

## Model for the the photoluminescence behavior of porous silicon

George C. John and Vijay A. Singh

Physics Department, Indian Institute of Technology (I.I.T.)–Kanpur, Uttar Pradesh 208106, India

(Received 10 May 1996)

We outline a simple framework to explain the vast amount of data on the photoluminescence (PL) behavior of porous silicon. Our model involves the competition between an activated radiative process and a Berthelot-type nonradiative process. Our framework successfully explains a wide range of observations by various groups on the temperature, pressure and emission energy dependence of PL. The temperature dependence of luminescence intensity and decay time as predicted by this model is observed for a variety of materials such as amorphous silicon and chalcogenide glasses. The model is transparent, analytic, and does not take recourse to computer modeling or simulation. [S0163-1829(96)11031-6]

Nanocrystalline forms of semiconductors, particularly porous silicon (PS), have been a focus of attention in recent years. Several microscopic mechanisms have been proposed to explain the visible photoluminescence (PL) in PS. The most popular among these is the quantum confinement model.<sup>1</sup> While considerable effort has been devoted to these microscopic mechanisms, attempts to explain the vast amount of accumulated data regarding the dependence of PL on temperature, pressure and luminescence energy have been scattered and sporadic.<sup>2</sup> The present work is an attempt to present a simple, unified framework to explain and systematize this large body of data.

PS is a disordered system, and its properties have been known to depend on factors ranging from preparation conditions, size distribution of crystallites and post anodization surface treatments. There is, however, a consensus about visible PL from high porosity samples. Further, our survey of the existing literature reveals some systematics in the PL behavior under various conditions.<sup>2,3</sup> These are (i) the luminescence decay time falls by an order of magnitude or more as the temperature is increased from 10 K to 300 K, (ii) the PL intensity shows a maximum with temperature, the peak being in the range 50 K–150 K, (iii) the PL intensity falls steeply with pressure, (iv) the luminescence decay time decreases systematically with emission energy in the range 1.4–2.5 eV (v) the PL peak position exhibits an anomalous behavior (both blueshifts and redshifts) with temperature, and (vi) the PL peak position exhibits a redshift with pressure, with an initial blueshift being discernible in some cases.

PL from PS has been attributed to the recombination of electron-hole pairs within nanocrystallites.<sup>4</sup> A localized carrier can (i) recombine radiatively, (ii) recombine nonradiatively, or (iii) escape to another site. Electronic transport in PS has been observed to follow a surface-based mechanism.<sup>5,6</sup> Considering the low efficiency of electroluminescence from PS, we believe that the surface current is linked to the nonradiative process.

Some studies have reported a Berthelot-type behavior<sup>7</sup> of the conductivity.<sup>5,8</sup> The PL intensity  $I(T)$  has also been reported to vary with temperature as

$$\frac{I_0}{I(T)} - 1 \propto \exp\left[\frac{T}{T_n}\right] \quad (1)$$

in PS (Ref. 9) as well as in siloxene,<sup>10</sup> amorphous semiconductors, and chalcogenides.<sup>11</sup> In the light of these observations, we *hypothesize* that the nonradiative rate  $R_n$  varies as  $\exp(T/T_n)$ . We also note that the radiative rate  $R_r$  has an activated behavior.<sup>12</sup> Therefore, the luminescence decay time in our model can be expressed as

$$\frac{1}{\tau} = R_r + R_n = \nu_r \exp\left(\frac{-T_r}{T}\right) + \nu_n \exp\left(\frac{T}{T_n}\right), \quad (2)$$

where  $\{\nu_r, \nu_n, T_r, T_n\}$  are characteristic constants.

Within the context of transport, the Berthelot behavior is attributed<sup>13,14</sup> to carrier tunneling across a barrier of width  $S$  vibrating with a frequency  $\Omega$ . The characteristic constants of the nonradiative process will then be given by

$$\nu_n = \Gamma_0 \exp(-2\alpha S), \quad (3a)$$

$$T_n = \frac{M\Omega^2}{2\alpha^2 k}, \quad (3b)$$

where  $k, M, \Gamma_0$  are the Boltzmann constant, the inertia of the vibrating system, and the jump frequency,<sup>15</sup> respectively.  $\alpha^{-1}$  is the extent of the carrier wave function.

The characteristic constants assume a range of numerical values, reflecting the disordered nature of the PS system. In the present study, we fix their ranges in an *a priori* fashion by examining data from transport (not PL) measurements.<sup>5,8,14</sup> The wave-function extent  $\alpha^{-1} \in 2-7 \text{ \AA}$ , the width of the barrier  $S \in 8-20 \text{ \AA}$ , and the characteristic nonradiative temperature  $T_n \in 50-150 \text{ K}$ . For the radiative process,  $\nu_r \sim 10^4 \text{ s}^{-1}$  and  $T_r \in 25-125 \text{ K}$ .<sup>12</sup> Our model thus attains a firm predictive value.

The luminescence decay time is found to fall by more than an order of magnitude when the temperature is increased from 10 K to 300 K. This behavior is accurately reproduced by Eq. (2). Figure 1 depicts a log-log plot of the lifetime vs temperature. The boxes represent experimental data from the work of Finkbeiner and Weber.<sup>16</sup> The lifetime falls by two orders of magnitude. If the radiative rate is higher, the fall is less steep. This is depicted by crosses in Fig. 1, which represent the data due to Mauckner and co-workers.<sup>17</sup> This trend is also depicted by curves based on Eq. (2) (Fig. 1). The agreement with experiment is excellent.

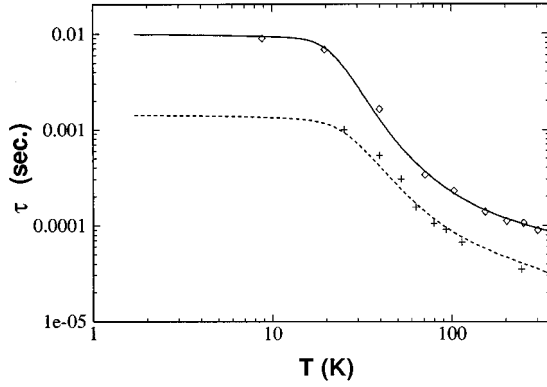


FIG. 1. The temperature dependence of the luminescence decay time. Shown are the experimental values obtained from Ref. 16 (boxes) and Ref. 17 (crosses). The solid (dashed) line represents a theoretical fit based on Eq. (2) with  $\nu_r=15000$  (35000)  $s^{-1}$ ,  $\nu_n=100$  (700)  $s^{-1}$ ,  $T_r=125$  (125) K, and  $T_n=150$  (150) K.

Besides these two representative examples from literature, several other investigations of the temperature dependence of the lifetime have been carried out.<sup>18</sup> Our model can successfully explain these results, working within a circumscribed set of parameters whose values have been fixed in an *a priori* fashion.

The time-integrated PL intensity is given by<sup>12</sup>

$$I(T) = \frac{I_0 R_r}{R_n + R_r} = \frac{I_0}{1 + \nu_0 \exp\left(\frac{T}{T_n} + \frac{T_r}{T}\right)}, \quad (4)$$

where we have used Eq. (2) and defined a reduced frequency  $\nu_0 = \nu_n / \nu_r$ .  $I_0$  is the initial intensity.  $I(T)$  clearly has a maximum with temperature

$$T_m = \sqrt{T_r T_n}.$$

From our initial assignment of numerical values, the maxima is found to lie in the range 30–140 K. The detailed behavior of  $I(T)$  is depicted in Fig. 2. The boxes denote data on the

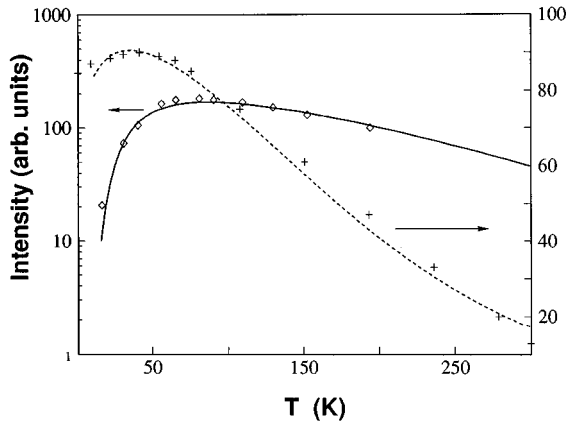


FIG. 2. The variation of the luminescence intensity with temperature. The boxes denote data from Ref. 19 and crosses, data from Ref. 20. The solid (dashed) line shows a theoretical plot based on Eq. (4) with  $\nu_r=9000$  (6000)  $s^{-1}$ ,  $\nu_n=5000$  (1000)  $s^{-1}$ ,  $T_r=75$  (20) K and  $T_n=100$  (50) K.

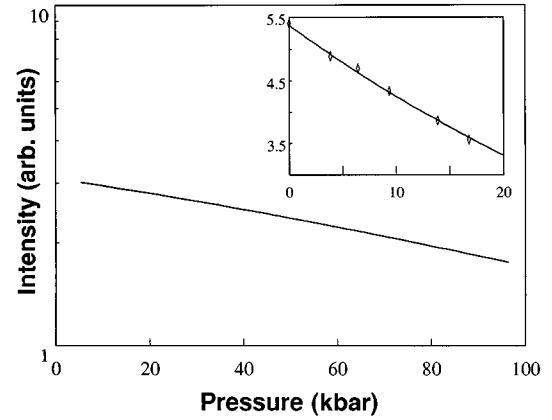


FIG. 3. The variation of luminescence intensity with pressure, computed from Eq. (5) with  $(\Gamma_0/\nu_r)=1000$ ,  $T_r=75$  K,  $T_n=100$  K,  $\alpha=0.25 \text{ \AA}^{-1}$ ,  $S=20 \text{ \AA}$ , and  $K=1 \text{ meV/kbar}$ . The inset shows a fit to the data reported by Zhou and co-workers (Ref. 24).

temperature dependence of luminescence intensity reported by Kanemitsu and co-workers.<sup>19</sup> To illustrate the extent of disorder in PS, we also depict the data due to Banerjee (crosses),<sup>20</sup> which has a maximum at a much lower temperature. The curves calculated from Eq. (4) reveal an excellent agreement with the theory. Similar temperature dependence of PL has been reported by a large number of workers.<sup>12,17,21</sup> We also note that if the characteristic radiative temperature ( $T_r$ ) is very low, the PL intensity remains nearly constant at  $T < T_m$ . This behavior has also been experimentally observed.<sup>22</sup> The fall in intensity at low temperatures has been attributed by some workers to Auger recombination.<sup>23</sup> Our model does not explicitly invoke an Auger mechanism. Further, we note that in general,  $T_r < T_n$ . Hence, for  $T > T_n$ , Eq. (4) reduces to

$$I(T) \rightarrow \frac{I_0}{1 + \nu_0 \exp\left(\frac{T}{T_n}\right)}, \quad T > T_n$$

which is the behavior reported in Eq. (1) for PS,<sup>9</sup> siloxene,<sup>10</sup> and amorphous semiconductors.<sup>11</sup>

Using Eq. (3a) in Eq. (4), the pressure dependence of PL intensity can be explicitly stated,

$$I(P) = \frac{I_0}{1 + \frac{\Gamma_0}{\nu_r} \exp\left\{\frac{T_r}{T} + \frac{T}{T_n}\right\} \exp[-2\alpha S(1-KP)]}, \quad (5)$$

where we have assumed that the barrier width  $S$  varies with pressure as  $S \rightarrow S(1-KP)$ ,  $K$  being the isothermal compressibility. Figure 3 is a plot of  $I(P)$  based on Eq. (5). The qualitative behavior predicted by our model is experimentally observed. In the inset of Fig. 3, we compare a theoretical plot with the experimental data due to Zhou and co-workers,<sup>24</sup> which shows a rapid fall in intensity with increasing pressure. A detailed quantitative comparison with experiment is not possible given the uncertainty in the value of  $K$  for PS and the arbitrary scale for intensity. Our model is in agreement with other reported works in the literature.<sup>25</sup>

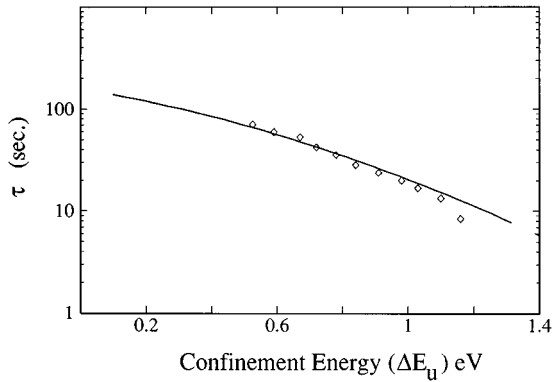


FIG. 4. The variation of the luminescence decay time  $\tau$  with confinement energy  $\Delta E_u$ . The experimental data (boxes) are from Ref. 26. The solid line depicts a theoretical plot based on Eq. (6) with  $R_r=4000 \text{ s}^{-1}$ ,  $\Gamma_0=5 \times 10^8 \text{ s}^{-1}$ ,  $\gamma_1=8 \text{ (eV)}^{-1/2}$ ,  $\gamma_2=0.4 \text{ (eV)}^{-1}$  and  $V=2.5 \text{ eV}$ .

This model, as described thus far, relies solely on the competition between an activated radiative rate  $R_r$  and a Berthelot-type nonradiative rate  $R_n$  and is not premised on any microscopic mechanism of photoluminescence. We can also view our model in the light of a quantum confinement scheme. Employing a tunneling model similar to that of Vial *et al.*,<sup>26</sup> but with the incorporation of a vibrating barrier we obtain, from Eqs. (2) and (3),

$$\frac{1}{\tau} = R_r + \Gamma_0 \exp[\gamma_1(V - \Delta E_u)^{1/2} + \gamma_2(V - \Delta E_u)], \quad (6)$$

where  $\gamma_1, \gamma_2$  are energy-independent factors,  $V$  is the height of the vibrating barrier,  $m$  is the effective mass of the confined carrier, and  $E_u$  is the energy upshift due to confinement. In Fig. 4, we compare a plot (solid line) of  $\tau$  vs  $\Delta E_u$  based on Eq. (6) with the experimental data of Pavesi and co-workers<sup>27</sup> measured on an 87% porosity sample. The theoretical curve [Eq. (6)], is almost linear on a semilog scale, indicating a nearly exponential fall of the lifetime with confinement energy in the range 0.3–1.0 eV.

Employing Eqs. (3) and (5), the PL intensity in terms of the tunneling parameters  $\alpha, S$  and temperature  $T$  can be written as

$$I(T) = \frac{I_0}{1 + \frac{\Gamma_0}{\nu_r} \exp\left(\frac{T_r}{T}\right) \exp(-2\alpha S) \exp\left[\frac{2\alpha^2 kT}{M\Omega^2}\right]}. \quad (7)$$

This expression exhibits a maximum with varying  $\alpha$ . The peak position

$$\alpha_p = \frac{SM\Omega^2}{2kT} \sim \frac{1}{T}. \quad (8)$$

Using the relations  $\hbar\omega = E_g + \Delta E_u$ ,  $\alpha^2 \propto (V - \Delta E_u)$ , and (8), we can examine the temperature dependence of the PL peak,

$$\hbar\omega_p = V + E_g - c_1 T - \frac{c_2}{T^2}, \quad (9)$$

where  $E_g$  is assumed to decrease linearly with temperature, with a slope  $c_1 = 2.3 \times 10^{-4} \text{ eV/K}$ .  $c_2 = \hbar^2/2m(SM\Omega^2/2k)^2$

falls in the range  $3 \times 10^3 - 3 \times 10^5 \text{ eV K}^2$ . This expression implies an initial blueshift, followed by a redshift, with the cross-over temperature  $T_c = (2c_2/c_1)^{1/3}$ . Working within the allowed range of disorder, we find that  $T_c$  may range from 20 K to 1000 K, the large variation being caused by the  $\Omega^4$  term in  $c_2$ . This can explain the observed anomalous behavior of the PL peak position with temperature as reported in several works.<sup>21,22,28</sup>

From Eq. (8) one can also obtain the pressure dependence of the PL peak

$$\hbar\omega_p = \left( V + E_g - \frac{c_2}{T^2} \right) + P \left( \frac{2Kc_2}{T^2} - \eta \right) - \frac{P^2 K^2 c_2}{T^2}, \quad (10)$$

where we assume the bulk energy gap to vary as  $E_g(P) = E_g - \eta P$ ,  $\eta$  being in the range 0.1–2 meV/kbar.<sup>29</sup> The PL peak will show an initial blueshift only when the coefficient of the term linear in  $P$  is positive. This is permissible within the preassigned range of values. The observed surface dependence of the initial peak shift can be understood in this fashion.<sup>30</sup>

The key hypothesis in our model is the presence of a Berthelot component in the PL lifetime. Note that we have assumed a single  $\Omega$ , the frequency of the vibrating barrier. Therefore, the source of vibration could be a defect such as a silicon oxygen complex,<sup>26</sup> a dangling bond, or some other vibrating species. The phenomenological models for PL behavior by some<sup>26</sup> have suggested that carriers tunnel across an  $\text{SiO}_x$  coating surrounding the crystallite. In the present study, we refrain from speculating further on the nature of the barrier. The surface-dependence of PL can be explained by invoking a surface-dependent tunneling mechanism. Our model basically employs a set of four parameters  $\{\nu_r, \nu_n, T_r, T_n\}$ , which clearly define the competition between the radiative and nonradiative processes. These parameters can assume a range of values reflecting the disordered nature of the PS system.

Our model enables us to make several predictions. The values assigned to  $\{\nu_r, \nu_n, T_r, T_n\}$  can be further refined on the basis of these predictions. Based on an examination of Eqs. (2) and (3), one can expect the lifetime to decrease with pressure. The increase in nonradiative recombination due to an increase in pressure may also lead to an enhanced conductivity. Summing up, we have presented a transparent, analytic framework (without recourse to computer simulation or modeling) to explain a diverse range of experimental studies on the PL behavior in PS. Extensions of our model are possible. We have worked with a fixed frequency  $\Omega$ . The dependence of PL on excitation intensity and energy are yet to be addressed. We hope that this model will provide workers in this field with a systematic, unified perspective. Experimental studies to verify and critique our model are possible. We hope to extend our model to other aspects of PS such as electroluminescence and to related disordered materials.

This work was supported in part by grants from the Department of Science & Technology and the Council of Scientific and Industrial Research, Government of India. The authors wish to thank Dr. S. Sinha, Dr. K.L. Narasimhan, and Dr. B.M. Arora of the Tata Institute of Fundamental Research, Bombay, where this work was initiated.

- <sup>1</sup>L.T. Canham, *Appl. Phys. Lett.* **57**, 1046 (1990); V. Lehmann and U. Gosele, *ibid.* **58**, 856 (1991).
- <sup>2</sup>G.C. John and V.A. Singh, *Phys. Rep.* **263**, 93 (1995).
- <sup>3</sup>Y. Kanemitsu, *Phys. Rep.* **263**, 1 (1995); D.J. Lockwood, *Solid State Commun.* **92**, 101 (1994); B. Hamilton, *Semicond. Sci. Technol.* **10**, 1187 (1995); S. Schuppler *et al.*, *Phys. Rev. B* **52**, 4910 (1995).
- <sup>4</sup>P.D.J. Calcott *et al.*, *J. Phys. Condens. Matter* **5**, L91 (1993).
- <sup>5</sup>J.J. Mares, J. Kristofik, J. Pangrac, and A. Hospodkova, *Appl. Phys. Lett.* **63**, 180 (1993).
- <sup>6</sup>Z. Chen, T.-Y. Lee, and G. Bosman, *Appl. Phys. Lett.* **76**, 2499 (1994).
- <sup>7</sup>H. Berthelot, *Ann. Chim. Phys.* **66**, 110 (1862).
- <sup>8</sup>D. Deresmes, V. Marissael, D. Stievenard, and C. Ortega, *Thin Solid Films* **255**, 258 (1995).
- <sup>9</sup>M. Stutzmann *et al.*, *J. Lumin.* **57**, 321 (1993).
- <sup>10</sup>I. Hirabayashi, K. Morigaki, and S. Yamanaka, *J. Phys. Soc. Jpn.* **52**, 671 (1983); *J. Non-Cryst. Solids* **59-60**, 645 (1983).
- <sup>11</sup>R.A. Street, *Adv. Phys.* **25**, 397 (1976).
- <sup>12</sup>T. Suemoto, K. Tanaka, and A. Nakajima, *Phys. Rev. B* **49**, 11 005 (1994).
- <sup>13</sup>R.H. Tredgold, *Proc. Phys. Soc.* **80**, 807 (1962).
- <sup>14</sup>C.M. Hurd, *J. Phys. C* **18**, 6487 (1985).
- <sup>15</sup>D. Emin, *Phys. Today* **35** (6), 34 (1982).
- <sup>16</sup>S. Finkbeiner and J. Weber, *Thin Solid Films* **255**, 254 (1995).
- <sup>17</sup>G. Mauckner *et al.*, *J. Appl. Phys.* **75**, 4167 (1994).
- <sup>18</sup>R. Laiho, A. Pavlov, O. Hovi, and T. Tsuboi, *Appl. Phys. Lett.* **63**, 275 (1993); G. Amato, G. Francia, and P. Menna, *Thin Solid Films* **255**, 204 (1995); T. Tsuboi, R. Laiho, and A. Pavlov, *Thin Solid Films* **255**, 216 (1995).
- <sup>19</sup>Y. Kanemitsu *et al.*, *Phys. Rev. B* **48**, 2827 (1993).
- <sup>20</sup>S. Banerjee, *Bull. Mater. Sci.* **17**, 533 (1994).
- <sup>21</sup>X.L. Zheng, W. Wang, and H.C. Chen, *Appl. Phys. Lett.* **60**, 986 (1992).
- <sup>22</sup>Z.Y. Xu, M. Gal, and M. Gross, *Appl. Phys. Lett.* **60**, 1375 (1992); Y.H. Xie *et al.*, *Phys. Rev. B* **49**, 5386 (1994).
- <sup>23</sup>C. Delerue *et al.*, *Phys. Rev. Lett.* **75**, 2228 (1995); R.A. Street, *Phys. Rev. B* **23**, 861 (1981).
- <sup>24</sup>W. Zhou *et al.*, *Appl. Phys. Lett.* **61**, 1435 (1992).
- <sup>25</sup>J.M. Ryan, P.R. Wamsley, and K.L. Bray, *Appl. Phys. Lett.* **63**, 2260 (1993); N. Ookubo, *J. Appl. Phys.* **74**, 6375 (1993).
- <sup>26</sup>J.C. Vial *et al.*, *Phys. Rev. B* **45**, 14 171 (1992); M. Sacilotti *et al.*, *Electron. Lett.* **29**, 790 (1993); G.G. Qin and Y.Q. Jia, *Solid State Commun.* **86**, 559 (1993).
- <sup>27</sup>L. Pavesi, M. Ceschini, and H.E. Roman, *Thin Solid Films* **255**, 67 (1995).
- <sup>28</sup>K.L. Narasimhan, S. Banerjee, A.K. Srivastava, and A. Sardesai, *Appl. Phys. Lett.* **62**, 331 (1993).
- <sup>29</sup>W. Paul and G.L. Pearson, *Phys. Rev.* **98**, 1755 (1995); C.-Y. Yeh, S.B. Zhang, and A. Zunger, *Appl. Phys. Lett.* **64**, 3545 (1994).
- <sup>30</sup>H.M. Cheong *et al.*, *Phys. Rev. B* **52**, R11 577 (1995); A.K. Sood, K. Jayaram, and D.V.S. Muthu, *J. Appl. Phys.* **72**, 4963 (1992); N. Ookubo, Y. Matsuda, and N. Kuroda, *Appl. Phys. Lett.* **63**, 346 (1993).