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

Akihito Taguchi and Kenichiro Takahi

NTT Basic Research Laboratories
3-1, Morinosato Wakamiya, Atsugi-shi, Kanagawa 243-01 JAPAN

The energy transfer mechanism between an Yb 4f-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 4f-shell luminescence decay time was compared with the experimentally obtained one. In this procedure, the transition probability between the Yb 4f-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-4f-shell transitions. Since the 4f-shell is well shielded by outer 5s and 5p 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 4f-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 Yb3+ 4f-shell has only one excited state, 2F5/2. 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 (NRMPPT) process as the energy compensation mechanism in the InP:Yb system. The time decay of the intra-4f-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 4f-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.

The energy transfer model is schematically shown in Fig. 1 by using a configuration coordinate diagram. The energy transfer between the Yb 4f-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 4f-shell is in the ground state 4F7/2. 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 ion2) (the state III). Then, a hole is attracted by

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Fig. 1 The configuration coordinate diagram of InP:Yb.
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, the transition probabilities between two localized electronic states are analytically expressed by

\[ W_e = W_0(n_q + 1)\exp(-2n_{ps}), \]  \( (1) \)

\[ W_a = W_0(n_p)\exp(-2n_{qs}). \]  \( (2) \)

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.

\[ dN_{eh}/dt = g_e - W_eN_{eh} - e_pN_{eh} + W_aN_{4f}, \]  \( (3) \)

\[ dN_{4f}/dt = W_eN_{eh} - W_aN_{4f} - \tau_{4f}^{-1}N_{4f}. \]  \( (4) \)

Here, \( g_e \) 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. \( \tau_{4f} \) is the radiative decay time of the 4f-shell, which has been experimentally obtained as \( \sim 13 \mu s \). 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 \( e_p = \sigma_p\nu_{eh}N_{eh}\exp(-E_b/kT) \). Here, \( \sigma_p \) is the hole capture cross section and \( \nu_{eh} \) is the thermal velocity of the free hole. \( N_e \) 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 \( \nu_{eh} \) and \( N_e \) can be estimated by using physical parameters such as the hole effective mass. Since the value of \( \sigma_p \) can not be estimated, it is used as an adjusting parameter.

Assuming that \( g_e = 0 \) 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.

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

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

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. \( \alpha \) and \( \beta \) show the decay rates, which are the functions of \( W_e, W_a, \tau_{4f} \), and \( e_p \).

Since the intra-4f-shell luminescence is expressed as \( \tau_{4f}^{-1}N_{4f} \) and \( \tau_{4f} \) 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 \( \sigma_p \), were treated as fitting parameters. It was found that the best fit values of \( W_0 \) and \( \sigma_p \) are
3 × 10^{13} \, \text{s}^{-1} \text{ and } 2 \times 10^{-11} \, \text{cm}^2, \text{ 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 \text{ and } \sigma_\alpha \text{ are rather large. This means that the energy transfer between the electron-hole pair at the AE trap and the Yb 4f-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 4f-shell luminescence at that temperature.\(^{11}\) The band-edge related luminescence intensity \(I_b\) can be expressed by \(I_b = Bn_\alpha\). \(B\) 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 \(\sigma_\alpha N_{\text{eh}}\). Since \(\sigma_\alpha\) is independent of time, the time decay of \(I_b\) should be proportional to that of \(N_{\text{eh}}\) given by Eq. (5).

Figure 4 shows calculated time dependence of \(N_{\text{eh}}\) and \(N_{\text{df}}\) at 10 and 150 K. The values of \(W_0\) and \(\sigma_\alpha\) were the same as those used in the calculations for Fig. 3. The decay of \(N_{\text{df}}\) can be expressed essentially by a single exponential at both temperatures. This is consistent with the assumption made before that the 4f-shell decay time is equal to \(1/\alpha\). The decay of \(N_{\text{eh}}\) 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, \(N_{\text{eh}}\) 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-4f-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 4f-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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References