Environment of Er doped in a-Si:H and its relation with photoluminescence spectra

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ABSTRACT

The crystal-field potential at the Er^{3+} ion surrounded by six oxygen ions is expanded in terms of polynomials. After converting it into equivalent angular momentum operators, the Stark-splitting of the $^4I_{15/2}$ ground state of the Er^{3+} ion is calculated. Influence of the change in the environment of the Er^{3+} ion on the shift of the energy levels is investigated and compared with the observed Er photoluminescence spectrum in a-Si:H. The scattering of the calculated energy levels by the structural fluctuation around the Er^{3+} ion is also compared with the linewidth of the component photoluminescence lines.

INTRODUCTION

Emission of the light at 1540 nm of an Er ion is matched with the wavelength region of the lowest loss of the optical fiber, and many studies have been done on Er ions doped in various host materials. Hydrogenated amorphous silicon (a-Si:H) films are a suitable host material because many Er atoms can be added without segregation and the inversion symmetry inhibiting the optical transition among 4f electronic states is destroyed in the amorphous network. Er atoms tends to get O atoms as nearest neighbors and three- to six-fold coordinations with O are reported by EXAFS measurements[1]. A DV-Xα calculation also suggests that the Er atom is slightly lifted from the plane where the four O atoms are located [2]. However, it is not clear whether such an Er environment is consistent with the observed Er photoluminescence (PL) spectrum.

The environment of the Er atom has been analyzed in crystalline materials by fitting the observed PL spectra or ESR spectra with calculated results [3-6]. The calculations are based on the Stevens equivalent operator method [7] and parameters associated with the crystal-field potential are adjusted to fit the observed spectra. Although a fairly well fitted result is obtained, it is not directly evident whether the obtained values of the parameters are reasonable in connection with the wavefunction of the Er atom or the bond-lengths between the neighboring atoms. Especially for Er atoms which are incorporated in amorphous network, the environmental fluctuation gives rise to changes in the parameters of the crystal-field potential, but the extent of the effect on the PL spectra has not been clear.

We try to fit the PL spectra of Er which is doped in a-Si:H, starting with the simple crystal-field potential and using the wavefunction of 4f electrons of the Er atom. This is the first study to fit the Er PL spectrum based on the wavefunction to the authors knowledge. We investigate the effect of the change in the location of the neighboring atoms on the PL spectra.

EXPERIMENTS AND CALCULATIONS

Er-doped a-Si:H films were prepared by a magnetron sputtering method. The Si-Er alloy films which had been prepared in advance was put on the crystalline Si target and were sputtered with an rf power of 200 W in an atmosphere of Ar + H_2 gas [8]. The substrate temperature was 200 °C. The film thickness is about 800 nm. The films contain O atoms unintentionally introduced during the preparation process. The PL spectrum around 1540 nm arising from the Er ion was observed at low temperature (19 K) and decomposed into several Gaussian lines.

Calculations of the crystal-field splitting of the $^4I_{15/2}$ ground state of the Er^{3+} ion were done based on the point charge model. As is well known, the crystal-field potential around the magnetic ion can be expanded using spherical harmonic functions, and the matrix elements of the crystal-filed potential perturbation can be calculated using the equivalent angular momentum operators O_n^m. We first consider a crystal-field potential around the Er^{3+} ion which is located at the center of a cage of an octahedron of O^{2-} ions. The crystal-field potential at the site of the Er^{3+} is

$$V(x,y,z)=\frac{2e}{4\pi\varepsilon_0}\left\{\frac{1}{\sqrt{(x\pm a)^2+y^2+z^2}}+\frac{1}{\sqrt{x^2+(y\pm a)^2+z^2}}+\frac{1}{\sqrt{x^2+y^2+(z\pm a)^2}}\right\}$$

where the O^{2-} ions are located at (±a,0,0), (0, ±a,0) and (0,0, ±a), e is the charge of an electron and ε_0 is the dielectric constant in vacuum. Expanding $V(x,y,z)$ up to the sixth order and using the equivalent operator description, the perturbation potential is given by

$$V_{octa}=\frac{2e^2}{4\pi\varepsilon_0}\left\{\frac{7}{16}\frac{1}{a^5}\beta<r^4>(O_4^0+5O_4^4)+\frac{3}{63}\frac{1}{a^7}\gamma<r^6>(O_6^0-21O_6^4)\right\}$$

where a_0 is the Bohr radius, β and γ are constants (β= 4.44 x 10^{-5} and γ= 2.07 x 10^{-6}), O_n^m are functions of the angular-momentum operators [7], and $<r^n>$ is the expectation value of r^n using the radial part of the wavefunction $R(r)$ for 4f electrons of the Er^{3+} ion. We assume the Slater-type orbital [9] for $R(r)$ as

$$R(r)=Nr^{k-1}\exp\left(-\frac{Z}{k}\frac{r}{a_0}\right)$$

where N is the normalization factor and k and Z are constants reflecting the screening effect. k=3.7 and Z = 15.5 in the present case for 4f electrons in the Er^{3+} ion. $<r^2>$, $<r^4>$ and $<r^6>$ are thus calculated to be 1.1 a_0^2, 1.9 a_0^4 and 4.5 a_0^6, respectively.

The matrix elements of V_{octa} in the J=15/2 state are calculated and the matrix is diagonalized. In the cubic-symmetry crystal-filed potential, only five levels appear in accordance with a group theoretical prediction. Next the octahedral cage is elongated along the z-axes by a length ε and another distortion around the Er ion is given by lifting the Er ion by a length δ from the x-y plane of four O atoms as shown in Figure. 1. The perturbation potential for this structure is given by

$$V = V_{octa} - \frac{2e^2}{4\pi\varepsilon_0}\left\{3\frac{1}{a^3}\alpha < r^2 > O_2^0 + \frac{5}{4}\frac{1}{a^5}\beta < r^4 > O_4^0 + \frac{7}{8}\frac{1}{a^7}\gamma < r^6 > O_6^0\right\}\frac{\varepsilon}{a}$$

$$+ \frac{2e^2}{4\pi\varepsilon_0}\left\{\frac{21}{2}\frac{1}{a^3}\alpha < r^2 > O_2^0 + \frac{45}{32}\frac{1}{a^5}\beta < r^4 > (O_4^0 - 7O_4^4) + \frac{693}{128}\frac{1}{a^7}\gamma < r^6 > (O_6^0 + 3O_6^4)\right\}\left(\frac{\delta}{a}\right)^2$$

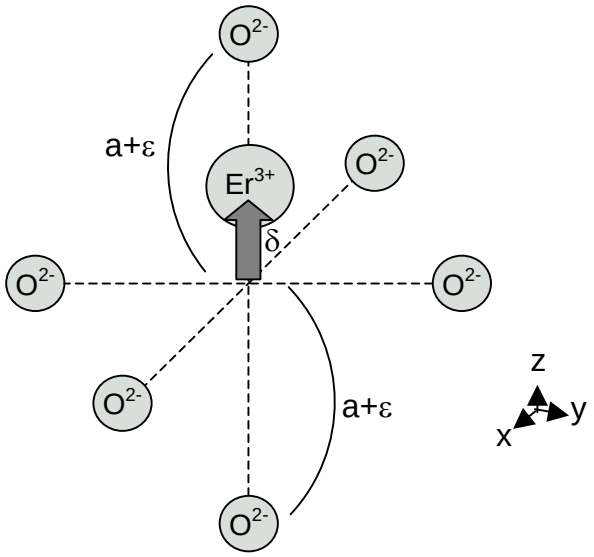

Figure 1. The structural model used for calculation.

where $\alpha = 2.54 \times 10^{-3}$ is a constant.

It should be noticed that the inversion symmetry around the Er^{3+} ion is maintained by only the axial distortion caused by ε. Therefore, the optical transition between f electrons is still inhibited in this distortion[1]. But the other distortion caused by δ destroys the inversion symmetry and makes the optical transition possible.

RESULTS AND DISCUSSION

Only the lowest one of the Stark-split levels in the upper $^4I_{13/2}$ is thought to be populated at 19 K and so the observed PL component lines are attributed to the splitting of the $^4I_{15/2}$ ground state. Hence the observed PL spectrum is compared with the calculated Stark-splitting of the $^4I_{15/2}$ ground state.

Since the odd-order polynomials in the expansion of the crystal-field potential have zero matrix elements, terms such as O_2^0, O_4^0, O_4^4, O_6^0, O_6^4 appear in addition to the terms in the cubic-symmetry case. The perturbation matrix of the crystal-field potential with 16 x 16 elements is diagonalized and the energy levels separated by the Stark splitting are obtained for the $^4I_{15/2}$ ground state. Figure 2 shows the comparison between the observed PL peak energies of the component lines and the calculated energy levels of the $^4I_{15/2}$ ground state in which the energy of the lowest level is taken to be zero. The calculated

results are obtained by setting the parameters as a = 0.228 nm, ε/a = 0.11 and δ/a = 0.04. The value of a is taken from the Er-O distance in Er_2O_3 crystal, the value of ε/a is settled so as to fit the observed data and the value of δ/a is one in the literature using DV-Xα calculation [2]. It is seen that the lowest four calculated levels agree fairly well with the observed ones. The calculated Stark-split levels have eight components but the experimental data show only four lines probably because the linewidths of the PL lines arising from the upper four levels of the eight Stark-split levels are too broad to be decomposed. It should be noticed that only adjusting the value of ε/a gives an almost satisfactory fit to the observed data. But the optical transition for f electrons is inhibited by the selection rule when the inversion symmetry exists. The effect of the distortion of δ/a on the shift of the energy levels is rather small but is effective to break the inversion symmetry and to give none-zero transition probability. Pulling the two apical O ions away from the central Er ion means that the coordination number of Er is four, which is consistent with the EXAFS results that the Er ions responsible for the strong PL have the coordination number of nearly four although the coordination number and the PL intensity change with annealing [1].

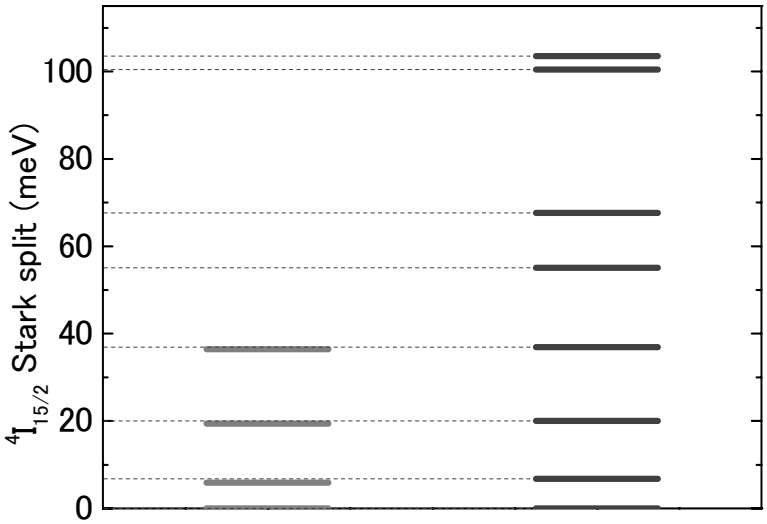

Figure 2. The location of the Stark-split levels for the $^4I_{15/2}$ deduced from the observed PL spectrum at 19 K (left) and those obtained by calculation (right).

We tried to check the influence of another deformation from the regular octahedron on the Stark splitting of the ground state $^4I_{15/2}$. A line connecting the center of one of the eight triangle planes of the octahedron with the corresponding center of the inverted triangle plane parallel to the former passes the Er site. It is found that the distortion along this line by a length of 0.1 a gives the Stark-split levels of $^4I_{15/2}$ in which the lower four levels agree with the observed data. In this case, however, the number of O atoms

coordinated around Er remains six which appears to be inconsistent with the EXAFS results [1]. We can expect that other types of structural deformation around Er could give a similar fit and an ensemble of different environments around Er could cause the linewidth of the observed PL spectrum.

In order to see the influence of the structural fluctuation on the PL linewidth, the value of ε was changed by ±5 % from the value which gives the best fit (ε/a =0.11). Figure 3 shows the range of the change in the energy levels of the $^4I_{15/2}$ ground state together with the observed and decomposed PL spectrum. It can be seen that the scattering of the energy levels due to the fluctuation of ε becomes larger for the smaller photon energy. The result appears to be consistent with the observed tendency of the linewidth change of the component lines. The fact suggests that the structural flucturation is one of the origins of the linewidth for Er PL spectrum in the host of amorphous materials. However, we must consider other factors influencing the linewidth; (1) the lowest one of the Stark-split levels of the upper $^4I_{13/2}$ state should be shifted by the structural fluctuation and (2) the lifetime may be different for each energy level to give different linewidth.

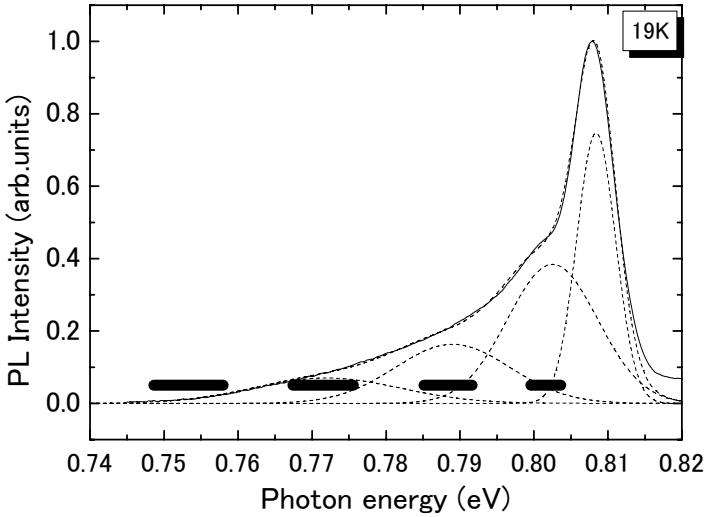

Figure 3. The Er PL spectrum at 19 K and its decomposition to the component lines. The horizontal bars show the range of scattered energy levels calculated for the structural fluctuation of ± 5% toward the tetragonal axes.

In conclusion, the Stark-splitting of the $^4I_{15/2}$ ground state of the Er ion surrounded by O ions is calculated starting from the crystal-field potential at the Er site and using the wavefunction of the Er atom. The observed photoluminescence spectrum of Er in a-Si:H agrees fairly well with the calculated results based on the configuration of oxygen ions around the Er ion which is not inconsistent with the DV-Xα calculation. The linewidth of the photoluminescence lines is possible to be originated from the structural fluctuation of

the amorphous structure but further studies are needed to verify this.

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