Magnetic properties of magnetic semiconductor GaAs:Er,O studied by ESR

Masashi Fujisawa¹, Atsushi Asakura², Fatma Elmasry², Susumu Okubo¹, Hitoshi Ohta¹,³, and Yasufumi Fujiwara⁴

¹Molecular Photoscience Research Center, Kobe University, Kobe 657-8501, Japan
²Graduate School of Sciences, Kobe University, Kobe 657-8501, Japan
³Division of Frontier Research and Technology, Kobe University, Kobe 657-8501, Japan
⁴Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan
E-mail: fujisawa@crystal.kobe-u.ac.jp

Abstract. In order to investigate the magnetic properties of GaAs:Er,O, we performed X-band ESR measurement on three different Er-concentration samples in the temperature region from $T = 4.6$ K to 18 K. Three types of Er-related ESR signals were observed below 18 K. The temperature dependence of the signal intensities and the result of the line shape analyses suggest that the luminescent related Er centers have a singlet-like ground state: that is, the Er-related centers are not homogenously distributed in GaAs:Er,O, and Er³⁺ ions can be antiferromagnetically coupled via the super exchange interaction. Moreover, we have shown that the Er-concentration dependence of intensities of ESR absorption has a strong correlation with the Er-concentration dependence of the PL intensities of GaAs:Er,O.

1. Introduction

Rare earth ions incorporated in semiconductors show the photoluminescence (PL) originating the intra-4f-shell transition by the photo excitation of the host semiconductor. Er-doped III-V semiconductors has attracted particular attention because the temperature-stable PL transition from the first excited state ($^4I_{13/2}$) to the ground state ($^4I_{15/2}$) occurs at the wavelength of 1.54 μm, which is important for the application. The wavelength of 1.54 μm lies in the minimum loss region in silica-based optical fibers and is thus important for optical communication. However, it has been found that the PL of Er³⁺ ions doped in semiconductors have various fine structures, indicating that different kinds of Er centers with different atomic configurations are formed in a semiconductor. Therefore, selective formation of highly efficient Er centers for PL has been desired for applications of Er-related luminescence to light-emitting devices. Recently, oxygen has been recognized to influence the Er-related PL in semiconductors. The magnetic semiconductor GaAs:Er,O, which is Er-doped GaAs with O₂ co-doping, exhibits a sharp, simple PL spectrum of Er³⁺ [1]. The PL center has been identified as Er³⁺⁺ at the Ga sublattice with two adjacent oxygen atoms (Er-2O center) from polarized PL spectroscopy [2], extended X-ray absorption fine structure (EXAFS) measurement [3], Zeeman analysis [4], and electron spin resonance (ESR) measurement [5, 6, 7].

However, some unsolved problems remain with respect to the magnetic properties of GaAs:Er,O. Takahei et al. [8, 9] have pointed out that a large proportion of Er atoms in GaAs
do not participate in the host-excited PL. Photoluminescence excitation (PLE) spectroscopy has revealed that there are many kinds of Er centers having different atomic configurations in one GaAs:Er,O sample, while its host-exited PL spectrum is dominated by the luminescence of the Er-2O center [8]. Therefore, it is important to understand the difference between the luminescent Er center and the other Er centers. However, the atomic configurations between them are still unclear.

Recently, Fujiwara et al. [10] have reported that the PL intensity still remains even at a very low concentration of Er ($\sim 10^{17}$ cm$^{-3}$). This result seems to be a clue to distinguish the luminescent Er center from the other Er centers in GaAs:Er,O. ESR measurement is one of the most powerful experimental techniques for examining the electronic states of the magnetic ions in semiconductors. In this study we performed X-band ESR measurement in order to clarify the local configuration of the Er-2O center and its spin state. Based on the line shape analysis and the temperature dependence of integrated intensity, we show the existence of the exchange interaction between the Er-2O centers.

2. Experimental

The GaAs:Er,O epitaxial films were grown on (001) SI-GaAs substrates using the organometallic vapor phase epitaxy (OMVPE) method [11, 12]. As an Er source, tris-isopropylcyclopentadienylerbium Er([i-PrCp]$_3$, was used, and was maintained at 90°C under 76 Torr. The Er-concentration $C_{Er}$ of GA05529, GA05522, and GA030278 was estimated to be 9.2x10$^{18}$ cm$^{-3}$, 8.3x10$^{17}$ cm$^{-3}$, and less than 1.0x10$^{17}$ cm$^{-3}$, respectively, by the secondary ion mass spectroscopy (SIMS) measurement. For simplicity, we abbreviated ‘GA05529, GA05522, and GA030278’ to ‘GA-19, GA-18, and GA-17.’ The ESR measurements were performed using a Bruker ESR spectrometer EMX081 with a TE$_{103}$ rectangular cavity at Kobe University. The microwave frequency was approximately 9.66 GHz. The external magnetic field was swept up to 9000 G. Samples were cooled from $T = 18.0$ K to 4.6 K using an Oxford He flow cryostat ESR 900.

3. Results and Discussion

Three types of Er-related ESR signals were observed in GA-17 at low temperature. We labeled them A, B, and C, respectively, according to Ishiyama et al. [5] and Yoshida et al. [6]. Signals A, B and C are at the same resonance fields in GA-19 and GA-18. The resonance fields observed in GA-19, GA-18, and GA-17 were consistent with those reported previously [5, 6, 7]. In other words, Er-concentration dependence of the resonance fields are negligible. Figure 1 shows the temperature dependence of ESR spectra of the B and C signals for GaAs:Er,O(GA-17). An ESR signal was observed from 4.6 K to 11.0 K. Here the magnetic field was applied approximately 9.66 GHz. The external magnetic field was swept up to 9000 G. Samples were cooled from $T = 18.0$ K to 4.6 K using an Oxford He flow cryostat ESR 900.

If Er$^{3+}$ ions are homogeneously distributed in GaAs, the distance between Er$^{3+}$ ions is quite large compared to the length of the lattice parameter of GaAs, $a_{GaAs} = 0.565$ nm; i.e., the average distance between Er ions is 22 nm in the case of GA-17 ($C_{Er} < 1.0x10^{17}$ cm$^{-3}$). In this case, the exchange interaction between Er$^{3+}$ ions is negligible. Therefore, in the homogeneously distributed case, the dominant interaction between the magnetic moment is magnetic a dipolar interaction. If the exchange interaction is dominant between magnetic moments, the line shape of ESR spectra should be a Lorentzian curve. On the other hand, if the magnetic dipolar interaction is dominant, the line shape is Gaussian. In order to clarify the dominant interaction in the system, we performed a line shape analysis. By using the normalized magnetic field (horizontal axis) and intensity (vertical axis) as shown in Fig. 2, we can readily compare the experimental data.
Figure 1. Temperature dependence of the ESR spectra of B and C signals of GaAs:Er,O (GA-17). The magnetic field was applied approximately along the [110] direction.

Figure 2. Comparison between the experimental absorption line for GaAs:Er,O (GA-17) and the theoretical curves. Open circles correspond to the experimental data of signal B observed at $T = 8.0$ K. Solid and dashed lines correspond to Lorentzian and Gaussian curves, respectively. $B_0$, $\Delta B_{pp}$, $I'_m$ and $I'(B)$ are the resonance center field, the line width, the peak intensity, and the magnetic field dependence of the absorption intensity, respectively.

Figure 3. Relative integrated intensity of GaAs:Er,O as a function of Er-concentration at 8.0 K. The integrated intensity was normalized by the total number of Er atoms in each sample. The left (center, right) side data near $10^{17}$ ($10^{18}$, $10^{19}$)cm$^{-3}$ are obtained from the experiments for GA-17 (GA-18, GA-19). The broken lines are included as visual guides.

The intensities of the signals B and C show maxima around 6.5 K. These behaviors indicate that the ground state of signals B and C is nonmagnetic —e.g., a singlet state— and these resonances are coming from the excited states. The paramagnetic Er centers expected from the assumption with theoretical curves. Solid and dashed lines indicate Lorentzian and Gaussian curves. The normalized experimental data of GA-17 are in good agreement with a Lorentzian curve. The result clearly indicates that the exchange interaction is dominant, and it is not consistent with the first assumption, that Er$^{3+}$ ions are homogenously distributed in GaAs. As shown in Fig. 1,
that they are homogeneously distributed in GaAs seem to change to a singlet-like non-magnetic ground state below 6.5 K. This mechanism is unclear under the assumption of a homogeneously distributed model. A possible interpretation of this result is that the Er centers form pairs with exchange interaction. If the exchange interaction is antiferromagnetic, the ground state may be the singlet state and the temperature dependence of the integrated intensity can be interpreted.

Figure 3 shows the Er-concentration dependence of the relative integrated intensity $I^\text{nor}$, which is normalized by the total number of Er atoms in each sample. First, in spite of the different values of Er-concentration $C_{\text{Er}}$—e.g., $C_{\text{Er}} = 9.2 \times 10^{18} \text{ cm}^{-3}$, $8.3 \times 10^{17} \text{ cm}^{-3}$ and less than $1 \times 10^{17} \text{ cm}^{-3}$—all of three samples have almost the same ratio of $I^\text{nor}_A : I^\text{nor}_B : I^\text{nor}_C$, which is roughly estimated to be $I^\text{nor}_A : I^\text{nor}_B : I^\text{nor}_C = 1:10:10$. Second, the $I^\text{nor}_A$, $I^\text{nor}_B$, and $I^\text{nor}_C$ for $C_{\text{Er}} \leq 1 \times 10^{17} \text{ cm}^{-3}$ (GA-17) are comparable with those for $C_{\text{Er}} = 8.3 \times 10^{17} \text{ cm}^{-3}$ (GA-18), while those for $C_{\text{Er}} = 9.2 \times 10^{18} \text{ cm}^{-3}$ (GA-19) are considerably smaller than the others. Fujiwara [10] reports that for the sample in the region of $C_{\text{Er}} = 10^{17}$ to $10^{18} \text{ cm}^{-3}$ the relative PL intensity is strong and the Er-concentration dependence of the PL intensity is almost constant, while it decreases to about $1\%$ for the sample in the region of $C_{\text{Er}} = 10^{18}$ to $10^{19} \text{ cm}^{-3}$. Thus the Er-concentration dependence of ESR intensity is similar to that of PL intensity. Therefore the similarity suggests that there is a close relation between the integrated intensity of ESR absorption and the PL intensity.

4. Conclusion
ESR measurements of GaAs:Er,O grown by OMVPE were performed at 9.49 GHz, and the Er-concentration effect was investigated. Several anisotropic ESR signals (A, B and C) were observed. The resonance fields of the A, B, and C signals are quite consistent with those of observed previously. From the line shape analysis, the dominant interaction between Er spins turns out to be not the magnetic dipole interaction but the exchange interaction. From the temperature dependence of the integrated intensity, the exchange interaction between adjacent Er ions is antiferromagnetic and the signal suggests a singlet-like ground state. Furthermore, we pointed out the possibility that the Er-2O center is not homogeneously distributed in GaAs. We observed Er-concentration dependence of ESR intensity. By comparing Er-concentration dependence of the ESR intensity and that of the previously-reported PL intensity, we suggested that there was a close relation between the PL intensity and the ESR intensity.

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References
[1] Takahei K and Taguchi A, 1993 J. Appl. Phys. 74 1979.
[2] Takahei K, Taguchi A, Horikoshi Y, and Nakata J, 1994 J. Appl. Phys. 76 4332.
[3] Tabuchi M, Ohuchi H, Kubo T, Takahei K, and Takeda Y, 1977 Mater. Sci. Forum 258-263 1571.
[4] Haase D, Dornen A, Takahei K, and Taguchi A, 1996 Mater. Res. Soc. Symp. Proc. 422 179.
[5] Ishiyama T, Katayama E, Murakami K, Takahei K, and Taguchi A, 1998 J. Appl. Phys. 84 6782.
[6] Yoshida M, Hiraka K, Fujiwara Y, Koizumi A, and Takeda Y, 2004 J. Appl. Phys. 96 4189.
[7] Yoshikawa J, Urawaka C, Ohta H, Koide T, Kawamoto T, Fujiwara Y, and Takeda Y, 2001 Physica E (Amsterdam) 10 395.
[8] Takahei K, and Taguchi A, 1995 J. Appl. Phys. 77 1735.
[9] Takahei K and Taguchi A, 1997 J. Appl. Phys. 82 3997.
[10] Fujiwara Y, private communication.
[11] Fujiwara Y, Kawamoto T, Koide T, and Takeda Y, 1999 Physica B 273-274 770.
[12] Koizumi A, Fujiwara Y, Inoue K, Urakami A, Yoshikane T, and Takeda Y, 2001 Physica E (Amsterdam) 10 391.