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On the temperature dependence of point-defect-mediated luminescence in silicon

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We present a model of the temperature dependence of point-defect-mediated luminescence in silicon derived from basic kinetics and semiconductor physics and based on the kinetics of bound exciton formation. The model provides a good fit to data for *W* line electroluminescence and *G* line photoluminescence in silicon. Strategies are discussed for extending luminescence to room temperature. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3157277]

Despite silicon's indirect band gap, the potential cost and scale benefits of developing a silicon device that displays efficient electroluminescence at room temperature make the search for such a device an active area of research.[1] One approach is the use of point defects as light emission centers.[2–4] Recently, light-emitting devices have been produced using two different zero-phonon emission lines originating at point defects, the *W* line at 1.018 eV and the *G* line at 969 meV. The *G* line arises from the presence of carbon in silicon.[3,4] The *W* line from a small self-interstitial complex.[2,5]

Point-defect luminescence devices are not yet practical because the intensity of emitted light decreases to a small fraction of its maximum value as the temperature is raised from 4 to 77 K and is undetectable at room temperature.[2,3,5] The most detailed phenomenological model of this temperature dependence, developed by Davies *et al.*[6] to describe *G* line photoluminescence, is not based on specific physical mechanisms. It relies on two unknown energies: an unspecified trap level and an energy barrier for a general nonradiative process. While this model was able to fit experimental observations, it does not provide the detail necessary to consider the feasibility of this type of device. This letter presents an initial attempt to build on the work of Davies *et al.*[6] by describing the observed luminescence using familiar concepts from semiconductor physics. Employing this approach is an initial step toward addressing questions of materials design for point-defect luminescence in silicon.

Previous experiments have suggested that *G* line luminescence is due to a two energy level system whose upper level is slightly below the conduction band.[6] These levels likely arise from bound exciton formation at the neutral carbon complex responsible for the *G* line. Because the data are qualitatively similar, we hypothesize that the same is true of the neutral self-interstitial complex responsible for the *W* line.

A neutral point defect capable of binding excitons can be in one of three states:[7] it can have no carriers bound to it, one bound carrier (in which case it is charged), or two bound carriers of opposite signs (a bound exciton). These will be referred to as states 0, 1, and 2, respectively. It must be true that

$$n_D = n_0 + n_1 + n_2, \tag{1}$$

where n_D is the total concentration of defects and n_0, n_1, and n_2 are the concentrations of defects in states 0, 1, and 2. The defect is capable of transitioning between any pair of these states. It is thus possible to define transition rates between the three states per unit volume such as R_{20} for the transition from state 2 to state 0 (e.g., by radiative recombination). The intensity of luminescence will be proportional to n_2 and thus the goal of this model is to determine n_2 as a function of temperature. Under steady state conditions, n_0, n_1, and n_2 must be constant. For n_2 this implies that $R_{02}+R_{12}=R_{20}+R_{21}$. Similar consideration of n_0 and n_1 yields a total of two independent equations.

Table I lists all the physical processes that can occur in this system and ties each of them to one of the transition rates. Several processes are ignored based on the following assumptions: (1) the concentration of free excitons is negligible compared to the concentration of free carriers. This is reasonable because the purpose of the model is to describe an electrically or optically pumped device. (2) The rate of recombination of a bound carrier with a free carrier is small relative to the rates of capture and emission of free carriers. This assumption reflects the notion that a localized state and a delocalized state have a small interaction probability. Finally, (3) pair generation processes localized at a defect can be ignored. In the case of electrical pumping this is a modest assumption because the only carrier generation is thermal and so all pair generation events can be neglected relative to the electrical pumping. For optical pumping, this assumption is essentially equivalent to stating that the rate at which pump photons generate carriers at the luminescent defects is small relative to the rate at which the defects capture free carriers.

Assumption (1) means that it is not necessary to track the number of free excitons. Similarly, if the concentration of defects is small relative to the concentrations of free electrons and free holes, applying charge neutrality[8] allows free carriers to be removed from the bookkeeping according to

$$n_{\text{free } e-} \approx n_{\text{free } h+} \equiv n_c, \tag{2}$$

which is independent of temperature and of the concentrations of other species and is controlled independently by the experimenter using the pump intensity. Consequently, n_0, n_1,

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TABLE I. Physical processes contributing to each transition rate, associated changes in concentrations of all species, and inclusion/neglect of process in the model. For clarity in this table it is assumed that the defect captures a hole and then an electron even though the model makes no distinction. Processes listed as not in the model are excluded based on the three numbered assumptions given in the text.

Rate	Process	Δn_0	Δn_1	Δn_2	$\Delta n_{\text{free } e-}$	$\Delta n_{\text{free } h+}$	$\Delta n_{\text{free exciton}}$	In model? (reason neglected)
R_{01}	h^+ capture	−1	+1	0	0	−1	0	Yes
R_{01}	Bound h^+/free e^- generation	−1	+1	0	+1	0	0	No (3)
R_{12}	e^- capture	0	−1	+1	−1	0	0	Yes
R_{12}	Bound e^-/free h^+ generation	0	−1	+1	0	+1	0	No (3)
R_{02}	Free exciton capture	−1	0	+1	0	0	−1	No (1)
R_{02}	Bound exciton generation	−1	0	+1	0	0	0	No (3)
R_{10}	h^+ emission	+1	−1	0	0	+1	0	Yes
R_{10}	Bound h^+/free e^- recombination	+1	−1	0	−1	0	0	No (2)
R_{21}	e^- emission	0	+1	−1	+1	0	0	Yes
R_{21}	Bound e^-/free h^+ recombination	0	+1	−1	0	−1	0	No (2)
R_{20}	Nonradiative bound exciton recombination	+1	0	−1	0	0	0	Yes
R_{20}	Radiative bound exciton recombination	+1	0	−1	0	0	0	Yes
R_{20}	Bound exciton emission	+1	0	−1	0	0	+1	Yes

and n_2 are the only temperature dependent concentrations in this model.

Under these assumptions and assuming linear kinetics, Table I translates into the following equations:

$$R_{01} = n_0 n_c c_{01}; \quad R_{12} = n_1 n_c c_{12}; \quad R_{02} \approx 0;$$

$$R_{10} = n_1 e_{10}; \quad R_{21} = n_2 e_{21}; \quad R_{20} = n_2 e_{20}, \tag{3}$$

where the c_{ij}'s and e_{ij}'s are capture and emission coefficients, respectively. Detailed balance (e.g., Ref. 9) eliminates the emission coefficients according to

$$e_{10} = c_{01} n_0^* n_C^* / n_1^* = c_{01} K_{01} \tag{4}$$

and

$$e_{21} = c_{12} n_1^* n_C^* / n_2^* = c_{12} K_{12}, \tag{5}$$

where * denotes an equilibrium value and the K_{ij}'s are calculable equilibrium constants for their respective processes. Making these substitutions and solving the steady state problem for n_2 yields

$$n_2 = \frac{\beta n_D n_C^2}{\beta(K_{01}K_{12} + K_{12}n_C + n_C^2) + \alpha(K_{01} + n_C) + \alpha\beta n_C}, \tag{6}$$

in which $\alpha \equiv e_{20}/c_{01}$ and $\beta \equiv c_{12}/c_{01}$ are fitting parameters with units of concentration and no units, respectively. Assuming that the defect always binds a hole from the valence band (set to $E=0$) and then an electron from the conduction band,[10] Eq. (6) becomes

$$n_2 = \frac{\beta n_D n_C^2}{\beta\left(\frac{N_V}{g_h}\frac{N_C}{g_e}e^{(E_e-E_h-E_g)/k_BT} + n_C\frac{N_C}{g_e}e^{(E_e-E_g)/k_BT} + n_C^2\right) + \alpha\left(\frac{N_V}{g_h}e^{-E_h/k_BT} + n_C\right) + \alpha\beta n_C}, \tag{7}$$

where N_C and N_V are the conduction and valence band effective densities of states ($\propto T^{3/2}$), g_h, and g_e are the hole and electron degeneracy factors, respectively, E_g is the band gap, and E_h and $E_g - E_e$ are the hole and electron binding energies, respectively, such that $E_e - E_h$ is the energy of the emitted photons.

Dividing Eq. (7) by n_D provides a functional form for the temperature dependence that can be compared with and fit to photo and electroluminescence intensity data. The main portion of Fig. 1 shows three least-squares fits (for three different carrier concentrations) of this model to the data of Bao *et al.*[2] for the temperature dependence of electroluminescence intensity from a *W* line light-emitting diode (LED). The inset shows a least-squares fit to the data of Davies *et al.*[6] for the temperature dependence of *G* line photoluminescence intensity for an assumed carrier concentration of 10^{15}/cm. This data series is truncated below 20 K to exclude points influenced by a trap state not contained in this model. Both sets of data have been normalized to a maximum of 1. All fits ignore the temperature dependences of α, β, and n_C, and silicon's band gap. α, β, and n_C are considered constants to prevent a proliferation of fitting parameters. The band gap is set to its low-temperature value of 1.17 eV. Including its temperature dependence would represent false precision because the (unknown) temperature dependence of the defect levels is neglected. $E_e - E_h$ is taken to be 1.02 eV for the *W* line and 0.969 eV for the *G* line. Finally, the silicon samples in both references are assumed to be undoped. This is accurate for Ref. 6 but the active region of the *W* line LED in Ref. 2 was lightly *p*-doped to a resistivity of 5 Ω cm.[2,6] This resistivity corresponds to a boron concentration of roughly $3 \times 10^{15}/\text{cm}^2$, which is on the order of the smallest carrier concentration assumed in fitting the *W* line data.[2]

The model presented above provides an accurate fit to the *G* line data from Ref. 6 and a reasonable fit to the *W* line data in Ref. 2. In the latter case, higher carrier concentrations produce a better fit at low temperatures and lower carrier concentrations produce a better fit at high temperatures. This

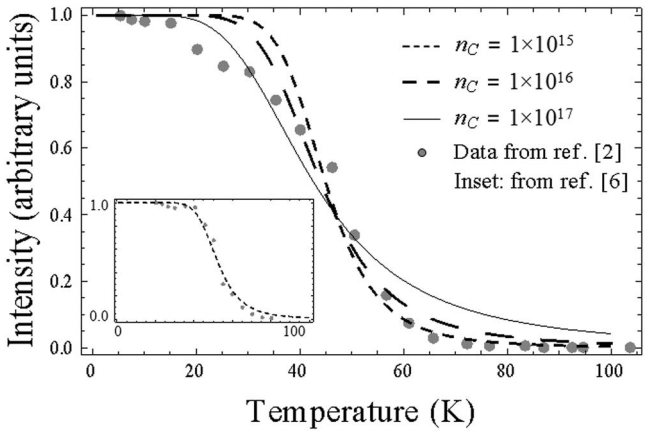

FIG. 1. Plot of a least-squares fit of the model to the *W* line electroluminescence data in Ref. 2 for three assumed carrier concentrations: 10^{15}, 10^{16}, and $10^{17}/\mathrm{cm}^2$. The temperature dependences of the fitting parameters and band gap were ignored. Inset: plot of a least-squares fit of the model to the *G* line photoluminescence data in Ref. 6 for an assumed carrier concentration of $10^{15}/\mathrm{cm}^2$. Data for temperatures below 20 K were disregarded because they reflect an additional trap level not described in this model (see Ref. 6).

could be a consequence of one or more of the temperature dependences ignored in this calculation. The results of fitting were highly insensitive to variations in several orders of magnitude in the values of α and β. Table II reports the values of E_e computed by the least-squares fits. For both defects it is evident that one carrier, assumed by Eq. (7) to be an electron, is bound much more loosely than the other. The result for the *G* line is in quantitative agreement with Ref. 6, which fits a model of a defect binding a single carrier to the same data.

Given the model's reasonable fit to the data, it is possible to use the model to consider whether devices relying on defect-mediated luminescence in silicon will ever operate at room temperature. Equation (7) implies that that the dominant influence on the temperature dependence is the smaller of the carrier binding energies $E_g - E_e$ and E_h. Whereas it would be difficult to manipulate the binding energy for a given defect, the model provides grounds for optimism if we can utilize a defect with trap states at least 100 meV from both band edges, leading to luminescence at around 800 meV—an energy that would be ideal for telecom applications at 1.55 μm. This would allow for tighter binding of carriers, which is necessary for room-temperature operation. Such a defect would bind electrons and holes with roughly equal energies and would thus be beyond the scope of the model presented in Ref. 6 but tractable using the model presented above. Temperature dependent photoluminescence measurements on a system with comparable electron and hole binding energies would thus be a natural way to experimentally test the additional complexity of Eqs. (6) and (7) relative to the model in Ref. 6.

TABLE II. Trap energy calculated from a least-squares fit of the model to the data in Refs. 2 and 6 assuming the stated values for n_C.

n_C (atoms/cm^3)	*G* line E_e (eV)	*W* line E_e (eV)
10^{15}	1.138	1.144
10^{16}	N/A	1.153
10^{17}	N/A	1.162

In addition to changing defects, one could also potentially increase the number of defects through materials processing. Although the model presented above is normalized with respect to defect concentration, the absolute intensity scales with defect concentration. Furthermore, one could raise the carrier concentration by increasing the level of optical or electrical pumping. Nevertheless, the priority should be manipulating the defect energy if possible because varying the defect and carrier concentrations provides linear and sublinear[11] enhancement in luminescence, respectively.

It is worth noting that if the defect binding energies increase enough, bound exciton escape (contained within α) might come to dominate the temperature dependence. Although including this effect in the model would have been possible, the temperature dependence of α was ignored, as noted above, to reduce the total number of fitting parameters.

In summary, we have presented a model of defect-mediated luminescence in silicon based on the kinetics of carrier emission and capture that is consistent with past experimental observations. The model was used to suggest that the most effective way to make a device based on these principles operate at room temperature would be to utilize a defect with trap states at least 100 meV from the conduction and valence band edges.

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[10] To consider the opposite case, interchange $(N_C/g_e)e^{(E_e-E_g)/k_BT}$ and $(N_V/g_h)e^{-E_h/k_BT}$ in Eq. (6).
[11] Ignoring stimulated emission.