

Environment of Erbium in a -Si:H and a -SiO_x:H

C. Piamonteze, A. C. Iñiguez, and L. R. Tessler

Instituto de Física "Gleb Wataghin," UNICAMP, CP 6165, 13083-970, Campinas, São Paulo, Brazil

M. C. Martins Alves and H. Tolentino

Laboratório Nacional de Luz Síncrotron, CP 6192, 13083-970, Campinas, São Paulo, Brazil

(Received 17 June 1998)

The chemical environment of Er in a -Si:H and a -SiO_x:H was determined by extended x-ray absorption fine structure. Only one family of Er sites is found, coordinated on average with two to three O atoms (compared to six in Er₂O₃). We devised a new model for the incorporation of Er in a -Si:H and a -SiO_x:H. According to the model, Er is incorporated in the form of [ErO_δ]^{+3-2δ} complexes, with δ ≤ 3. The minimum configuration energy is achieved for δ = 3 when the valence requirements of Er are fulfilled. The complexes are low symmetry environments that allow the Er³⁺ luminescent transition at 1.54 μm and make Er an acceptor in a -Si:H whereas it is donor in crystalline silicon. [S0031-9007(98)07668-6]

PACS numbers: 61.43.Dq, 61.10.Ht, 73.61.Jc

The study of triply ionized erbium (Er³⁺) luminescence in semiconductors has been an intensive area of research over the last few years mainly because of possible photonic applications [1]. The Er³⁺ ions exhibit atomlike luminescence that arises from electronic transitions within its incomplete internal 4*f* shell. In particular, the ⁴I_{13/2} → ⁴I_{15/2} transition from the first excited to the fundamental state emits photons with a wavelength of ~1.54 μm. Because of the shielding provided by the outer filled 5*s*² and 5*p*⁶ shells, the transition wavelength depends very weakly on the details of the host. This wavelength is especially important because it corresponds to the window of minimum attenuation in the silica based optical fibers currently used in optical communications. Silicon has been one of the most studied hosts for Er, because of the enormous technological benefit that would result from a silicon based photonic technology. Erbium luminescence has been reported in crystalline, porous, and hydrogenated amorphous silicon (a -Si:H). Nevertheless, the understanding of the process of luminescence of Er in silicon is far from complete. The *f*-*f* transitions are electric dipole forbidden in the free ion. They become at least partially allowed in solid hosts where states of different angular momentum are admixed to the *f* wave functions. In pure float zone (FZ) crystalline Si the Er luminescence yield is relatively low, and this has been attributed to a highly symmetrical 12-fold coordinated Er site very similar to the Er site in ErSi₂ [2]. The addition of a co-dopant such as O, N, C, or F strongly enhances the luminescence yield [3]. In a -Si:H the Er³⁺ luminescence yield is high and temperature quenching is smaller even without co-doping [4] when compared to crystalline Si, although O co-doping slightly enhances the luminescence yield [5]. The reason for this is not completely clear. Furthermore, Er³⁺ is an anomalous dopant in silicon. Early reports on crystalline

silicon have found unexplained *p*-type doping [6], while more recent results indicated the expected *n*-type doping [7,8]. For unhydrogenated amorphous silicon it has been reported that many rare earths have acceptor character [9] and thus *p*-type doping is obtained, while for a -Si:H erbium doping has been classified as *n* type [10], although in this study a detailed doping characterization was not reported.

The chemical environment of Er in FZ and Czochralski (Cz) crystalline silicon has been investigated by extended x-ray absorption fine structure (EXAFS) [2,11]. The main result is that efficient Er luminescence is associated with a local environment very similar to that of Er in Er₂O₃, which led to the conclusion that the effect of oxygen is to provide a 6-fold coordinated, noncentrosymmetric O cage for Er that replaces the highly symmetric 12-fold coordinated Si cage. More recently, a dramatic reduction of the fraction of Er atoms in Si tetrahedral cages in Cz silicon has been associated with the reaction of Er with O during annealing and formation of Er-O complexes [12]. In Er doped a -Si:H, the only study of the local Er environment has been by emission Mössbauer spectroscopy [13]. This study concluded that the Er³⁺ environment in a -Si:H is similar to that in Er₂O₃. In this Letter we report on the determination of the Er³⁺ chemical environment in Er doped a -Si:H and a -SiO_x:H by EXAFS. We show that the Er local environment in a -Si:H is similar to that in Er₂O₃ only in the sense that the first Er neighbors are O atoms. The average coordination is much lower (saturating at a value of ~3) and the Er-O distance is significantly shorter. Based on this we propose a model that accounts for the luminescence properties of Er in a -Si:H and also for the observed *p*-type doping effect of Er in a -Si:H.

Erbium doped a -Si:H and a -SiO_x:H samples were prepared in a conventional rf sputtering system following

a procedure described elsewhere [14]. The lowest O concentration [O] measured by Rutherford backscattering spectroscopy (RBS) was 0.2 at. % of the same order of the Er concentration [Er], which was between 0.1 and 0.3 at. %. This residual O contamination is normally found in *a*-Si:H samples prepared in conventional plasma deposition systems [4,5], and thus we refer to nonintentionally O contaminated samples as *a*-Si:H. It turns out that Er is such a strong getter for O that most of the contaminant O is bonded to Er. In the present study we used samples containing up to 7.6 at. % [O]/[Si]. No postdeposition thermal treatments were necessary to detect room temperature photoluminescence at 1.54 μm in all samples when excited by the 514.5 nm line of an Ar⁺ laser, the maximum yield being for 1.1 at. % [O]/[Si].

Thermopower measurements at room temperature indicated a negative Seebeck coefficient S for undoped samples (undoped *a*-Si:H is normally slightly *n* type) and positive S for the Er doped samples up to 1.1 at. % [O]. For higher [O] the value of S is too small to be reliably measured, but we have no reason to presume it would not be positive. Er doping clearly produced *p*-type *a*-Si:H samples.

Erbium L_{III} -edge EXAFS was measured with total secondary electron yield detection at the XAFS beam line of the Laboratório Nacional de Luz Síncrotron (LNLS) in Campinas, Brazil [15]. The experimental details are described in [16]. Reference samples of bulk Er_2O_3 and a thin film of ErSi_2 were used as model standards for determining coordination numbers and bond lengths. EXAFS data were processed following the recommendations of the International Committee [17].

In Fig. 1 we show Er L_{III} -edge EXAFS data $\chi(k)$ for representative samples and for the model compounds. The corresponding pseudo-radial-distribution functions

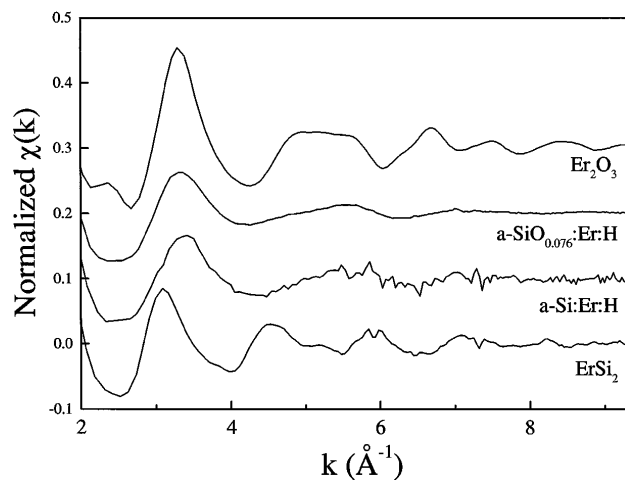


FIG. 1. Erbium L_{III} -edge EXAFS $\chi(k)$ of Er-doped *a*-Si:H and *a*-SiO_{0.076}:H (see text). The data from the reference samples are also shown. The upper curves were displaced for clarity.

(*p*-RDF) obtained from the Fourier transforms of $\chi(k)k^2$ between 2.1 and 8.6 \AA^{-1} are shown in Fig. 2. Samples with different oxygen contents in the range studied provided similar results. From the experimental curves it is clear that the average first neighbor shell of Er in *a*-Si:H is similar to that in Er_2O_3 , indicating that the first neighbors of Er are mostly O atoms. The maximum of the second peak is closer to the Er-Si separation in ErSi_2 and could result either from second neighbor shell scattering or from the presence of two different Er neighborhoods within the samples, one consisting of Er surrounded by O and the other consisting of Er surrounded by Si. We will show later that only the O neighborhood occurs. To obtain the average atomic separation r_0 , average coordination N_0 , and Debye-Waller factor σ_0^2 of the oxygen neighbor shell we calculated backtransforms of the isolated first peaks of the *p*-RDFs and compared them with EXAFS simulations using the amplitudes and phases obtained from the Er_2O_3 standard. The O shell parameters obtained for different samples are represented in Table I. Although the measurements were taken at room temperature, the values of the incremental Debye-Waller factors σ_0^2 were very small, typically in the range 0.003–0.005 \AA^2 relative to the Er_2O_3 standard. This indicates that the dispersion of the Er-O distances is small.

In Fig. 3 we represent the Er-O separation versus average coordination for samples with different O contents. The Er-O separation in the system is in the range 2.07 to 2.14 ± 0.02 \AA , significantly smaller than 2.26 \AA in Er_2O_3 and is minimum for the average coordination three within the experimental error. A decrease in the Er-O separation in Cz silicon relative to Er_2O_3 had already been reported [2], although it was 0.03 \AA , an order of magnitude smaller than the 0.2 \AA found in the present *a*-Si:H samples.

We have also calculated backtransforms of the *p*-RDF curves including the first and second peaks and compared them with EXAFS simulations using amplitude

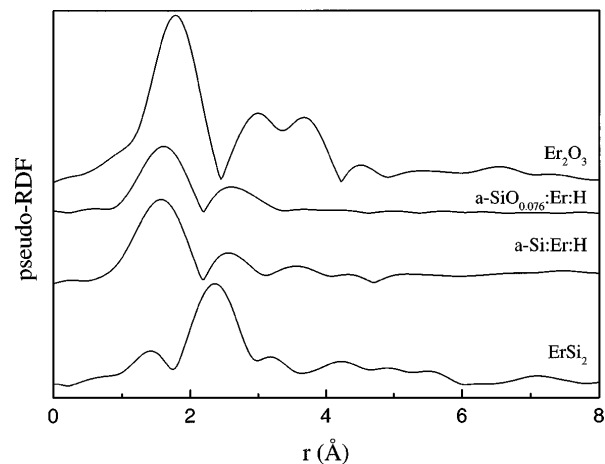


FIG. 2. Pseudo-RDF obtained from the k^2 weighted Fourier transforms of the data in Fig. 1.

TABLE I. Er first neighbor shell parameters average coordination N_O , average interatomic separation r_O , and Debye-Waller factor σ_O^2 assuming an O neighborhood obtained from EXAFS simulations for samples with different O concentrations. The estimated errors for N_O , r_O , and σ_O^2 are, respectively, 0.3, 0.02 Å, and 0.0004 Å².

[O]/[Si] (at. %)	N_O	r_O (Å)	σ_O^2 (Å ²)
0.2	2.0	2.137	0.0005
0.2	2.3	2.12	0.0004
0.3	2.4	2.18	0.0029
0.3	2.5	2.09	0.0006
0.3	2.5	2.14	0.0033
0.5	2.7	2.12	0.0072
0.9	2.7	2.05	0.0003
1.1	2.8	2.07	0.0027
3.2	3.3	2.14	0.0035
7.6	3.6	2.14	0.0097
Er ₂ O ₃	6	2.26	...

and phases from the Er₂O₃ and ErSi₂ standards to obtain Si shell parameters. The O shell parameters r_O , N_O , and σ_O^2 were fixed at the values obtained from the previous simulations. This procedure yielded the Si shell average atomic separations r_{Si} , average coordinations N_{Si} , and Debye-Waller factors σ_{Si}^2 . The result of both simulations for one sample is represented with the corresponding backtransforms (one and two peaks of the p -RDF) in Fig. 4. The calculated Er-Si atomic separations r_{Si} are between 3.10 and 3.17 ± 0.02 Å, up to 0.5 Å larger than in ErSi₂. This Er-Si interatomic distance is too large for direct bonding, but reasonable for Er-O-Si bonding. Moreover, N_{Si} increases with N_O and is in the range 5 to 10, reasonable values for a second neighbor shell. Together with the small Debye-Waller factors σ_O^2 of

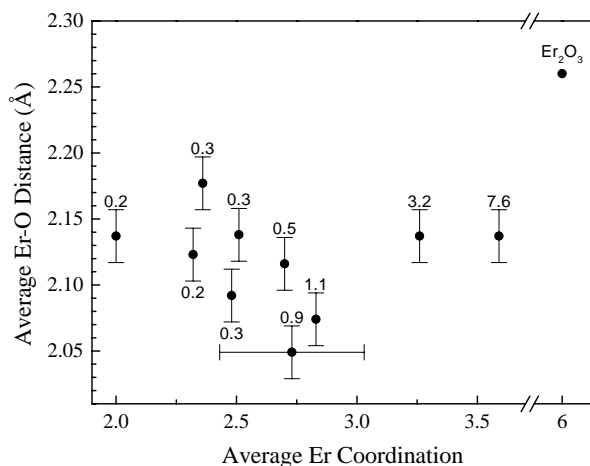


FIG. 3. Er-O separation in a -Si:H and a -SiO_x:H versus average Er coordination. The numbers indicate the [O]/[Si] atomic percentage. For clarity, only one x -axis error bar is represented. The values for Er₂O₃ are also indicated.

the O shell, this indicates that, in fact, only one family of Er sites occurs, the first Er neighbors being always O atoms. That in as-deposited luminescent Er-doped a -Si:H the immediate chemical neighborhood of Er is always composed of O atoms is a consequence of residual O contamination, normally found in plasma deposited a -Si:H, and the well-known gettering of O by Er in Si.

The data obtained allow us to formulate a model for Er incorporation in a -Si:H prepared in conventional plasma deposition systems, i.e., contaminated by residual O. Being a strong O getter, Er tends to be bonded to O. If the [O] is less than 3 times [Er], Er is bonded to virtually all the available O, forming ErO_δ complexes. The Er-O bonds have a highly ionic character, as the free energy is lowered by transferring electrons from Er to O. To fulfill the valence requirements of O, the ErO_δ complexes lower their energy further taking electrons from the host and becoming [ErO_δ]^{+3-2δ}. In fact, a mixture of complexes with different values of δ occurs. Acceptor character is expected when the average δ is greater than 1.5. We have found that the average δ is always greater than 2 in Er doped a -Si:H prepared in our plasma deposition system. Thus, the ErO_δ complexes behave as acceptors and p -type doping is observed. In pure FZ Si, however, O contamination levels are very small resulting in an average δ much smaller than 1. Then Er is a donor and n -type doping is observed.

The EXAFS data show that in a -SiO_x:H the value of δ saturates at approximately three, also when the Er-O interatomic distance is the shortest. The configurational energy is minimum for $\delta = 3$, when Er³⁺ transfers its three unpaired electrons to the neighboring O atoms. Not being constrained by crystalline long range order, Er will minimize the configurational energy by having three O first neighbors. Additional O atoms are then primarily bonded

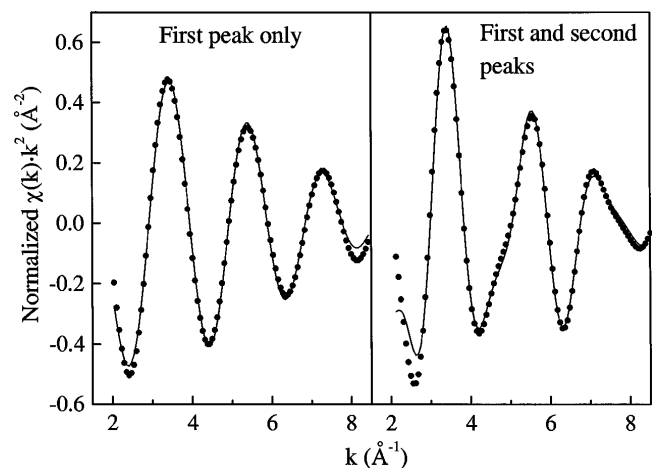


FIG. 4. Backtransforms of the first neighbor peak only and of the first and second neighbor peaks of the pseudo-RDF (dots) with the corresponding EXAFS simulations (lines) for a representative sample.

to Si, creating nonradiative recombination centers. As a result, the maximum p -type doping efficiency and maximum Er^{3+} luminescence yield occur when $\delta = 3$ and all the Er in the sample is in the form of $[\text{ErO}_3]^{13-}$ complexes. Indeed in our samples the maximum luminescence efficiency is found when $\delta \cong 3$ [14]. The short Er-O distances and their small dispersion indicate that the $[\text{ErO}_3]^{13-}$ complexes are strongly bonded internally and weakly coupled to the a -Si:H host. This reduces the probability of back-transfer of the luminescence excitation to the lattice by multiphonon processes, thus increasing the luminescence efficiency and reducing its temperature quenching [4,5]. It must also be noted that the 3-fold Er coordination in a -Si:H has a lower symmetry than the 6-fold coordination found in crystalline Si [2,11], increasing the probability of the normally forbidden intra- $4f$ transition.

Because of ErO_δ complex formation, the nature of Er doping in a -Si:H is different from FZ crystalline Si. Care must be taken when extending results from crystalline to amorphous silicon and n -type doping [10] cannot be assumed without a more detailed study. By the same reasoning, we believe that the p -type character of the crystalline samples of [6] was due to O contamination resulting in an average $\delta > 1.5$.

In conclusion, we have studied the chemical environment of erbium in samples of a -Si:H and a -SiO_x:H with up to 7.6 at. % O, which present Er^{3+} luminescence at room temperature as deposited. The general features deduced from EXAFS are the same in all samples: the first Er neighbor shell consists of O atoms and the second neighbor shell consists of Si. The average Er coordination increases with O concentration up to approximately three and saturates at this value. The average Er-O distance is significantly smaller than in Er_2O_3 and is minimum for coordination three. Er and O codoped a -Si:H samples with O concentration between 0.2 and 1.1 at. % O are p type. We propose a model in which Er forms $[\text{ErO}_\delta]^{+3-2\delta}$ complexes which behave as acceptors, whereas in FZ crystalline Si isolated Er^{3+} atoms (or perhaps $[\text{ErO}]^+$ complexes) present donor character. The $[\text{ErO}_\delta]^{+3-2\delta}$ complexes have lower symmetry than

the 6-fold coordinated Er^{3+} sites found in crystalline Si. They are strongly bonded internally and weakly coupled to the network, being the reason for the relatively high Er^{3+} luminescence yield in a -Si:H and small temperature quenching.

The authors are indebted to Dr. J. Michel for illuminating discussions and to Professor G.G. Kleiman and Professor C.E.T.G. da Silva for critical reading of the manuscript. RBS measurements were performed with M. Tabacniks at LAMFI, USP. The help of the staff at LNLS is gratefully acknowledged. This work was partially supported by CNPq, FAPESP, and PRONEX MCT/ME.

-
- [1] *Rare Earth Doped Semiconductors*, edited by G.S. Pomrenke, P.B. Klein, and D. W. Langer (Mater. Res. Soc., Pittsburgh, 1993), Vol. 301; *Rare Earth Doped Semiconductors II*, edited by A. Polman, S. Coffa, and R. Schwartz (Mater. Res. Soc., Pittsburgh, 1996), Vol. 422.
 - [2] D.L. Adler *et al.*, Appl. Phys. Lett. **61**, 2128 (1992).
 - [3] J. Michel *et al.*, J. Appl. Phys. **70**, 2672 (1991).
 - [4] M.S. Bressler *et al.*, Appl. Phys. Lett. **67**, 3599 (1995).
 - [5] J.H. Shin *et al.*, Appl. Phys. Lett. **68**, 997 (1996).
 - [6] H. Ennen *et al.*, Appl. Phys. Lett. **46**, 381 (1985).
 - [7] J.L. Benton *et al.*, J. Appl. Phys. **70**, 2667 (1991).
 - [8] S. Libertino *et al.*, J. Appl. Phys. **78**, 3867 (1995).
 - [9] J.H. Castilho *et al.*, Phys. Rev. B **43**, 8946 (1991).
 - [10] W. Fuhs *et al.*, Phys. Rev. B **56**, 9545 (1997).
 - [11] A. Terrasi *et al.*, Appl. Phys. Lett. **70**, 1712 (1997).
 - [12] U. Wahl *et al.*, Phys. Rev. Lett. **79**, 2069 (1997).
 - [13] V.F. Masterov *et al.*, Appl. Phys. Lett. **72**, 728 (1998).
 - [14] L.R. Tessler and A.C. Iñiguez, in *Amorphous and Microcrystalline Silicon Technology-1998* (Mater. Res. Soc., Pittsburgh, to be published).
 - [15] H. Tolentino *et al.*, J. Synchrotron Radiat. (to be published).
 - [16] L.R. Tessler *et al.*, in *Applications of Synchrotron Radiation Techniques to Materials Science IV* (Mater. Res. Soc., Pittsburgh, to be published).
 - [17] F.W. Lytle, D.E. Sayers, and E.A. Stern, Physica (Amsterdam) **158B**, 701 (1989).