensity vs energy incident intensity of 250 mW/cm^{-2}. The slope on the high-energy side of the peak indicates that the sample was heated to $\sim$380 K by the beam. The straight line labeled 300 K shows what the slope would have been if the sample had not been heated.

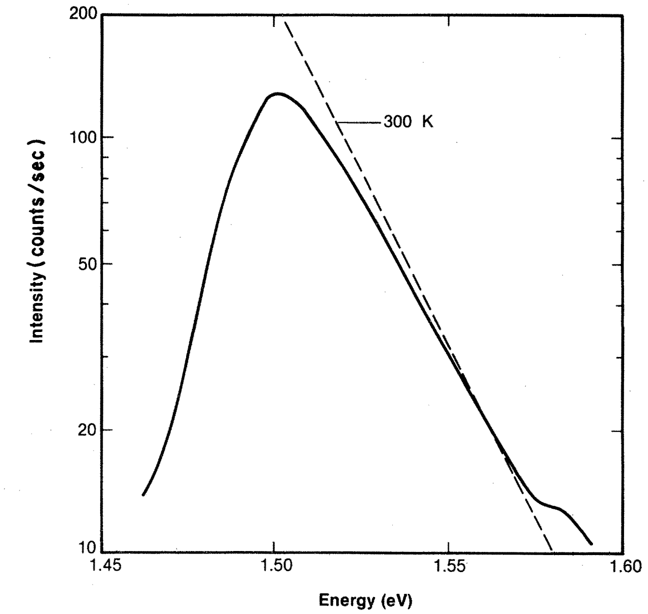

FIG. 6. CdTe luminescence intensity vs energy for an incident intensity of 68 mW/cm^2. The luminescing layer in this case is optically thin, and the shape of both sides of the peak is $\propto \alpha(E)\exp(-E/kT)$. The dashed line indicates the high-energy slope expected for an optically thick room-temperature luminescer.

the short diffusion length limits the surface sensitivity of the luminescence.

V. SUMMARY

It has been demonstrated that optical measurements—band-band photoluminescence and the absorption spectrum—on a semiconductor can be used to measure the electronic properties near its surface. Specifically (1) the unique temperature-dependent shape of this luminescent band identifies it in the presence of a background, (2) its intensity gives the quasi-Fermi-level separation μ, and (3) the position of its peak gives the minority-carrier diffusion length l, (4) μ, l and the equilibrium majority-carrier density gives an effective lifetime τ_{eff}, which is a convolution of bulk lifetime and surface recombination, (5) varying α_0 by changing the incident photon energy permits a separation of surface- and bulk-recombination rates. Since the surface is accessible, this enables studies of surface states and their modification. Finally, limits to semiconductors absorption strength and photon-detection equipment confine this technique to semiconductors for which $l \gtrsim 0.1$ μm and $\tau \gtrsim 10^{-10}$ sec.

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The samples of CdS and Zn_3P_2 were kindly given by Dr. J. D. Meakin and Dr. M. Bhushan of the Institute for Energy Conversion at the University of Delaware. Also, Dr. S. Garoff and M. Alvarez at Exxon Research and Engineering helped with the direct carrier-lifetime measurements in CdS. B. Brooks did the Zn_3P_2 absorption measurements.

APPENDIX A: CARRIER DISTRIBUTION IN AN ILLUMINATED SEMICONDUCTOR WITH SURFACE RECOMBINATION

For simplicity consider a material in which light is absorbed from the front surface and is absorbed with an extinction length $1/\alpha_0$ [i.e., $J(x)=J_0\exp(-\alpha_0 x)$]. The carriers recombine either at front surface with a recombination velocity S, or uniformly through the bulk with a diffusion length l. (See Ref. 3 for a derivation of the distribution in a thin film.)

The one-dimensional equation for this steady-state situation is

$$Du''+J_0\alpha_0\exp(-\alpha_0 x)-Du\,l^{-2}=0\,, \tag{A1}$$

where u is the excess carrier concentration, $D\equiv l^2/\tau$ is the diffusion constant, τ is the carrier lifetime in the bulk of the material, J_0 is the incident intensity inside the surface [this is $(1-r_f)I_0$ where I_0 is intensity outside the surface] and the prime indicates d/dx.

The surface recombination is included through the boundary condition

$$u'/u=S/D\,. \tag{A2}$$

The solution is

$$u(x)=\frac{(-r_f)I_0 l}{D[1-1/(\alpha_0 l)^2]}\left[\frac{[1+(1/\alpha_0 l)S\tau/l]\exp(-x/l)}{1+S\tau/l}-\frac{1}{\alpha_0 l}\exp(-\alpha_0 x)\right] \tag{A3}$$

and the total number of carriers generated is just

$$u_{\text{tot}}=\int_0^\infty u(x)dx=(1-r_f)\frac{I_0}{D}\frac{l^2}{[1-1/(\alpha_0 l)^2]}\left[\frac{[1+(1/\alpha_0 l)S\tau/l]}{1+S\tau/l}-\frac{1}{(\alpha_0 l)^2}\right]. \tag{A4}$$

In the absence of surface recombination ($S=0$) $u_{\text{tot}}=I_0 l^2/D=I_0\tau$. The average effect of surface recombination can be incorporated by introducing an effective lifetime, τ_{eff}:

$$\tau_{\text{eff}}=l^2/D\left[\frac{1+(1/\alpha_0 l)S\tau/l}{1+S\tau/l}-\frac{1}{(\alpha_0 l)^2}\right]; \tag{A5}$$

with this change, we can write $u(x)$ as

$$u(x)=\frac{J_0}{l}\tau_{\text{eff}}\left[\left[1+\frac{A}{\alpha_0 l}\right]\exp\left[-\frac{x}{l}\right]\right.$$
$$\left.-A\exp(-\alpha_0 x)\right](1-r_f), \tag{A6}$$

where

$$A=\frac{1}{\alpha_0 l}\left[\frac{1+(1/\alpha_0 l)S\tau/l}{1+S\tau/l}-1/(a_0 l)^2\right]^{-1} \tag{A7}$$

and is very small in the high mobility limit $\alpha_0 l\gg 1$ unless surface recombination gets too big ($S\tau/l>\alpha_0 l$).

APPENDIX B: LUMINESCENCE DETECTOR REQUIREMENTS

First, it is necessary to deal with the range of validity of the analysis. It contains the implicit assumption that $\alpha(E)$ is independent of incident-light intensity. Therefore, the photoexcited population density must never be allowed to get so large that photobleaching on darkening becomes significant. That is not a stringent limitation. For $\mu\sim E_g-0.25$ eV the excited population density is still $<10^{-4}$ of the band-edge degeneracy. Note that this is a limitation on μ, not the pump intensity. No matter how bad the semiconductor or short the lifetime of its carriers, one would be permitted to jack up the laser intensity until μ was sufficiently large to cause a detectable luminescence. It turns out that the incident-photon flux dumps enough heat into the sample that thermal problems will become important before $\alpha(E)$ starts changing.[22] A reasonable rule of thumb is that a sample can absorb power density of about 0.1 W/cm^2 (e.g., about the intensity of the Sun at noon on a clear day) without much of a temperature rise. That translates to a maximum absorbed flux of 4×10^{17} photons sec^{-1} cm^{-2} (for 1.5-eV photons).

The second set of limitations concerns the sensitivity, selectivity, and resolution of the detector system. A double monochromator will collect $\sim1\%$ of the emitted light ($f/4$ optics), transmit $\sim5\%$ of it (2–40% gratings, $\sim$6–80% mirrors) to a photomultiplier with a 10% quantum efficiency and a 10-cps dark count. For wavelengths longer than 850 nm, PMT's are useless so another factor of 100 is lost in going to a photodiode. We have then a throughput (including detector efficiency) of $\sim5\times10^{-5}$ for $\lambda<850$ nm and 5×10^{-7} for $\lambda>850$ nm.

The monochromator described will typically attenuate the incident laser wavelength by a factor of $\sim10^9$. Even the roughest sample will scatter less than 10% of the light scattered by a flat white surface, so one finds an effective rejection ratio $>10^{10}$.

Finally the monochromator is required to resolve a luminescence peak $\sim kT$ wide (room temperature is $\sim$0.025 eV$\sim$15 nm). A typical double monochromator with 2-mm slits and 1200-g/mm gratings gives a 4-nm bandwidth, or $dE=0.007$ eV through an aperture of 0.2 cm^2.

Now assume that E_g is about 1.5 eV, the sample is illuminated with 4×10^{17} photon cm^{-2} sec^{-1}, of which $\frac{1}{2}$ is absorbed, and the minority-carrier mobility is 100 cm^2/sec. Then the diffusion length l_{eff}, the required rejection ratio RR, and detector count rate I_{sig}, can be calculated as a function of μ.

Solving Eq. (17) for l_{eff} (defined as $l_{\text{eff}}^2\equiv D\tau_{\text{eff}}$),

$$\begin{aligned}l_{\text{eff}}&=\frac{Dn_0kT}{I_0(1-r_f)}\exp\left[\frac{\mu-E_g+E_c}{kT}\right]\\&=3.75\times10^2\exp\left[\frac{\mu-0.75E_g}{kT}\right],\end{aligned} \tag{B1}$$

E_c has arbitrarily been set to $E_g/4$, so the material will be in the low-intensity limit for $\mu<0.8$ eV (for $E_g=1.5$ eV). Dividing Eq. (21) by I_0, gives the relative luminescent/incident intensity ratio:

$$\begin{aligned}R&=\tfrac{1}{2}\pi I_0^{-1}\left[\frac{E_m}{hc}\right]^2\exp\left[\frac{\mu-E_m}{kT}\right]\frac{dE}{h}\\&=1.9\times10^2\exp\left[\frac{\mu-1.5}{kT}\right]\quad\text{for } E_m=1.5\text{ eV}\\&=1.2\times10^3\exp\left[\frac{\mu-1.2}{kT}\right]\quad\text{for } E_m=1.2\text{ eV},\end{aligned} \tag{B2}$$

where E_m is the peak of the luminescence signal [defined by $l\sim1/\alpha(E_m)$]. Multiplying Eq. (21) by the throughput (photons counted over photons emitted) of the detection system, g, gives the observed signal

$$I_{\mathrm{sig}}=\pi g\left[\frac{E_m}{hc}\right]^2\exp\left[\frac{\mu-E_m}{kT}\right]\frac{dE}{h}$$
$$=3.9\times10^{16}\exp\left[\frac{\mu-1.5}{kT}\right]\quad\text{for } E_m=1.5\text{ eV}$$
$$=2.5\times10^{14}\exp\left[\frac{\mu-1.2}{kT}\right]\quad\text{for } E_m=1.2\text{ eV}\,. \qquad \text{(B3)}$$

To get the numerical constants in Eqs. (B1), (B2), and (B3), the following values were used:

$$kT=0.025\text{ eV},\quad D=1\text{ cm}^2/\text{sec}\,,$$
$$dE=0.007\text{ eV},\quad n_0=6\times10^{19}\text{ eV cm}^3\,,$$
$$I_0=8\times10^{16}\text{ photons/sec},\quad r_f=0.5\,,$$
$$(\text{onto } 0.2\text{ cm}^2\text{ area}),\quad h=4.14\times10^{-15}\text{ eV sec}\,,$$
$$g=5\times10^{-5}\quad\text{at } E=1.5\text{ eV}$$
$$g=5\times10^{-17}\quad\text{at } E=1.2\text{ eV}\,.$$

The luminescence intensities and luminescent/incident ratios for a variety of E_g, μ, and l are presented in Table I.

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[10] μ is more than a computational convenience—it can be understood as the chemical potential of the carrier distribution, and as such defines the amount of work that this distribution can do. In a photovoltaic cell, for instance, it defines the maximum voltage obtainable from a photovoltaic device under the specified illumination conditions. See P. Würfel, J. Phys. C 45, 3967 (1982).

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