

X-ray-excited optical luminescence of impurity atom in semiconductor

M. Ishii,^a Y. Tanaka,^b S. Komuro,^c T. Morikawa,^c Y. Aoyagi^d and T. Ishikawa^b

^aJASRI, SPring-8, Mikaduki, Sayo-gun, Hyogo 679-5198, Japan, ^bRIKEN, Harima Institute/SPring-8, Mikaduki, Sayo-gun, Hyogo 679-5148, Japan, ^cFaculty of Engineering, Toyo University, Kawagoe, Saitama 350-8585, Japan, and ^dRIKEN, Wako, Saitama 351-0198, Japan. E-mail: ishiim@spring8.or.jp

We observed the x-ray-excited optical luminescence (XEOL) of erbium-doped silicon (Si:Er) thin films to make a site-selective x-ray absorption fine structure (XAFS) measurement of an optically active Er atom. The undulator beam was used for the increment of the electron population in the excited state, and following XEOL at an infrared wavelength of 1.54 μm with minimum absorption loss in the host Si was detected. The edge-jump and XAFS oscillation were successfully obtained at the Er L_{III} -edge. This spectrum originated from inner-shell excitation and relaxation of only the optically active Er atom, indicating that site-selectivity at an atomic level was achieved.

Keywords: site-selectivity at atomic level; XEOL; infrared; optically active Er atom; phonon-absorption

1. Introduction

X-ray-excited optical luminescence (XEOL) has been studied (Goulon *et al.*, 1983; Sham *et al.*, 1993) in order to acquire site-selectivity in x-ray absorption fine structure (XAFS) measurement. Since the luminescence wavelength is intrinsic to the materials, an x-ray photon energy dependence of the monochromatized XEOL yield indicates a site-selective XAFS spectrum (XEOL-XAFS). On the other hand, other pathways without luminescence are also involved in the relaxation of the x-ray-excited state. Although the relaxation processes depend on the materials, the poor signal-to-noise (S/N) ratio in XEOL-XAFS spectra generally suggests a high branching ratio of the relaxation pathways without luminescence to the optical de-excitation (Soderholm *et al.*, 1998). In spite of this simple idea of site-selectivity, the low emission efficiency of the luminescence restricts the observable material for the XEOL-XAFS measurement. In fact, almost all of the observable materials published in previous papers have been bulky, such as powder mixtures of semiconductors, indicating that sufficient volume was necessary to obtain a strong XEOL signal (Pettifer & Boutfillon, 1987).

Erbium-doped semiconductors have been studied over the last few decades (Coffa *et al.*, 1994), because of their inherent optical property of exhibiting an infrared (IR) luminescence peak at a wavelength of $\sim 1.54 \mu\text{m}$. This IR luminescence originates from the Er intra- $4f$ transition, which is forbidden in Er atoms. Therefore, a crystal field by a ligating atom such as oxygen, is considered to modify the electronic structure of Er, resulting in the intra- $4f$ transition. In previous studies, we demonstrated conventional XAFS analyses of an Er-doped Si (Si:Er) thin film, and concluded that a slightly distorted six fold O around Er with C_{4v} symmetry is the most probable structure for the optically active center (Ishii *et al.*, 1999). However, the intensity of Er-related photoluminescence (PL) sensitive to the Si:Er fabrication conditions, such as an annealing temperature and heating duration, suggests that not only the optically active Er but also inactive centers with different local structures are

constructed in actual Si:Er thin film. In order to analyze the unique structure of the optical center, site-selectivity at the atomic level is necessary in XEOL-XAFS measurements (Ishii *et al.*, 2000). In this paper, we demonstrate the site-selective XAFS measurement of only the optically active Er atom incorporated into host Si, and discuss influences of optical and x-ray absorptions at Si to observe the weak XEOL signal from the impurity atom.

2. Principle of XEOL measurement

XEOL-XAFS measurement has been performed for various optical materials. In addition to the site-selectivity of this method, anomalous optical-luminescence yield with a positive- and a negative-jump at absorption edge has been investigated by many groups (Emura *et al.*, 1993; Rogalev & Goulon, 1997). This phenomenon is caused by luminescence that arises from plural electron excitation and relaxation processes in a sample. Emura *et al.* proposed a theoretical model in which two excitation paths owing to K- and L-shell absorption are taken into account as an electron source for the optical transition at a valence state, and predicted the anomalous luminescence yield for the various sample thicknesses. In our system, the inner-shell excitation of Er, not the host Si, provides the site-selective XEOL-XAFS signal. Since the Si surrounds the Er atom as shown in Fig. 1, influences of (a) an absorption of XEOL and (b) an x-ray absorption at Si, should be considered. The absorption (a) simply attenuates the XEOL, so that it has nothing to do with the anomalous luminescence yield of XEOL. However, as discussed below, the absorption (a) is not negligible for the detection of the weak luminescence signal from the Er atom. Moreover, although the incident x-ray is absorbed in a separate area from the Er atom (Fig. 1 (b)), it is considered that an energy transfer from Si to Er is excite the valence state of Er, resulting in a background luminescence. The property of this long-range energy transfer has never been understood.

In order to discuss both the absorptions of XEOL and x-ray at the host Si, the incidence of the x-ray with the intensity of I_0 and following XEOL emission from the Er atom at the depth of x (Fig. 1) are considered. In this situation, a detectable XEOL yield from this Er atom, I_{XEOL} , is expressed as

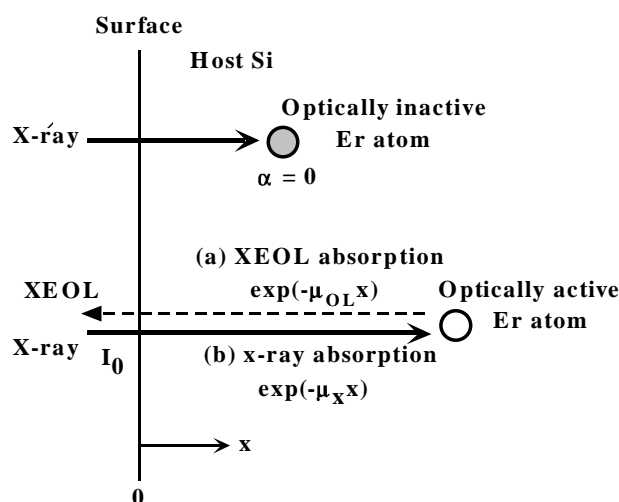


Figure 1

Model for the XEOL-XAFS. (a) and (b) indicate absorptions of XEOL and x-ray at host Si, respectively.

$$I_{\text{XEOL}} = \alpha I_0 \exp(-\mu_x x) \exp\{-\mu_{\text{OL}}(\lambda) x\}$$

$$= \alpha I_0 \exp[-\{\mu_x + \mu_{\text{OL}}(\lambda)\} x], \quad (1)$$

where α is the XEOL emission probability which is equal to multiplication of the x-ray absorption probability of the Er atom and its relaxation probability with the XEOL emission. The optically inactive Er atom has $\alpha = 0$ due to the forbidden transition of intra-4f electron. μ_x and $\mu_{\text{OL}}(\lambda)$ are the absorption coefficients of x-ray and optical luminescence in Si, respectively. The λ is the XEOL wavelength. The I_0 is attenuated by a factor of $\exp(-\mu_x x)$, and the XEOL given by $\alpha I_0 \exp(-\mu_x x)$ decreases further by XEOL absorption expressed as $\exp\{-\mu_{\text{OL}}(\lambda) x\}$ until it escapes from the sample surface. Note that α and μ_x are fixed values when the sample and the x-ray photon energy are given for the XAFS measurements. Therefore, the minimization of $\mu_{\text{OL}}(\lambda)$ by selection of λ is important for the increment of I_{XEOL} ; an escape depth of the luminescence deeper than a penetration depth of x-ray is advantageous for sensitive detection. In the ideal case, the maximum total XEOL yield is given by summation of Eq. (1) for all the Er atoms in the x-ray penetration depth.

The closed circle in Fig. 2 shows the $\mu_{\text{OL}}(\lambda)$ of the host Si for various λ between 0.1 and 1.6 μm (Edwards, 1985; Hulthen, 1975). According to the Eq. (1), the detectable depth of XEOL, $d_{1/e}$, defined by $1/\{\mu_x + \mu_{\text{OL}}(\lambda)\}$ is also indicated by open circle in this figure. Assuming that $\alpha = 1$, the $d_{1/e}$ indicates the depth with a detection efficiency, I_{XEOL}/I_0 , of $1/e$. The x-ray penetration depth at Er L_{III}-edge, $1/\mu_x \sim 79.3 \mu\text{m}$ ($\mu_x \sim 0.0126 \mu\text{m}^{-1}$), is used for the calculation of $d_{1/e}$. As shown in Fig. 2, the host Si has the maximum $\mu_{\text{OL}} \sim 238.1 \mu\text{m}^{-1}$ at the wavelength λ , of 0.287 μm (Edwards, 1985). Since μ_x is negligible in this ultraviolet (UV) region, $d_{1/e}$ is approximately given by an escape depth of the luminescence, $\sim 1/\mu_{\text{OL}}(\lambda)$. Despite of the large penetration depth of x-ray, the $d_{1/e}$ is limited to the sample surface region $< 0.01 \mu\text{m}$. The $\mu_{\text{OL}}(\lambda)$ decreases with increasing λ , and becomes $\sim 0.599 \mu\text{m}^{-1}$ in the typical visible light with $\lambda = 0.619 \mu\text{m}$ (Hulthen, 1975). In this wavelength region, $\mu_{\text{OL}} > \mu_x$ still limits the detectable depth of XEOL. Finally, the infrared (IR) luminescence at $\lambda = 1.54 \mu\text{m}$ has the smaller μ_{OL} due to the photon energy being less than the band gap of Si. In this case, the μ_{OL} is $< 10^{-7} \mu\text{m}^{-1}$ (Edwards, 1985), so that $d_{1/e}$ is roughly

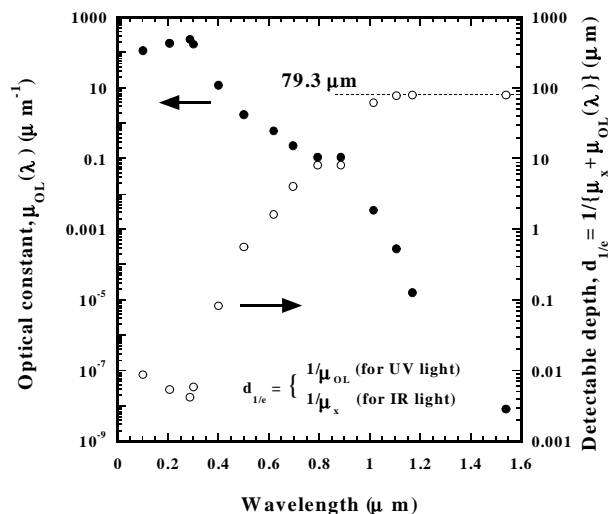


Figure 2

Optical constant of Si, μ_{OL} , and detectable depth of XEOL, $d_{1/e}$. Convergence of $d_{1/e}$ to $1/\mu_{\text{OL}}$ and $1/\mu_x$ is obtained for UV and IR lights, respectively.

given by $\sim 1/\mu_x$. Actually, $d_{1/e}$ converges to the x-ray penetration depth of $\sim 79.3 \mu\text{m}$ in the IR region of $\lambda > 1.1 \mu\text{m}$. In this case, all the optically active Er atoms in the x-ray penetration depth can be detected, resulting in maximum I_{XEOL} . This finding indicates that detection of XEOL in the IR region is desirable for XEOL-XAFS measurement of low-density impurity atoms in Si.

3. Experiment

The beamline used in this study was the BL29XU RIKEN beamline, which has an in-vacuum undulator (Kitamura, 1995) as its light source. For an efficient emission of XEOL from the impurity atom, a useful technique is the population increment of an excited state by the irradiation of an intense x-ray beam. The increment of I_0 in Eq. (1) resulted in enhancement of I_{XEOL} . X-ray beams with a narrow bandwidth demand continuous tuning of the undulator gap width during XAFS measurement. Despite this complicated procedure, an x-ray photon flux with two orders of magnitude stronger than that from a standard bending magnet is obtained.

In our experiments, the photon flux at the sample was estimated to $\sim 10^{13}$ photons/s. A monochromator equipped with a Si (111) double crystal was used to monochromatize the x-ray beam from the undulator. The sample was Si:Er thin film deposited by the laser ablation technique (Komuro *et al.*, 1999). An ablation target was made by a powder mixture of Si and Er_2O_3 with a density of 10 wt%. The Er_2O_3 was decomposed into Er atoms during laser ablation, and forms the optically inactive center in as-ablated sample. After annealing for 3 min at 600° in N_2 ambience, part of the Er atoms were activated, and laser induced PL at 1.54 μm was observed.

In the experiments using SR, the XEOL emitted from the sample was condensed onto the slit of an IR monochromator (Acton Research Corporation, SpectaPro 300i) with 300 groove/mm grating by collimator and focus lenses. An optical chopper for sensitive IR detection using a lock-in amplifier was mounted in front of the IR monochromator slit. The Ge p-i-n photodiode (Applied Detector Corporation, 403L) was used as the IR detector.

4. Results and discussion

Fig. 3 (a) shows the XEOL-XAFS spectrum of Si:Er thin film at the Er L_{III}-edge. The wavelength for the XEOL observation was fixed at 1.54 μm . The substrate temperature was 300 K. Although the difficulty of the XEOL-XAFS observation for the impurity atom has been pointed out (Soderholm *et al.*, 1998), the photon energy dependence of the XEOL signal indicates a positive absorption peak at the Er L_{III}-edge (white line) and following XAFS oscillation. Unfortunately, the S/N ratio of this spectrum is insufficient for the Fourier transform to obtain structural information. Nevertheless, the bonding state of Er with the ligand can be analyzed from the shape of the white line (Ishii *et al.*, 1999). In conventional XAFS measurements, a convoluted spectrum of the optically active and the inactive centers is obtained. In contrast to x-ray fluorescence and photoelectrons observed in conventional XAFS, the XEOL emission is induced at only the optically active atom, indicating that Fig 3 (a) is site-selective XAFS spectrum of the optically active Er. The structural information evaluated by the comparison between conventional and XEOL-XAFS spectra will be discussed elsewhere.

Fig. 3 (b) indicates the XEOL-XAFS spectrum at 20 K. In this case, the edge-jump is not obtained. This finding indicates that

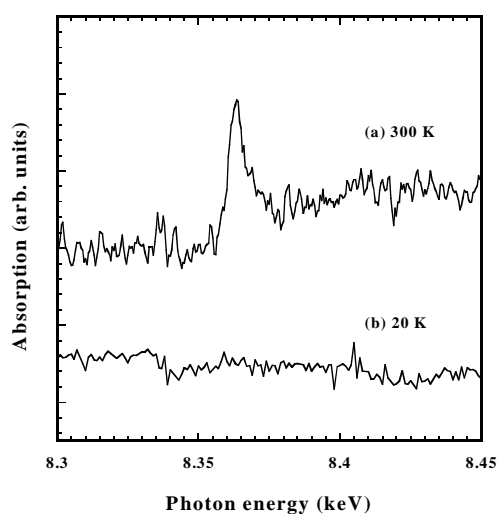


Figure 3
XEOL-XAFS spectrum of Si:Er thin film. The substrate temperatures were (a) 300 K and (b) 20 K.

the XEOL emission is sensitive to the sample temperature, which can be explained as follows. The x-ray absorption at host Si as shown in Fig. 1 (b) induces the electron-hole pair in the valence state of Si, and its recombination energy is transferred from Si to Er. The recombination energy excites the $4f$ electron of Er, resulting in an extra luminescence independent of XAFS signal. Hence, the weak XEOL due to the direct inner-shell excitation of Er atoms vanishes into the background luminescence. On the other hand, since energy back-transfer from Er to Si becomes dominant by a phonon-absorption, the background luminescence is suppressed in high temperature regions. At 300 K, the XEOL signal is equivalently enhanced by the phonon-absorption, so that the site-selective XAFS spectrum is obtained as shown in Fig. 3 (a). This long-range energy transfer is similar to the process observed in conventional PL (van den Hoven *et al.*, 1995). In XEOL-XAFS measurement of impurity atoms, since the energy transfer process determines the signal amplitude of XAFS, control of energy transfer is necessary for the sensitive detection of XEOL signals.

5. Summary

A continuous tuning of the undulator gap width and infrared (IR) luminescence detection were performed for site-selective x-ray absorption fine structure (XAFS) measurement of Er-doped Si thin film. The photon energy dependence of the x-ray excited optical luminescence (XEOL) yield at the wavelength of $1.54 \mu\text{m}$ indicates an XAFS spectrum at 300 K. Since the spectrum was obtained by inner-shell excitation and relaxation of only the optically active Er atoms, site-selectivity at an atomic level was achieved. On the other hand, the XAFS spectrum is not observed at 20 K. This temperature dependence can be explained by energy exchange between Si and Er.

References

- Coffa, S., Franzo G., Priolo, F., Polman, A. & Serena, R. (1994). *Phys. Rev. B* **49**, 16313-16320.
- Edwards, D. F. (1985). *Handbook of Optical Constants of Solids*, edited by E. D. Palik, pp. 547-569. Orland: Academic Press, Inc..
- Emura, S., Morinaga, T., Takizawa, J., Nomura, M., Bauchspiess, K. R., Murata, T., Harada, K. & Maeda, H. (1993). *Phys. Rev. B* **47**, 6918-6930.
- Goulon, J., Tola, P., Lemonnier, M. & Dexpert-gheys, J. (1983). *Chem. Phys.* **78**, 347-356.
- Hulthen, R. (1975). *Physica Scripta*. **12**, 342-344.
- Ishii, M., Komuro, S., Morikawa, T., Aoyagi, Y., Ishikawa, T. & Ueki, T. (1999). *J. Appl. Phys.* **85**, 4024-4031.
- Ishii, M., Komuro, S., Morikawa, T., Aoyagi, Y., Ishikawa, T. & Ueki, T. (1999). *Jpn. J. Appl. Phys. Suppl.* **38-1**, 191-194.
- Ishii, M., Tanaka, Y., Komuro, S., Morikawa, T., Aoyagi, Y. & Ishikawa, T. (2000). In preparation.
- Kitamura, H. (1995). *Rev. Sci. Instrum.* **66**, 2007-2010.
- Komuro, S., Katsumata, T., Morikawa, T., Zhao, X., Isshiki, H. & Aoyagi, Y. (1999). *Appl. Phys. Lett.* **74**, 377-379.
- Pettifer, R. F. & Bourdillon, A. J. (1987). *J. Phys. C: Solid State Phys.* **20**, 329-335.
- Rogalev, A. & Goulon, J. (1997). *J. Phys. IV France* **7**, C2-565-568.
- Sham, T. K., Jiang, D. T., Coulthard, I., Lorimer, J. W., Feng, X. H., Tan, K. H., Frigo, S. P., Rosenberg, R. A., Houghton, D. C. & Bryskiewicz, B. (1993). *Nature (London)* **363**, 331-334.
- Soderholm, L., Liu, G. K., Antonio, M. R. & Lytle, F. W. (1998). *J. Chem. Phys.* **109**, 6745-6752.
- van den Hoven, G. N., Shin, J. H., Polman, A., Lombardo, S. & Campisano (1995). *J. Appl. Phys.* **78**, 2642-2650.