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Excitation and Relaxation of Yb 4*f*-Shell in InP Host — Energy Compensation by a Multi-Phonon Process

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The energy transfer mechanism between an Yb 4*f*-shell and an InP host was investigated by assuming that the energy transfer is assisted by a non-radiative multi-phonon process. Rate equations were solved and the temperature dependence of the calculated 4*f*-shell luminescence decay time was compared with the experimentally obtained one. In this procedure, the transition probability between the Yb 4*f*-shell and the InP host was estimated. It was found that the energy transfer is very efficient, although an energy as large as 140 meV has to be compensated. The time decay of the band-edge related luminescence was also calculated. The results agree with the experimental results.

Rare-earth (RE) doped semiconductors have received much attention, because the doped RE ions emit luminescence due to the intra-4*f*-shell transitions. Since the 4*f*-shell is well shielded by outer 5*s* and 5*p* electrons, the luminescence is sharp and temperature stable, and their wave length is not sensitive to host materials. Light emitting devices have been fabricated, but their luminescence efficiencies are still low and their intensity rapidly decreases at elevated temperature, which is called thermal quenching. To overcome these problems, it is necessary to understand luminescence mechanisms of RE in semiconductor hosts.

Yb-doped InP has been the most widely used material to investigate the excitation and relaxation mechanisms of an RE 4*f*-shell in a semiconductor host. This is because Yb ions form only one kind of luminescence center in an InP host, and also because an Yb^{3+} 4*f*-shell has only one excited state, $^2F_{5/2}$. We have proposed a model for the excitation and relaxation processes based on the electrical and optical properties of InP:Yb.[1] Although the model qualitatively explains the experimental results, there remains an open question. Since there is an energy mismatch in the excitation and the thermal quenching processes, an energy compensation mechanism is required. However, such mechanism is not clear yet. In this paper, we assume a non-radiative multi-phonon transition (NRMPT) process as the energy compensation mechanism in the InP:Yb system . The time decay of the intra-4*f*-shell luminescence was calculated based on this assumption and the calculated results were compared with the experimental ones. Using this model, the transition probability between the Yb 4*f*-shell and the InP host was estimated. The time decay of the band-edge related luminescence was also calculated and found to agree with the experimentally obtained results.

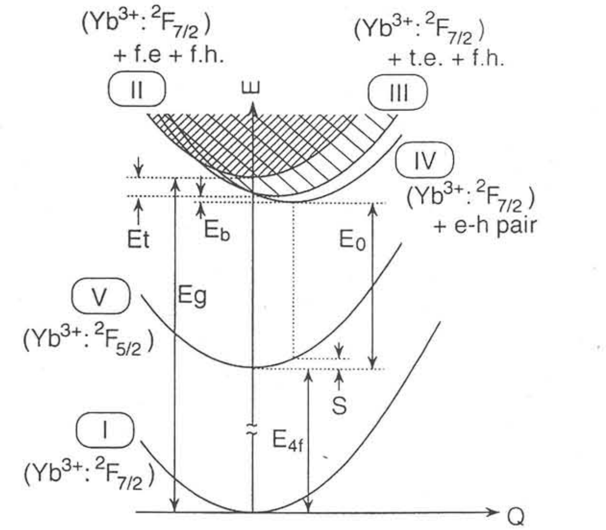

Fig. 1 The configuration coordinate diagram of InP:Yb.

The energy transfer model is schematically shown in Fig. 1 by using a configuration coordinate diagram. The energy transfer between the Yb 4*f*-shell and the InP host is explained as follows. In the ground state of the system (the state I), there is no free electron and free hole and the Yb 4*f*-shell is in the ground state $^2F_{7/2}$. When one free electron and one free hole are generated, the state becomes the state II. The free electron in the conduction band is trapped by an acceptor-like electron (AE) trap formed by the Yb ion[2] (the state III). Then, a hole is attracted by

Coulombic force to the trapped electron. As a result, an electron-hole pair is created at the AE trap, which is the state IV. A transition from the state IV to the state V is the excitation process of the 4f-shell. The recombination energy of the electron-hole pair is transferred to the 4f-shell. A transition from the state V to the ground state I results in the intra-4f-shell luminescence. The thermal quenching of the 4f-shell is due to the back transition from the state V to the state IV and subsequent relaxation outside the 4f-shell. This process, the reverse process to the excitation process, is called the energy back-transfer. The energy difference between the states IV and V is the energy mismatch to be compensated in the transition processes.

According to the theory of NRMPT,[3] the transition probabilities between two localized electronic states are analytically expressed by

$$W_e = W_0(n_q+1)^p exp(-2n_q s), \quad (1)$$

$$W_a = W_0(n_q)^p exp(-2n_q s). \quad (2)$$

Here, W_e is the transition probability for a phonon emission process and W_a is that for a phonon absorption process. n_q is the phonon number, which is expressed as $n_q = (exp(\hbar\omega/kT)-1)^{-1}$. $\hbar\omega$ is the phonon energy. Parameters p and s are defined as $p \equiv E_0/\hbar\omega$ and $s \equiv S/\hbar\omega$, respectively. The parameter s corresponds to the Huang-Rhys factor. Energies corresponding to E_0 and S are shown in Fig. 1. E_0 is the energy mismatch. W_0 is a temperature-independent term containing the matrix element of the transition.

The phonon emission and absorption processes correspond to the transitions between the states IV and V. Hence, Eqs. (1) and (2) express the transition probabilities for the 4f-shell excitation and the energy back-transfer processes, respectively. The energies of $\hbar\omega$, S, and E_0, which are necessary to estimate the probabilities, were determined from the experimental results. The values of W_0 can not be determined, since neither the wave functions of the states IV, V nor the interaction Hamiltonian are known. However, the temperature dependence of the transition probabilities can be obtained from Eqs.(1) and (2), since W_0 is independent of temperature.

It is a good test of the validity of applying NRMPT to the InP:Yb system to compare the calculated temperature dependence of the decay time of the intra-4f-shell luminescence with the experimental results. To estimate the decay time, the simple model shown in Fig. 2 was used. In this model, the energy back-transfer from the excited 4f-shell creates an electron-hole pair and it subsequently dissociates. The dissociation may occur easily above the temperature where the back-transfer occurs, which is about 100 K, since the binding energy of the electron-hole pair is expected to be about 10 meV or less. Another energy dissipation process of the electron-hole pair is a radiative recombination, but the luminescence due to such recombination has not been observed. Hence, this process is not included in the model.

The rate equations of the model are as follows.

$$dN_{eh}/dt = g_r - W_e N_{eh} - e_p N_{eh} + W_a N_{4f}, \quad (3)$$

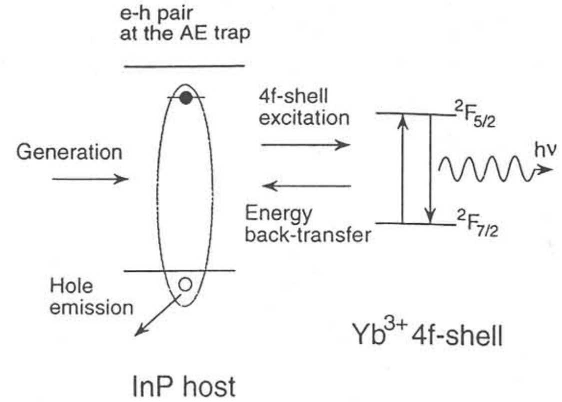

Fig. 2 The model used in the estimation of the decay time.

$$dN_{4f}/dt = W_e N_{eh} - W_a N_{4f} - \tau_{4f}^{-1} N_{4f}. \quad (4)$$

Here, g_r is the generation rate of the electron-hole pair. N_{eh} and N_{4f} are the concentration of the electron-hole pair and the excited 4f-shell, respectively. τ_{4f} is the radiative decay time of the 4f-shell, which has been experimentally obtained as ~13 μs.[4] Since no experiments have been done on the hole emission process, we assumed that the AE trap with an electron behaves like a conventional acceptor. Hence, we assumed that $e_p = \sigma_p v_{th}^p N_v exp(-E_b/kT)$. Here, σ_p is the hole capture cross section and v_{th}^p is the thermal velocity of the free hole. N_v is the effective density of state of the valence band. E_b is the binding energy of the hole to the AE trap. The values of v_{th}^p and N_v can be estimated by using physical parameters such as the hole effective mass. Since the value of σ_p can not be estimated, it is used as an adjusting parameter.

Assuming that $g_r = 0$ for $t \geq 0$ (which corresponds to the time after a pulsed excitation), the solutions of the coupled rate equations (3) and (4) were analytically obtained.

$$N_{eh}(t) = C_1 exp(-\alpha t) + C_2 exp(-\beta t), \quad (5)$$

$$N_{4f}(t) = C_3 exp(-\alpha t) + C_4 exp(-\beta t). \quad (6)$$

Here, C_i (i = 1, 2, 3, and 4) are time-independent constants determined by the initial condition. The equilibrium state, $dN_{eh}/dt = dN_{4f}/dt = 0$, was taken as the initial state. α and β show the decay rates, which are the functions of W_e, W_a, τ_{4f}, and e_p.

Since the intra-4f-shell luminescence is expressed as $\tau_{4f}^{-1} N_{4f}$, and τ_{4f} is independent of time, its time decay can be expressed by Eq. (6). Although Eq. (6) indicates that the 4f-shell luminescence has a bi-exponential nature, it was found that the decay of N_{4f} can be expressed essentially by a single exponential, which will be shown later. The 4f-shell decay time is essentially the same as $1/\alpha$.

Figure 3 shows a comparison of the calculated and experimentally obtained temperature dependence of the 4f-shell decay time. The values of two parameters, W_0 and σ_p, were treated as fitting parameters. It was found that the best fit values of W_0 and σ_p are

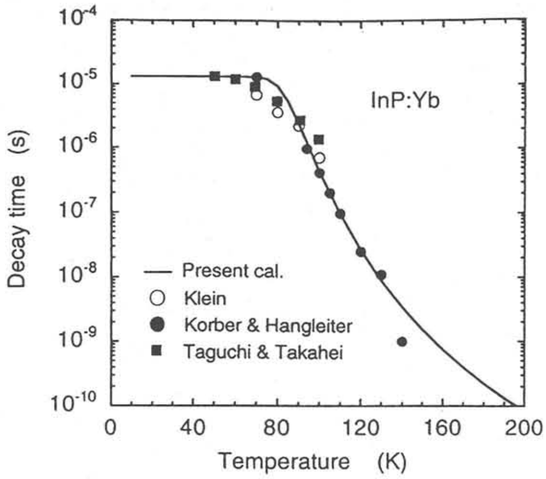

Fig. 3 Calculated and experimentally obtained decay time.

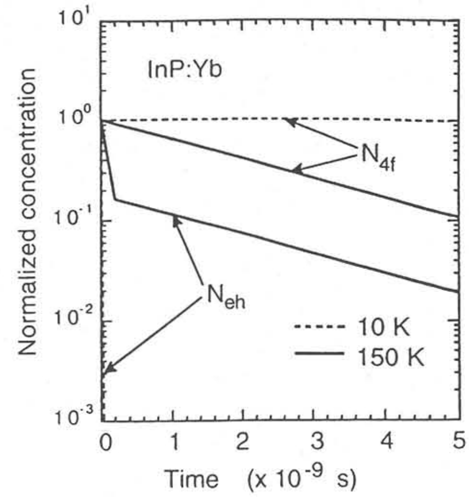

Fig. 4 Calculated time decay of N_{eh} and N_{4f}.

3x10^{13} s^{-1} and 2x10^{-11} cm^2, respectively. The calculated decay time shows good agreement with the experiments in wide ranges of temperature and decay time. The obtained values of W_0 and σ_p are rather large. This means that the energy transfer between the electron-hole pair at the AE trap and the Yb 4*f*-shell, and the hole emission to the valence band are very efficient. The high transition rate is consistent with the experimental result that is no luminescence from the electron-hole pair at the AE trap.

It has been experimentally observed that, at temperatures where the energy back-transfer occurs, the time decay curve of the band-edge related luminescence has a slowly decaying component, which has the same time decay constant as that of the 4*f*-shell luminescence at that temperature.[1] The band-edge related luminescence intensity I_b can be expressed by $I_b = Bnp$. B is the recombination rate of the electron and hole, and n is the free electron concentration. B is independent of time and temperature. When a sample is n type, n can be taken as constant. Hence, I_b is proportional to the free hole concentration p. The hole generation rate in the energy back-transfer process is expressed as $e_p N_{eh}$. Since e_p is independent of time, the time decay of I_b should be proportional to that of N_{eh} given by Eq. (5).

Figure 4 shows calculated time dependence of N_{eh} and N_{4f} at 10 and 150 K. The values of W_0 and σ_p were the same as those used in the calculations for Fig. 3. The decay of N_{4f} can be expressed essentially by a single exponential at both temperatures. This is consistent with the assumption made before that the 4*f*-shell decay time is equal to $1/\alpha$. The decay of N_{eh} at 10 K can be expressed by a single fast exponential, but at 150 K, the decay clearly shows bi-exponential nature. At 150 K, due to a high rate of energy back-transfer, a large number of electron-hole pairs is generated. Hence, N_{eh} shows bi-exponential nature. In actual experiments, there is the intrinsic band-edge related luminescence which is not due to the energy back-transfer. Such intrinsic luminescence process was not included in the model. However, the decay time of such luminescence would be on the nanosecond order or less. Therefore, the calculated results shown in Fig. 4 qualitatively explain the experimentally obtained properties of the band-edge related luminescence after the decay of such fast decaying component.

In conclusion, we investigated the optical properties of the InP:Yb by assuming that the energy compensation mechanism is NRMPT. The calculated decay time of the intra-4*f*-shell luminescence shows good agreement with the experimental results. The time decay of the band-edge related luminescence was also calculated and the results qualitatively agree with those obtained in experiments. These results strongly suggest that the energy compensation mechanism is NRMPT. It was found that the transition probability between the 4*f*-shell and the InP host is very efficient, although there is an energy mismatch as large as 140 meV. The calculated results also show that the excitation process is not sensitive to the energy mismatch, but that the thermal quenching is. Details of this topic will be discussed elsewhere.

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