Energy levels and interaction between Er³⁺-ions located at the two crystalographic sites of Er₂O₃ grown on Si(111)

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1. Introduction

Erbium oxide (Er₂O₃) has great potential as a light amplifier material in silicon photonics [1-3]. The unit cell of erbium oxide has symmetry T_h^7 and contains 32 erbium ions, 24 at sites with C_2 symmetry and 8 at sites with C_{3i} symmetry (see Fig. 1). The ions at the C_2 sites absorb radiation by electric-dipole transitions, but for ions at C_{3i} sites only magnetic-dipole transitions are allowed. The nearest neighbor distances of Er^{3+} -ions between $C_2 - C_2$, $C_2 - C_{3i}$, and C_{3i} - C_{3i} sites are 3.509, 3.987, and 5.268Å, respectively. Recently, Gruber et al. precisely determined the energy levels of Er³⁺-ions, including Stark-splittings due to the crystal field, located at the C_2 and C_{3i} sites from calculations, and assigned the origin of photoluminescence (PL) peaks on the basis of the site-dependent energy levels [2]. On the other hand, Michael et al. have succeeded in creating cavity polaritons using a micro-disk cavity of Er₂O₃ on Si(111) at a high temperature (T > 361 K) and suggested the existence of asymmetric energy transfer or diffusion between the two sites on the basis of the Gruber's PL peak assignments, They also pointed out some issues with respect to enhancing the intensity of cavity polaritons in the Er₂O₃ cavity; for example, understanding the carrier dynamics at the C_2 and C_{3i} sites and interactions between the sites and suppression of non-radiative transfer between them [3].

In this work, we first confirmed the energy levels of Er^{3+} -ion in Er_2O_3 determined by Gruber et al. by PL measurements on Er_2O_3 grown on Si(111). We then explored PL from Er^{3+} -ions located at the C_2 and C_{3i} sites as a function of temperature by time-resolved PL measurements and investigated the energy transfer between the C_2 and C_{3i} .

2. Experiments

The 100-nm-thick erbium oxides were deposited on Si(111) substrates by rf-magnetron sputtering at room temperature and annealed at the temperatures of up to 1000 $^{\circ}$ C in Ar ambience in a furnace for 30 min. Prior to the PL measurements, we performed synchrotron grazing incidence X-ray diffraction (GIXD) experiments at the BL24 in SPring-8. Photoluminescence measurements were mainly performed on the annealed samples by pumping a semiconductor laser at 532 nm with excitation power of 4.5 mW between 4 and 300 K. A near-infrared streak camera was used for the detection of Er³⁺ emission from the samples for the time-resolved PL measurements.

3. Results and discussion

Figure 2 shows a typical X-ray powder pattern obtained from the samples annealed in Ar ambience at 1000 °C. The peaks are assigned to erbium oxide, according to the joint committee for powder diffraction standards (JCPDS) cards no. 43-1007, indicating that the thermal annealing actually produced poly crystalline Er_2O_3 on Si(111).

Figure 3(a) shows a typical PL spectrum obtained from the Er_2O_3 on Si(111). The PL spectrum is almost identical to the one obtained by Gruber *et al.* The peaks at 1535 and 1548 nm can then be assigned to the transitions between the Y_1 level in the ${}^4I_{13/2}$ and the X_1 level in the ${}^4I_{15/2}$ at the C_2 site and the Y'_1 level in the ${}^4I_{13/2}$ and the X'_1 level in the ${}_4I_{15/2}$ at the C_{3i} site. From the other peaks, we determined the energy levels of Er^{+3} -ions, including Stark splitting of ${}^4I_{15/2}$ and ${}^4I_{13/2}$ for the two sites, which confirm the validity of the energy levels determined by Gruber *et al*, but not to the ones calculated by others.

Figure 3(b) shows the temperature-dependence of the PL peak intensity ratio of I_{1535} to I_{1548} . The ratios monotonically increase with increasing temperature, which can be explained by a simple theory allowing a phonon-assisted energy transfer between the C_2 and C_{3i} sites. The solid line is the fitting curve obtained from the theory [4]. As can be seen in this figure, the experimental results are in good accordance with the theory as described below.

In Fig. 4, we show the temporal dependence of the spectrally resolved PL emission of Er_2O_3 grown on Si(111). The right panel shows that the PL decays at 1535 nm (red) and 1548 nm (blue). The effective decay time of the peaks are in the range of microseconds and the decay time of peak at 1548 nm (C_2 origin) is 1.1 times larger than that at 1535 nm (C_{3i} origin), indicating the ratio of the decay times obtained from the different sites is nearly unity ($\gamma_2 / \gamma_1 \approx 1.1$).

To understand the dynamics of the energy transfer between the C_2 and C_{3i} sites, we consider a simple model. In the model, according to ref. 4, the rate of change of the probability that the *i* th site of type α (1 or 2) is in the excited ${}^4I_{13/2}$ state is expressed as

 $\frac{dP_{ai}}{dt} = g_{\alpha} - \gamma_{\alpha} P_{ai} + \sum_{j} D_{ji} P_{aj} - \sum_{j} D_{ij} P_{ai} + \sum_{j} X_{ji} (\bar{a} \to \alpha) P_{\bar{a}_{j}} - \sum_{j} X_{ij} (\bar{a} \to \alpha) P_{\bar{a}_{i}}$ where g_{α} is the pumping rate, γ_{α} the decay rate for isolated ions at sites of type α , D_{ij} the transfer rate between equivalent sites, and X_{ij} the transfer rate between ions at inequivalent sites (if α is 1, then $\overline{\alpha}$ is 2 and vice versa). Energy transfer between inequivalent sites involves absorption or emission of a phonon and since the energy of site 1 (C_2 site) is higher than that of site 2 (C_{3i} site) by $\Delta E \approx 51$ cm⁻¹, the transfer rates are

 $X_{ij}(1 \to 2) = \eta W(R_{ij})[n(|\Delta E| + 1)]$

 $X_{ji}(2 \to 1) = \eta W(R_{ij}) n \left(\left| \Delta E \right| \right)$

where $n(E) = 1/[\exp(E/kT) - 1]$ is the number of phonons per mode. W(R) is the resonant transfer rate, and η is a positive constant related to electron-phonon coupling. We assumed here that energy transfer between the equivalent sites is resonant and therefore much faster than transfer between inequivalent sites, and that the excitation is always equally distributed amongst equivalent sites. The ratio of the intensities of luminescence from site $1(C_2)$ and site 2 (C_{3i}) is

$$R = \frac{I_1}{I_2} = \frac{\gamma_1 N_1 P_1}{\gamma_2 N_2 P_2} = C \frac{An(|\Delta E|) + \beta \gamma_2}{A[1 + n(|\Delta E| + 1)] + (1 - \beta)\gamma_1}$$

where $C = N_1 \gamma_1 / N_2 \gamma_2$, $\beta = g_1 / (g_1 + g_2)$, and the transfer coefficient

$$A = \left(\frac{\beta}{N_2} + \frac{1-\beta}{N_1}\right) \sum_{ij} \eta W(R_{ij})$$

A fit to our experimental results gives A = 88.6 (s⁻¹) and C = 1.72. The value of the transfer rate (A) is eight times larger than that of radiation life time of isolated Er^{3+} -ion. From the value of C, we derived $N_1/N_2 = 1.9$ using the experimental result $\gamma_2/\gamma_1 \approx 1.1$ (**Fig. 4**). The value is not equal to 3, which means that the energy transfer between the sites partially occurs in the sample. We also derived $\beta = 0.32$ and then $g_2/g_1 = 2.2$, which indicates that the pumping rate of site 2 is about two times larger than that of site 1 at the excitation wavelength of 532 nm.

3. Conclusion

We grew crystalline erbium oxide films on Si(111) by rf-sputtering and subsequent thermal annealing at 1000 °C and performed PL experiments in spectral and time domains to understand the energy transfers between the Er^{+3} -ions at the lattice sites of symmetry C_2 and symmetry C_{3i} in polycrystalline Er_2O_3 . We found that phonon assisted-energy transfer occurs between the two different sites. A simple theory suggests that pumping rates for the two sites are not identical and the energy transfers between the Er^{+3} -ions located at the two sites occur partially in the samples.

Acknowledgement

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References

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Figure 1: Oxygen surrounding the two Er^{3+} sites in Er_2O_3 .



Figure 2: X-ray powder diffraction pattern obtained at $\alpha = 1.0^{\circ}$ from the sample annealed at 1000 °C in Ar ambience. The X-ray wavelength was 0.124 nm.



Figure 3: (a) Photoluminescence spectra from Er_2O_3 grown on Si(111), obtained at room temperature at the excitation wavelength of 532 nm. (b) Temperature-dependence of intensity ratios of I₁₅₃₅/I₁₅₄₈.



Figure 4: Typical spectral dependence of the time-resolved PL signal decay of the sample, obtained at room temperature.