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Stark Splitting in Photoluminescence Spectra of Er in a-Si:H

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ABSTRACT

The photoluminescence spectra due to Er ions doped in a-Si:H were decomposed into several lines. The 19-K spectrum was reproduced by adding four Gaussian lines whose linewidths were increased with decreasing the photon energy. Since only the lowest energy level of $^4I_{13/2}$ contributes to the radiative transition at this low temperature, the energy levels in $^4I_{15/2}$ split by the Stark effect can be determined. These splittings are not largely different from those for Er in aluminosilicate glass. This implies that the all nearest neighbors of Er are oxygens which have been introduced unintentionally in the sample during preparation. The change in the photoluminescence intensity by annealing is discussed in relation with the spectral change and the results of ESR measurements.

INTRODUCTION

The wavelength 1540 nm of the optical transition of Er ions coincides with a minimum loss of silica optical fibers and many works on Er-doped materials have been done aiming applications to optical devices [1]. Since the optical transition between states with f orbitals is inhibited by symmetry, we need a lack of inversion symmetry around the Er ion to make mixing of orbitals with different symmetries (say d orbitals) possible. a-Si:H films are useful as a host material because the disorder of the amorphous network promotes mixing of the orbitals with different symmetries and the flexibility of amorphous network makes possible a higher amount of Er ions incorporated in the host. Understanding of the excitation mechanism for Er ions [2] is important to get a strong emission. Fuhs et al. reported that the excitation spectrum of the photoluminescence (PL) has a correlation with the absorption coefficient, indicating that Er centers are not excited by direct resonant absorption process but by the absorption in the matrix, and they compared their results with the theoretical work [3]. The incorporation scheme of Er ions is useful for clarifying the excitation mechanism, and should be reflected in the PL spectra. We tried to decompose the PL spectra and pursue the change by annealing.

EXPERIMENTAL

Er-doped a-Si:H films were prepared by magnetron cosputtering. In order to get a small ratio of Er to Si, a very small chip of Er metal should be placed on the c-Si target.

However, it is difficult to deal with such a small chip of Er metal. Therefore, we prepared thick Si-Er films in advance by cosputtering in an atmosphere of Ar using Er metals on the c-Si target. The content of Er in the Si-Er films was determined by an electron probe micro-analysis. Then small chips of the Si-Er films were placed on the c-Si target and the cosputtering was performed in an atmosphere of Ar and H₂ mixture at a nominal substrate temperature of 200 C. By changing the target area of the Si-Er films, samples with different Er contents were prepared. The Er content was estimated from the ratio of the target area of the Si-Er film to that of c-Si target by considering the sputtering coefficient ratio between Er and Si. Aluminum substrates were used for the PL measurements in order to get a good thermal contact between the cryostat finger and the sample film. On the other hand, silica substrates were used for the ESR measurements. The thickness of the films was around 600 nm. The PL measurements were performed at temperatures between 19 K and room temperature using a He-Ne laser (30 mW) as an excitation source chopped with a frequency of 27 Hz. A 25-cm monochrometer, an InGaAs detector and a lock-in amplifier were used to detect the photoluminescent light.

RESULTS AND DISCUSSION

The results of a-Si:H films with different Er contents are shown for sample 1 and sample 2, whose estimated Er contents are 0.2 and 0.08 at. %, respectively. Figure 1 shows the PL spectrum for sample 2 at 19 K. The PL spectrum $g(\lambda)$ which was recorded as the PL intensity against the wavelength λ was converted to a spectrum $f(E)$ on the photon energy abscissa using a relation

$$f(E) dE = g(\lambda) d\lambda,$$

where $E = h c/\lambda$. Figure 2 shows the PL spectrum due to Er³⁺ ions for sample 1 at 19 K on the photon energy abscissa. The PL spectrum was decomposed into component lines which are also shown in Fig. 2. As seen from the figure, the observed PL

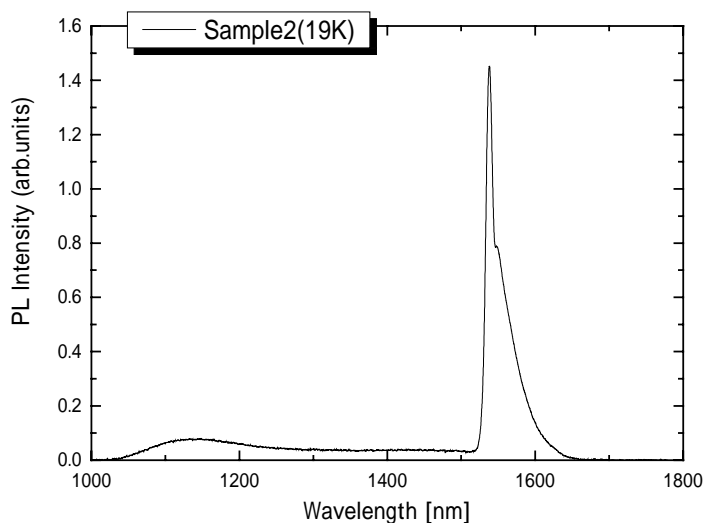


Figure 1. PL spectrum for sample 2 observed at 19K.

spectrum can be reproduced by four component lines with Gaussian shape whose linewidths are increased with decreasing the photon energy.

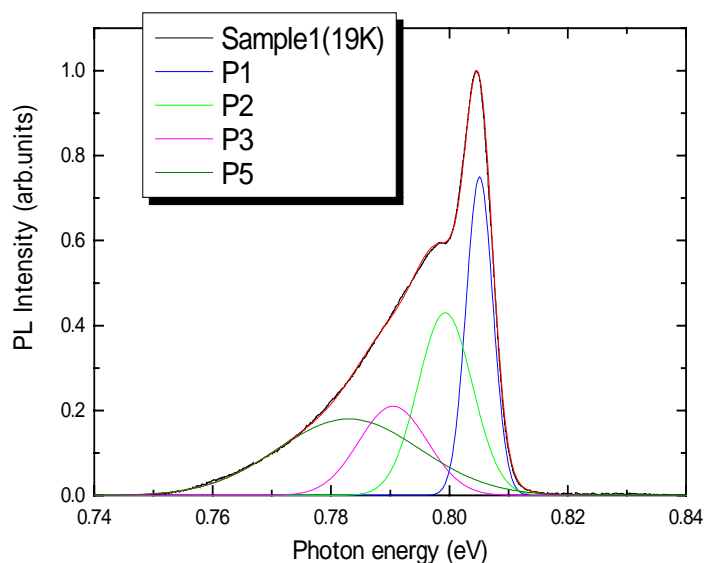


Figure 2. PL spectrum due to Er on the photon energy abscissa for sample1 at 19K. Component Gaussian lines P1, P2, P3 and P4 and the sum of them are also shown.

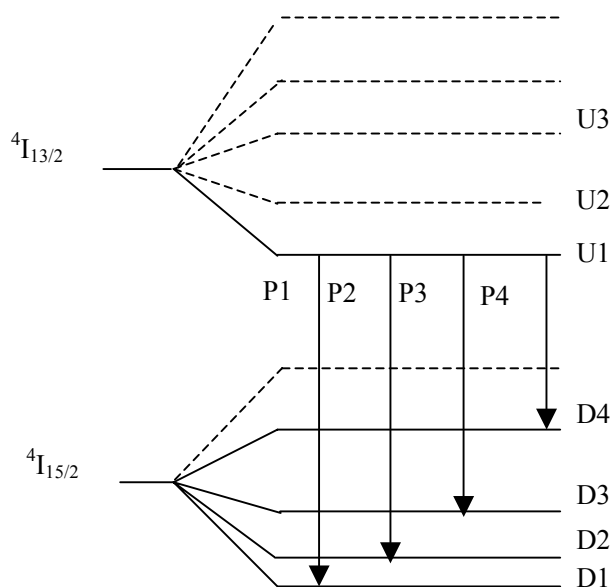


Figure 3. A schematic energy diagram for Er^{3+} ions as a result of the Stark splitting.

These four component lines are assigned to the transitions from the lowest level of the ${}^4I_{13/2}$ to the Stark-split levels of ${}^4I_{15/2}$ as schematically shown in Fig. 3, because only the lowest level of ${}^4I_{13/2}$ is expected to be populated at this low temperature. The Stark splitting of ${}^4I_{15/2}$ for sample 2 was also deduced in the same way and the obtained

values of the energy levels are shown in Table 1 together with the energy levels for other samples published in literatures [4-6]. If the local environment of Er is close to that in the crystalline counterpart, the PL spectrum of Er in amorphous matrix should be close to the superposition of Gaussian lines whose peaks are at the Stark levels of Er in the crystal and the linewidths are determined by randomness. Hence, for the sake of comparison, data for crystalline hosts are also given in Table 1.

Table 1. Stark splitting of $^4I_{15/2}$ term of Er ions in units of meV. Energy levels higher than 60 meV in Er_2O_3 are omitted in this table.

level	present work		Desurvire[4]	Wortman[5]	Huang[6]
	sample 1	sample 2	aluminosilicate glass	c-Si	Er_2O_3
D4	22.1	21.6	25.4	30.5 25.3	32.9
D3	14.6	12.5	16	21.6 15.1	19.7 10.9
D2	5.8	4.9	6.8	8.9 1.5	9.3 4.7
D1	0	0	0	0	0

The linewidth of the component P1 is probably determined by the distribution of the energy levels U1 and D1 due to the randomness of the amorphous network and the lifetime of the energy level U1. The components P2, P3 and P4 correspond to the transitions from U1 to D2, D3 and D4, respectively. The linewidths of these components are affected by the lifetime of D2, D3 and D4 in addition to the above mentioned origins so that the linewidths increase with decreasing the photon energy.

The energy levels of $^4I_{15/2}$ for samples 1 and 2 are slightly different as seen in Table 1, but overall features are similar and rather close to those for the aluminosilicate glass. The results suggest that Er ions are coordinated to oxygen atoms also in the present work. A small amount of oxygen atoms are thought to be incorporated during the sputtering process, but most oxygen atoms are brought from air after preparation. In fact, the infrared absorption peak due to Si-O stretching mode increases with elapse of time after preparation. These oxygen atoms, however, are thought to pile up in the surface layer of a-Si:H and not to affect Er in the bulk because the PL shows no discernible change with time. Similar conclusions about the environment of Er were reported: Masterov et al. reported the local environment of Er similar to Er_2O_3 from the Mössbauer spectroscopy [7], and EXAFS measurements revealed that 3- to 6-fold coordinated Er with oxygens depending on annealing[8].

The peak positions and the intensities of the component lines for sample 2 obtained by decomposing the PL spectrum at 19 K are shown in Figs. 4 and 5, respectively, as a function of annealing temperature. Annealing was done in vacuum for 1 h. The peak positions are almost unchanged except for 500 C annealing where the P1 peak shifts toward higher energy.

The PL intensity increases and the relative fractions of the component lines change

slightly by annealing up to 350 C. However, annealing at 500 C makes the PL intensity decrease more than 2 orders of magnitude, and the decrease in the P3 component is most prominent.

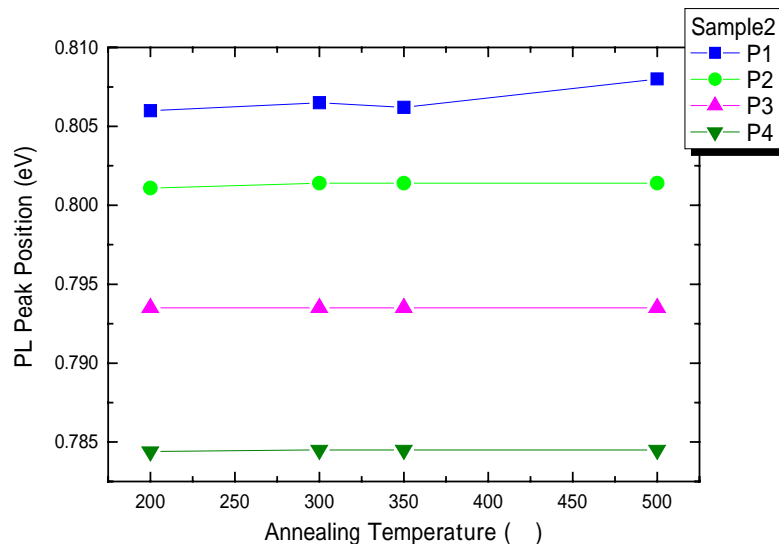


Figure 4. Change in the PL peak positions of the component lines with annealing temperature.

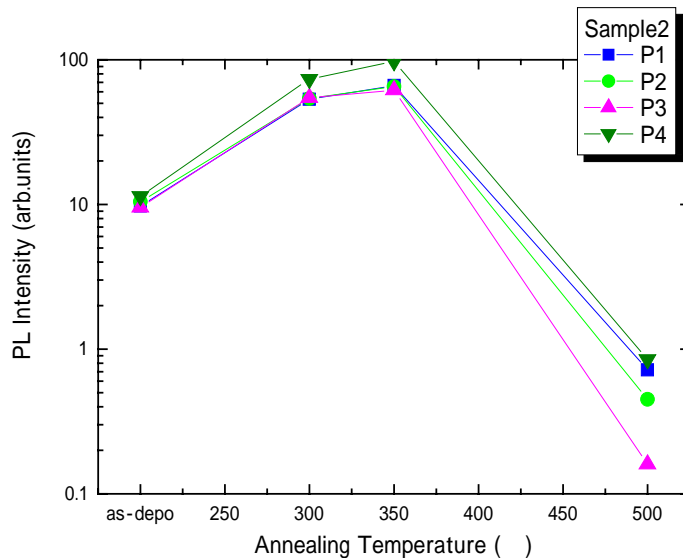


Figure 5. Change in the PL intensities of the component lines with annealing temperature.

From the results of ESR measurements, the density of Si dangling bonds are almost unchanged up to 300 C annealing ($3 \times 10^{17} \text{ cm}^{-3}$), and increases by higher temperature annealing due to the H effusion ($6 \times 10^{17} \text{ cm}^{-3}$ at 350 C and $1 \times 10^{19} \text{ cm}^{-3}$ at 500 C).

The PL intensity increases by annealing up to 350 C, although the dangling bond density does not decrease. This increase is thought to be due to a slight change in the environment of Er ions which does not cause a large change in the energy levels but causes a large change in the transition probability through a change in the mixture of d orbitals.

The prominent decrease in the PL intensity by 500 C annealing is thought to be due to the bypassing loss of the photoexcited carriers in the conduction band through the increased dangling bonds as well as via direct tunneling from the band tail states to the dangling bond states. The change in the peak position of the P1 peak at 500 C as shown in Fig. 4 and the large change in the relative fractions of the component lines at 500 C as shown in Fig. 5 indicate the change in the incorporation scheme of Er ions by annealing at 500 C, giving rise to the additional cause of the change in the mixture of d orbitals and so the change in the PL intensity.

Compared with the PL spectrum at 19 K, the PL spectra observed at higher temperatures have a higher energy tail because the higher energy levels of $^4I_{13/2}$ are populated and contribute to the higher energy part of the PL spectrum. However, it is difficult at present to determine the Stark-split levels of $^4I_{13/2}$ which give the component lines to fit the PL spectrum satisfactorily in consistent with the Boltzmann distribution among these energy levels.

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