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Author(s)	Johri, G. K.; Johri, M.; Sharma, Rajesh et al.
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The Study of Internal Quantum Efficiency and Size Dependence in Quantum Confinement Model for Photoluminescence

G.K. Johri, M. Johri , Rajesh Sharma and K. Yoshino*

Department of Physics and Electronics, D.A-V. College, 119/91, Darshanpurwa, Kanpur-208 012, INDIA * Department of Electronic Engineering, Graduate School of Engineering, Osaka University, 2-1, Yamada Oka, Suita, Osaka 565-0871, JAPAN.

The discovery of Canham [1] for the observation of strong visible photoluminescence (PL) in porous silicon (PS) has attracted much attention from the view point of fundamental physics involved and its applications. Recently, Kapoor, Singh and Johri (KSJ) [2] have given a model hereafter called as KSJ model using the WKB approximation. We are motivated to investigate the fundamental difference between non – radiative and radiative hopping rate processes. The internal quantum efficiency is calculated. A phenomenological quantum confinement model is formulated to find the size dependence.

The internal quantum efficiency (η) may be computed as $\eta = \tau R_r$ where $\tau = (R_r + R_{hop})^{-1}$ and the ratio of Berthelot – type anomalous temperature of R_{hop} and radiative rate (R_r) is given [2] as including disorder based on stretched exponential function.

$$\left(\frac{R_{hop}}{R_r}\right) = \frac{v_B}{v_r} Exp\left(\frac{T}{T_B} + \frac{T_r}{T}\right)$$
(1)

The values of E_{max} could be used for the computation of Berthelot – type temperature dependence using normalizable potential [2] and the formula proposed in this work is given below i.e.

$$E_{\max} T_{R} = kT^{2} \tag{2}$$

where T is any temperature and k is Boltzmann constant. The Berthelot – type temperature for $T = 100^{\circ}K$, $E_{max} = 0.008eV$ for effective mass of electron as $m^* = 0.1m_e$ is $114.9^{\circ}K$ while for $E_{max} = 0.036 - 0.038 \ eV$ for $m^* = 0.5m_e$ is $23.2^{\circ}K$. the values of E_{max} have been obtained from Fig.1 and 2. The barrier width (5nm) and barrier height (1eV) are the same for both the figures. Let us assume $T = \sqrt{T_r T_B}$ then $T_r = 87.03^{\circ}K$ for $T_B = 114.9^{\circ}K$ and $T_r = 431.03^{\circ}K$ for $T_B = 23.2^{\circ}K$. The internal quantum efficiency is $\eta = 99.99\%$ and 94.75% for two different values of T_B and T_r .

Let us assume ΔE_{hop} as energy change for hopping rate process, β as exponent of size, σ as disorder and d_m as mean size in the quantum confinement energy then the final form derived for the effective exponent is

$$\frac{\partial \ln(\Delta E_{kop})_{P}}{\partial \ln(d_{m})} = -\beta_{off} = -\frac{\beta}{2} \left[1 - \frac{2(\beta+6)}{2\left(\frac{d_{m}}{\sigma}\right)^{2} - (\beta+6)} \right]$$
(3)

i.e.
$$\beta_{eff} = \beta/2$$
 for $\sigma \to 0$ (4)

However, if the second term in Eq.(3) is not zero we get β_{eff} as a function of (d_m/σ) . For $\beta = 3$, $\sigma = 0.3$ nm, $\sigma/d_m = 0.1$ we get $\beta_{eff} = 1.36$. The general expression for quantum confinement energy proposed is

$$(\Delta E_{hop})_{P} = \frac{c'}{d_{\pi}^{\beta_{eff}}}$$
(5)

The values of c' and β_{eff} could be determined from the fitting process of $(\Delta E_{hop})_P$ and mean diameter d_m by changing σ . We assume quantum confinement energy as $E = \beta_0 + \beta_1 d + \beta_2 d^2$ which gives $\beta_0 = 7.26$, $\beta_1 = -2.25$, $\beta_2 = 0.25$, $d_{max} = 4.50nm$ and $E_{max} = 2.21eV$ for nanocrystallite passivated with hydrogen and for unpassivated situation these values are 4.10, -1.24, 0.13, 4.90nm and 1.06eV respectively. The values of E and d have been taken from the work in the reference [3].

It is found that consideration of normalizable potential with suitable parameters may provide size less than 4nm of nanocrystallite semiconductor and quantum confinement energy may have exponent of size as 1.36 including disorder and the combined effect of hopping and radiative processes. This work is fruitful to understand mechanism of photoluminescence.



Fig.1: Variation of the Transmission Coefficient (P_T) versus confinement energy (*E* in eV) for $T = 100^{\circ}K$. Multiplying factor are 10^{-5} and 10^{-9} for Arrhenius and Berthelot-type behaviour respectively.

Fig.2: Variation of the Transmission Coefficient (P_7) versus confinement energy (*E* in *eV*) for T = 100°*K*. Multiplying factor are 10⁻¹⁰ and 10⁻¹⁷ for Arrhenius and Berthelot-type behaviour respectively.

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