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Abstract
The 'S-shape' (decrease–increase–decrease) temperature dependence of luminescence peak shift from semiconductors is considered. A luminescence model for the localized state ensemble was employed to interpret this anomalous temperature dependence of the emission peak. The model provides a supplemental contribution from the thermal redistribution of localized carriers to the empirical Varshni relation describing the temperature dependence of the bandgap of perfect semiconductors. Excellent agreement between the theoretical calculation and the experiments was achieved over the whole studied temperature region. The physical origin of the 'S-shaped' shift is revealed.

Anomalous temperature dependence of luminescence peak position has been frequently observed in semiconductors [1–8]. A typical one of these phenomena is the so-called 'S-shaped' temperature dependence. That is, as the temperature continuously increases, the luminescence peak redshifts first, then blueshifts, and finally redshifts again. This unusual temperature dependence of the luminescence peak significantly deviates from that predicted by either the Varshni [9] or Bose–Einstein [10] formula. For an ideally perfect semiconductor, these formulae predict a monotonic decrease of the semiconductor bandgap with increasing temperature. The 'S-shaped' temperature-induced shift of luminescence peak has been known to be closely related to the carrier localization in semiconductors for a long time [1]. Several attempts have been made to interpret the phenomenon. For example, a band-tail emission model was proposed by Eliseev *et al* [2] to explain the frequently observed blueshift of the emission peak in InGaN QWs at higher temperatures. However, to our best knowledge, no model can reproduce the 'S-shaped' shift.

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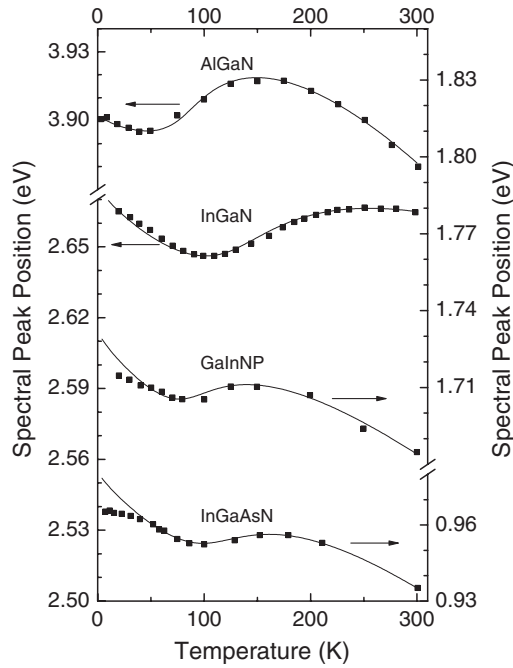
Figure 1. The 'S-shape' temperature dependence of luminescence peak positions of several semiconductor materials. From the bottom to the top: GaInNAs [3], GaInNP [4], InGaN [5] and AlGaN [6]. The scattered symbols are experimental data and the solid lines are the fitting results using equations (1) and (2).

In this paper, starting from a newly developed luminescence model for the localized state ensemble [11, 12], we quantitatively interpret the 'S-shaped' temperature dependence of luminescence peaks from several representative materials. It is found that the redistribution of carriers within the localized states due to the transfer between different localized states and the thermal escape of carriers from the higher energy states leads to the occurrence of the 'S-shaped' temperature dependence of the luminescence peak. Excellent agreement between the theoretical calculation and the experimental data is achieved over the whole studied temperature range.

Figure 1 shows the luminescence peak positions against temperature for four different materials of InGaAsN [3], GaInNP [4], InGaN [5], and AlGaN [6]. The solid squares represent the experimental data while the solid lines are the calculated results using the model described in detail in [12]. The emission colours of these materials vary from ultraviolet (AlGaN, 3.9 eV) to near-infrared (InGaAsN, 0.965 eV). In these materials, the emission spectra are from the radiative recombination of the localized excitons due to either large-scale inhomogeneity in composition or the N-induced localized states [3–6, 13]. Considering the radiative recombination, thermal escape, and re-capture of the excitons in a localized state ensemble, we derive a distribution function of localized carriers from a rate equation under quasi-steady state [12]. Assuming that the localized state ensemble has a Gaussian-type energetic distribution of density of states, the luminescence spectrum of the localized excitons is found. The temperature dependence of the luminescence peak positions can be given by [12]

$$E(T) = E_0 - \frac{\alpha T^2}{T + \Theta} - x(T) \cdot k_{\text{B}} T \tag{1}$$

Table 1. Parameters used to fit the temperature dependent energy peak positions in figures 1 and 2.

	E_0 (eV)	σ (meV)	$E_a - E_0$ (eV)	τ_{tr}/τ_r	α (meV K^{-1})	Θ (K)
GaInNAs	1.025	25.0	−0.044	0.025	0.44	300
GaInNP	1.763	20.0	−0.031	0.01	0.42	300
InGaN	2.733	30.6	−0.057	0.018	0.35	700
AlGaN	3.989	24.3	−0.086	0.2	0.94	700
A	2.78	31.5	−0.126	0.06	0.5	735
B	2.78	31.5	−0.112	0.04	0.5	735
C	2.78	31.5	−0.098	0.04	0.5	735
D	2.78	31.5	−0.088	0.04	0.5	735

where the second term on the right describes the bandgap shrinking according to Varshni's empirical formula. α is the Varshni parameter and Θ the Debye temperature. The third term represents the effect of thermal redistribution of localized carriers. k_B is the Boltzmann constant. The dimensionless coefficient $x(T)$ can be obtained by numerically solving the following equation [11, 12]:

$$x e^x = \left[\left(\frac{\sigma}{k_B T}\right)^2 - x\right]\left(\frac{\tau_r}{\tau_{tr}}\right) e^{(E_0 - E_a)/k_B T}, \tag{2}$$

where E_0 and σ are the central energy and broadening parameter for the distribution of the localized states, respectively. $1/\tau_{tr}$ is the escape rate and $1/\tau_r$ the radiative recombination rate of the localized carriers. Like the Fermi level in the Fermi–Dirac distribution function, E_a gives a special energy level below which the localized states are occupied by the excitons at 0 K. It is shown that the magnitude and sign of $E_a - E_0$ strongly affect the temperature dependence of the luminescence peak. When $E_a - E_0$ takes a negative value, the 'S-shaped' temperature dependence (the solid lines) of the luminescence peak can be well reproduced, as shown in figure 1. The parameters adopted in the calculations are summarized in table 1.

As mentioned earlier, $E_a - E_0$ plays an important role in determining the temperature behaviour of the luminescence peak of the localized excitons, particularly in the low temperature region. As the central energetic position of the localized state distribution, E_0 is determined for a given material. However, the energetic position of E_a is found to be dependent on both the concentration of carriers and the magnitude of the built-in electric field in the material. The magnitude and even the sign of $E_a - E_0$ can thus be changed through internally or externally adjusting the carrier density and the electric field. Figure 2 shows the electroluminescence peak positions (various symbols) as a function of temperature and injected current in an InGaN single-quantum-well light-emitting diode, reported by Eliseev et al [2]. The solid curves are the calculated results using equations (1) and (2). Excellent agreement between the theoretical results and the experimental data was obtained. The values of the parameters used in the calculations are also listed in table 1. From the table, an interesting observation is that the magnitude of $E_a - E_0$ systematically varies with increasing the injected electrical current during the measurements. It is known that the increase of the injected electric current can result in the increase of the carrier concentration. On the other hand, the increase of the injected electric current may cause a strength decrease of the effective electric field in the diode due to the screening out effect of the electrically injected carriers on the existing huge piezoelectric field [14–20]. Since the energetic position of E_a is dependent on both the carrier concentration and the magnitude of the effective electric field, it is not difficult for one to understand that the magnitude of $E_a - E_0$ changes with the injected electric current.
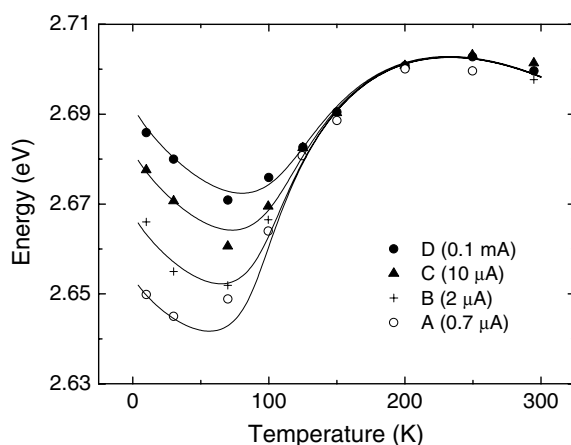
Figure 2. Electroluminescence peak positions (scattered symbols) of InGaN light-emitting diode under different injected currents as a function of temperature (from [2]). The solid lines are calculated results using equations (1) and (2).
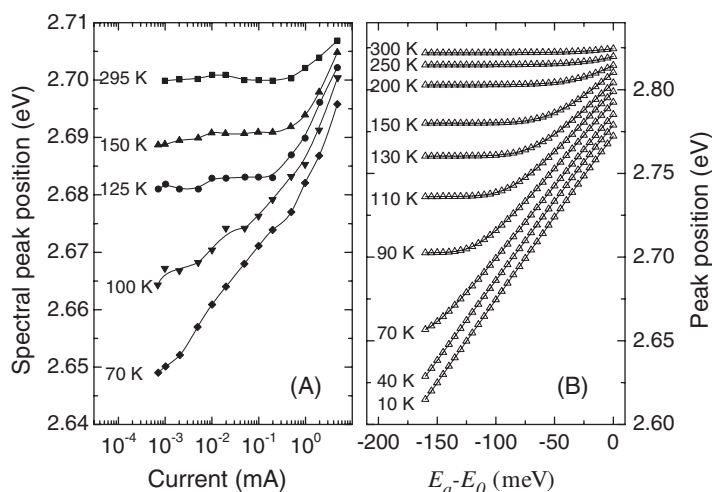

Figure 3. (A) Electroluminescence peak positions of InGaN light-emitting diode at several different temperatures as a function of injected current (from [21]). (B) Calculated spectral peak positions for different temperatures as a function of magnitude of $E_a - E_0$.

An interesting phenomenon in figure 2 is that the originally scattered electroluminescence peaks in the low temperature region for the different injected currents tend to converge at high temperatures. Figure 3(A) depicts the spectral peak positions of a blue InGaN single-quantum-well light-emitting diode at several different temperatures as a function of the injected current [21]. At 70 and 100 K, the peak position increases as the injected current increases. However, when the temperature $\geqslant 125$ K, a plateau region appears. In other words, the peak position does not change with the injected current in the region. This indicates that at higher temperatures the influence of the magnitude of $E_a - E_0$ on the temperature dependence of the peak positions will become weaker. This strange behaviour can be well interpreted using equations (1) and (2). At high temperatures, the solution of equation (2) can be found to be

$x \approx (\sigma / k_B T)^2$ and equation (1) becomes [11, 12]

$$E(T) = E_0 - \frac{\alpha T^2}{T + \Theta} - \frac{\sigma^2}{k_B T}. \tag{3}$$

Note that $E_a - E_0$ does not appear in the above equation, which indicates that the peak positions are no longer dependent on $E_a - E_0$ at high temperatures. Figure 3(B) shows the calculated peak positions as a function of $E_a - E_0$ for different temperatures using equations (1) and (2). Comparing figure 3(A) with (B), it can be concluded that the behaviours in the experimental data are quantitatively reproduced by the theoretical calculations.

Finally, we briefly discuss other parameters concerned with the model. The broadening parameter (σ) is essentially related to the distribution width of the localized states. For the nitride compounds studied in the present work, σ varies from 20 to about 30 meV, as shown in table 1. Another important parameter is the ratio of the escape time constant (τ_{tr}) and the radiative recombination time constant (τ_r). From table 1, it can be seen that the escape time of carriers is one or two orders shorter than the radiative recombination time. This is quite reasonable for semiconductor materials [12]. Moreover, the ratio (τ_{tr}/τ_r) seems to increase with the absolute value of $E_a - E_0$. If this phenomenon is real, it is not hard to understand. The larger the absolute value of $E_a - E_0$ is, the more difficulty the carriers have in escaping to the level E_a.

In conclusion, the 'S-shaped' temperature dependence of the luminescence peak positions, which is a frequently observed phenomenon in many semiconductors, is successfully modelled using a recently developed luminescence model for the localized state ensemble. The energetic difference between the quasi-Fermi level (E_a) and the central energy (E_0) of the localized state distribution essentially determines the details of temperature behaviour of the luminescence peaks. The model could be useful for experimentalists to quantitatively explain their experimental results in temperature dependent luminescence studies.

Acknowledgments

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