J. Synchrotron Rad. (1999). **6**, 477–479

The optically active center of Er-doped Si produced by laser ablation

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The local structure of Er-doped Si produced by a laser ablation technique is investigated by Er L_{III}-edge X-ray absorption fine structure (XAFS). The combination of an extended X-ray absorption fine structure (EXAFS) analysis and a X-ray absorption near edge structure (XANES) simulation indicate the atomic coordination of the optically active center; Er bonded with 6 oxygen atoms distorted form O_h symmetry such as a C_{4v} in this Si:Er system.

Key words: Er-doped Si, optically active center, Er-O local coordination, XANES simulation

1. Introduction

Erbium-doped Si (Ennen et al., 1985) is promising candidate as new optoelectronic devices (Xie, Fitzgerald & Mii, 1991) since an Er $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition produces a sharp photo-luminescence (PL) at a wavelength of ~1.54 μm with a minimum loss for silica-based optical fiber cables. A laser ablation (Komuro et al., 1988) is useful for the Er doping technique, because homogeneous and high-quality thin films with multiple elements can be deposited. Actually, Si:Er thin film with fine PL at room temperature has been successfully realized by this method (Komuro et al., 1996).

It is well known that oxygen enhances the Er related PL in this Si:Er system (Favennec et al., 1990). Extended X-ray absorption fine structure (EXAFS) of Er implanted into Czochralski-grown Si (CZ-Si) was measured by Adler et al (1992). They concluded that an optically active center in this system was the local sixfold coordination of the Er-O structure, and also suggested the possibility of a pseudo-octahedral structure as the optical center. However, it is not clear that this sixfold coordination is the unique center in the Si:Er system irrespective of the fabrication methods. Moreover, the actual local structure of the pseudo-octahedral center has never been understood.

In this report, the local structure of the optically active center of Si:Er produced by the laser ablation technique is discussed. A X-ray absorption near edge structure (XANES) simulation based on the multiple-scattering theory as well as a conventional EXAFS analysis are also used in this study. This combined analysis allows us to investigate more detailed local structures.

2. Experiments and local structure analysis

The details of the sample preparation and its optical properties were described by Komuro et al (1996). A KrF excimer laser (λ = 248 nm) was used for an ablation of 10 wt% Er_2O_3 bulk target prepared by a hot press technique from a Si and Er_2O_3 mixture. The substrate used in this study was a (100) oriented Si wafer. After Si:Er film deposition by the laser ablation, the sample was annealed in N_2 ambient to activate the Er in the films. The annealing temperature and duration were 600℃ and 3 min, respectively.

Experiments using synchrotron radiation (SR) were performed at SPring-8 located in Hyogo, Japan. The BL10XU beamline was used for X-ray absorption fine structure (XAFS) measurement. By using a standard in-vacuum type undulator, a high brilliance, quasi-monochromatized SR beam with a selectable energy above 5 keV is obtained by the undulator gap control. SPring-8 standard (111) oriented Si double-crystal monochromator was used. The energy resolution of this monochromator was estimated to be $\Delta E/E \sim 10^{-4}$. A rhodium coated double-mirror system for eliminating undesirable higher-order light was inserted after the monochromator. A total-conversion He ion-yield (TCY) cell (Watanabe, Tanida & Kawauchi, 1997) was used for the XAFS measurement of thin films. The photo-electrons ejected from the sample ionize the He gas continuously introduced into the cell, and as a result the X-ray absorption spectrum is obtained by measuring the ion current through the sample. The He flow rate and high voltage for collecting He ions were 300 sccm and 1 kV, respectively. The measurement temperature was room temperature. The X-ray incidence angle was 0.5°.

The EXAFS analysis was based on a published program, XAFS'93, developed by Maeda (1987). The backscattering amplitude and phase shift derived by McKale et al. (1988) were used for the parameters to obtain the chemical bond information. In addition to the conventional EXAFS analysis, XANES spectra were

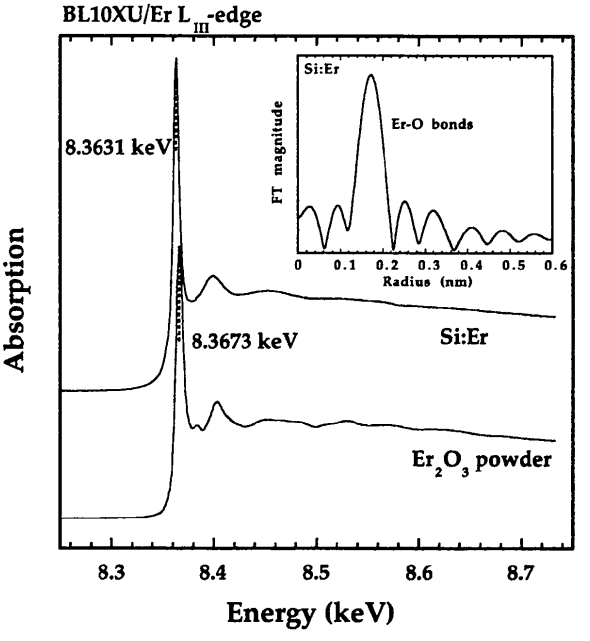

Figure 1
Er L_{III}-edge XAFS spectra of optically activated Si:Er thin film and Er_2O_3 powder for reference.

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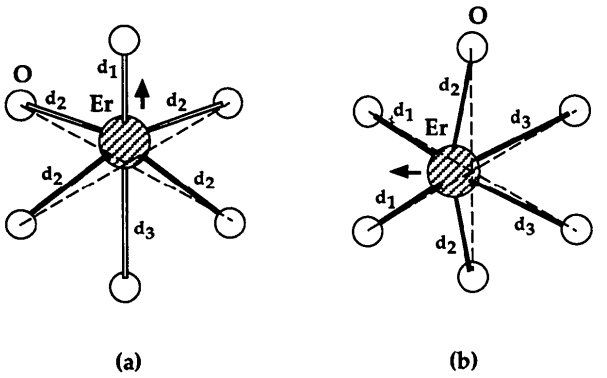

Figure 2
Schematic diagrams of (a) C_{4v} and (b) C_{2v} models proposed as the pseudo-octahedral structure.

simulated by a multiple-scattering theory (Fujikawa, 1986; Fujikawa & Yiwata, 1996).

3. Results and discussion

Fig. 1 shows the Er L_{III}-edge XAFS spectrum of a optically activated Si:Er thin film that is annealed after the laser ablation. The reference Er_2O_3 powder (99.9 %, High Purity Chemicals Co. Ltd.) spectrum is also indicated in this figure. The shapes of these spectra are quite similar even though the absorption edge energy is slightly different. The similarity of these spectra is considered to be caused by the principle sixfold coordination of O around Er in both samples. The absorption energy difference is caused by the difference of the local environment of the sixfold Er-O; 2nd nearest neighbor atoms are Si in optically activated sample. The inserted figure indicates radial structure function (RSF) derived by a Fourier-transform of $k^3\chi$ for Si:Er. The effect of the EXAFS phase shift is not included in this calculation. In this RSF, a peak at ~ 0.17 nm is caused by the O atoms bonded with Er rather than Si atoms with a larger covalent radius.

An octahedron of O with centered Er atom (O_h point group) is considered as a possible sixfold coordination. However, the symmetrical order of O_h is too high to explain the strong PL at ~1.54 μm in this system, so that the actual local structure that allows a more effective optical transition should be pseudo-octahedral. In order to identify the pseudo-octahedral structure, two models with a slight distortion are proposed as shown in Fig. 2. In the case of (a) the C_{4v} model, a certain O atom has a short bond length with Er, and the other 5 O atoms are relaxed from the octahedral coordination; this means a symmetrical degradation from O_h to C_{4v}. In the fitting of the back-transformed RSF, this C_{4v} model is expressed by 3 O shells with different Er-O bond lengths, in which 3 shells have 1, 4, and 1 O atoms, respectively. The three Er-O bond lengths are denoted as d_1, d_2, and d_3 in this figure. Another proposed coordination is (b) the C_{2v} model. An attraction of the two O atoms to Er results in a degradation from Oh to the C_{2v} point group. This model is also expressed by 3 shells with different bond lengths. In this case, all shells include 2 O atoms. The standard O_h structure without distortion is also calculated for the reference. The fitting results for the back-transformation of the nearest neighbor peak of RSF in Fig. 1 are shown in Fig. 3. The solid circles and solid line indicate the experimental result and theoretical calculation, respectively. The bond lengths estimated from these fittings are summarized in Table 1. The O_h model has a Er-O bond length of 0.220

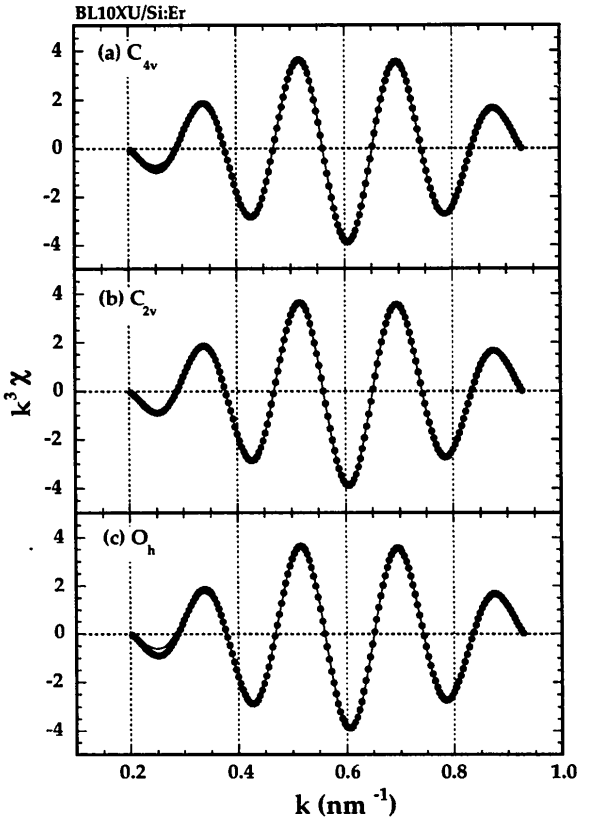

Figure 3
The fitting results of back-transformation of nearest neighbor peak of RSF at ~0.17 nm using back scattering amplitude and phase factor of McKale.

nm, which is almost the same as the Er-O bond length in the Er implanted CZ-Si (0.225 nm) estimated from a similar analysis (Adler et al., 1992); this suggests that the highly efficient optically active centers of Er in Si related to O have almost the same local structure irrespective of the fabrication methods. However, curve fitting results apparently indicate that all of the models of C_{4v}, C_{2v} and O_h agree well with the experimental result, so that another analytical method is necessary for specifying the pseudo-octahedral structure. XANES simulations based on a multiple-scattering theory are performed for an additional analysis. The atomic arrangements of O and Er in table 1 derived from EXAFS analysis were used for the XANES simulation; It is combination of EXAFS and XANES analyses. Fig. 4 shows the XANES simulations of the C_{4v}, C_{2v} and O_h models. The experimental result is also indicated in this figure. As shown in this figure, the second peak at ~ 8.398 keV is shifted toward the lower energy as a symmetrical degradation. Whereas the second peak in experiment is broader than the simulation, the peak position of the C_{4v} model corresponds with that of experiment,

Table 1
The bond lengths estimated from fittings.

	d_1 (nm)	d_2 (nm)	d_3 (nm)
(a) C_{4v}	0.2133	0.2233	0.2456
(b) C_{2v}	0.2214	0.2248	0.2460
(c) O_h	0.2200	-	-

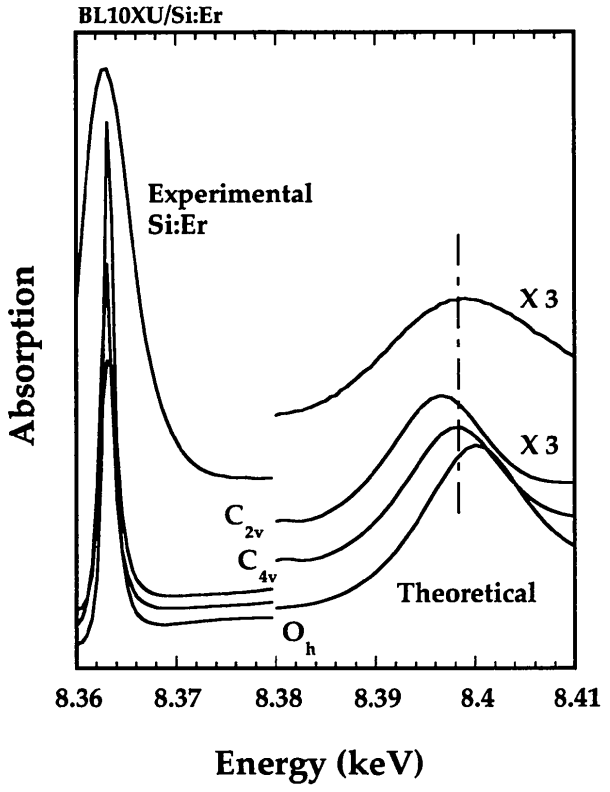

Figure 4
XANES simulations based on C_{4v}, C_{2v} and O_h model and experimental spectrum of optically activated Si:Er thin film.

indicating that the most probable center in Si:Er thin film produced by the laser ablation is C_{4v}. This symmetrical degradation is considered to induce the strong PL.

4. Summary

The optically active center in the Si:Er system produced by KrF excimer laser ablation was investigated. The combined analysis of an EXAFS fitting and a XANES simulation indicates that the most probable center in Si:Er thin film has C_{4v} symmetry; Er is surrounded by 6 oxygen atoms, and a certain O atom has a short bond length with Er while the other 5 atoms are in relaxed position from the octahedral coordination.

The synchrotron radiation experiments were performed at the SPring-8 with the approval of the JASRI (Proposal No. 1998A0134-NX-np).

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(Received 10 August 1998; accepted 18 January 1999)