

# Electron paramagnetic resonance of erbium doped silicon

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(Received 9 August 1996; accepted for publication 9 October 1996)

Electron paramagnetic resonance measurements have been made on samples of float zone silicon, implanted with  $10^{15}$  Er/cm<sup>2</sup>. One sample was coimplanted with oxygen to give an impurity concentration of  $10^{20}$  O/cm<sup>3</sup> and  $10^{19}$  Er/cm<sup>3</sup>. In this coimplanted sample, sharp lines are observed which are identified as arising from a single spin 1/2 Er<sup>3+</sup> center having a  $g$  tensor exhibiting monoclinic  $C_{1h}$  symmetry. The principal  $g$  values and tilt angle are  $g_1=0.80$ ,  $g_2=5.45$ ,  $g_3=12.60$ , and  $\tau=2.6^\circ$ . In the absence of O, the sharp lines are not observed. No Er<sup>3+</sup> cubic centers were detected in either sample. Possible structures for the center are discussed. © 1996 American Institute of Physics. [S0003-6951(96)02051-7]

Rare-earth doped semiconductors have attracted a great deal of attention because of their possible applications in optoelectronics.<sup>1–14</sup> The sharp intra  $4f$  shell transitions, which result from the  $4f$  electrons being shielded from the full effect of the crystal field, give rise to emissions which are largely independent of the surrounding environment. These emissions can be electrically excited which is important for device applications. Erbium doped silicon has attracted particular attention because the Er<sup>3+</sup> transition  $^4I_{13/2} \rightarrow ^4I_{15/2}$  at  $1.54 \mu\text{m}$  matches the minimum in the absorption of silica-based optical fibers. One of the major problems hampering future applications of Si:Er in optoelectronics is the strong quenching behavior of both the photo<sup>2</sup>- and electroluminescence<sup>1</sup> on going from 77 K to room temperature (RT). It has now been shown that the incorporation of other impurities, notably oxygen, can significantly increase the luminescence intensity<sup>2</sup> and help to suppress the temperature quenching of the luminescence.<sup>5</sup> Recently<sup>7–9</sup> RT electroluminescence has also been obtained from Er-doped Si  $p$ - $n$  diodes codoped with either O or F. Furthermore, it has been shown that, in spite of the low solid solubility<sup>10</sup> of Er in Si ( $\sim 2 \times 10^{16}/\text{cm}^3$  at  $900^\circ\text{C}$ ) higher Er concentrations (up to  $\sim 10^{20}/\text{cm}^3$ ) can be incorporated by chemical vapor deposition,<sup>11</sup> molecular beam epitaxy,<sup>12</sup> or by using the solid phase epitaxial regrowth of an amorphous layer produced by Er implantation.<sup>13</sup> Codoping with O or F allows the suppression of Er segregation at the moving crystal-amorphous interface and the regrowth of thick ( $\sim 2 \mu\text{m}$ ) recrystallized layers.<sup>14</sup> All of these beneficial effects have been attributed<sup>6</sup> to modifications in the local environment of Er produced by the codopants. Although strong evidence of the modifications of the electrical properties of Er in Si in the presence of O (or F) has been provided,<sup>4,15,16</sup> there is little experimental information on how the site location and coordination of Er in Si is altered by the presence of other impurities.

In this letter, we report on the first electron paramagnetic resonance (EPR) measurements made on Er implanted float

zone (FZ) Si coimplanted with O. We show that the presence of oxygen has a pronounced effect on the type of EPR signal observed. We believe that the presence of O is important in stabilizing well defined sites for Er<sup>3+</sup> ions within the Si host.

Samples of  $n$ -type (100) wafers (resistivity  $70 \Omega \text{ cm}$ ) were implanted with  $1 \times 10^{15}$  Er/cm<sup>2</sup> at various energies (in the range  $0.5$ – $5 \text{ MeV}$ ) and at  $77 \text{ K}$ . One sample was coimplanted with oxygen such that the impurity concentration was  $1 \times 10^{19}$  Er/cm<sup>3</sup> and  $1 \times 10^{20}$  O/cm<sup>3</sup> (this sample will be referred to as the O-rich sample). After implantation, a  $2\text{-}\mu\text{m}$ -thick amorphous layer is formed. A subsequent solid phase epitaxy at  $620^\circ\text{C}$  was then performed to restore the crystallinity and eventually a treatment at  $900^\circ\text{C}$  for  $30 \text{ s}$  under  $\text{N}_2$  flux was made. The O-rich sample has been shown<sup>16</sup> to give room temperature luminescence at  $1.54 \mu\text{m}$ , characteristic of Er<sup>3+</sup>, while in the noncoimplanted sample no RT luminescence was observed. Further details of the sample preparation and luminescence properties can be found elsewhere.<sup>16</sup> EPR measurements were performed in a modified Bruker EPR spectrometer with  $100 \text{ kHz}$  field modulation using a TE<sub>102</sub> rectangular cavity. The frequency of the microwaves was approximately  $9.228 \text{ GHz}$  and the samples were cooled to helium temperatures using an Oxford Instruments flow cryostat.

From the noncoimplanted sample, only a broad featureless resonance at a  $g$  value of  $10.5$ , with peak-to-peak width of  $23 \text{ mT}$  was detected. However, in the case of the O-rich sample sharp EPR spectra were observed. This sample was mounted with a  $[110]$  direction vertical, in order that the angular dependence of the spectrum could be recorded by rotation of the field in the  $(1\bar{1}0)$  plane of the sample. However, as will be seen from the discussion below, a slight misalignment of the sample occurred so that the magnetic field was not wholly in the  $(1\bar{1}0)$  plane. This misalignment is small ( $\sim 2^\circ$ ) and its effect has been taken into account in the analysis and does not affect the conclusions. Shown in Fig. 1 is the EPR spectrum from the O-rich sample at about  $10 \text{ K}$  with the magnetic field (a) nearly parallel to the  $[001]$  direction and (b) nearly parallel to the  $[110]$  direction. Figure

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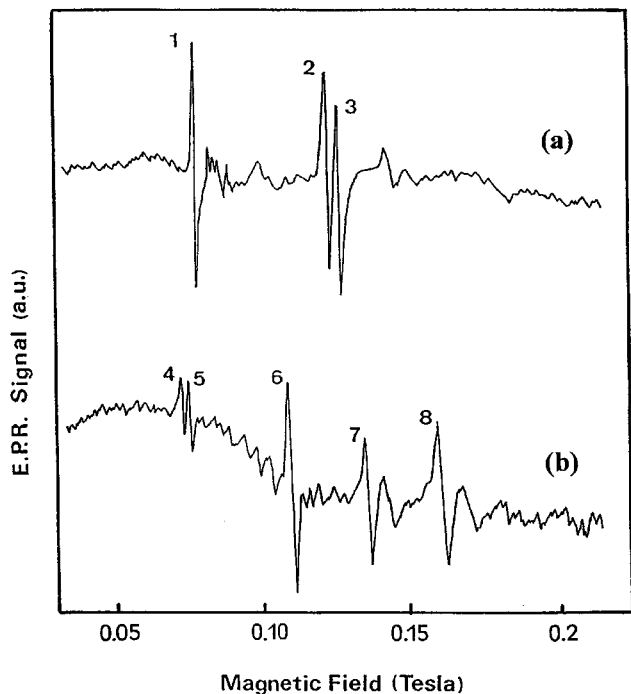


FIG. 1. Electron paramagnetic resonance spectrum of the O-rich sample measured at 10 K and at a microwave frequency of 9.228 GHz with the magnetic field (a) near the [001] direction and (b) near the [110] direction.

1(a) shows three intense lines, two of which are nearly coincident, along with a number of other weaker lines. The peak-to-peak linewidths of the most intense lines are 1.2 (line 1) and 1.9 mT (lines 2 and 3). The intensities of these lines are strongly temperature dependent and the spectrum is unobservable above about 20 K. When the field is nearly parallel to the [110] direction, the spectrum is as shown in Fig. 1(b). In Fig. 2, we show the angular dependence of all the intense lines observed. No isotropic lines are observed in the field range shown. Figure 2 shows that the complete angular dependence of the resonances can be fitted to that of a single center using the effective spin Hamiltonian<sup>17</sup>

$$H = \mu_B \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} \quad (1)$$

with spin  $S = 1/2$  and a  $g$  tensor exhibiting monoclinic  $C_{1h}$  symmetry. The principal  $g$  values are  $g_1 = 0.80$ ,  $g_2 = 5.45$ , and  $g_3 = 12.60$  and  $\tau$ , which is the angle the 1-axis is tilted away from nearest  $\langle 111 \rangle$  direction away from the  $\langle 001 \rangle$  direction, is  $2.6^\circ$ . The 2-axis is in a  $\langle 110 \rangle$  direction and both the 1- and 3-axis lie in the plane perpendicular to it. The  $C_{1h}$  point group has twelve inequivalent magnetic sites which reduce to seven when the field is confined to the  $(1\bar{1}0)$  plane and is further reduced to two, three, and four when the field is along the [001], [111], and [110] directions, respectively. Misalignment causes lines 2 and 3 in Fig. 1(a) and lines 4 and 5 in Fig. 1(b) to be noncoincident. Line 7 is the superposition of two accidentally coincident lines; one of which is split from line 8 as a result of the misalignment and whereas the other is a line unaffected by the misalignment.

The nature of this center is determined by the paramagnetic ground state and the crystal field. The possibility that the EPR resonances originate from  $\text{Er}^{2+}$ , can be ruled out since for a non-Kramers' ion a different Hamiltonian<sup>17</sup> to

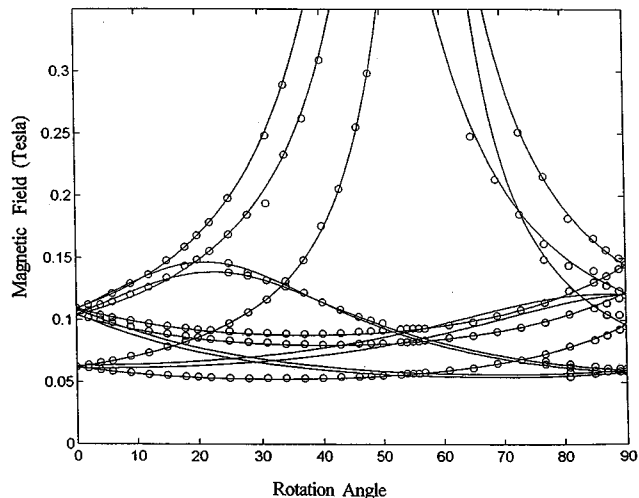


FIG. 2. Angular dependence of the observed resonances (open circles) from the O-rich sample with the field rotated in a plane near to the  $(1\bar{1}0)$  plane. The fit (solid lines) is obtained using the parameters given in the text and takes into account of the slight misorientation of the sample.

that used in Eq. (1) would have to be used. Furthermore, the similarity of the principal  $g$  values to those reported<sup>18–22</sup> for some  $\text{Er}^{3+}$  centers strongly suggest that the resonances are due to  $\text{Er}^{3+}$  although the hyperfine lines associated with the 23% abundant  $\text{Er}^{167}$  isotope with nuclear spin  $I = 7/2$  could not be clearly resolved above the noise level. Since  $\text{Er}^{3+}$  has eleven  $4f$  electrons, the ground state in a crystal field of any symmetry will be at least a doublet in accordance with Kramers' theorem. In the case of a cubic crystal field, the sixteen-fold degenerate ground state will split into five levels<sup>17</sup> given by  $\Gamma_6 + \Gamma_7 + 3\Gamma_8$ . Both the  $\Gamma_6$  and  $\Gamma_7$  representations are doublets with effective spin  $S = 1/2$  whereas the  $\Gamma_8$  representation is a quartet with  $S = 3/2$ . The relative positions of these levels have been determined by Lea, Leask, and Wolf<sup>23</sup> in terms of a parameter  $x$ , which is related to the ratio of the fourth to sixth order crystal field terms. With the labeling appropriate to  $T_d$  symmetry, they show, that a  $\Gamma_7$  level lies lowest for  $-1 < x < -0.46$ ,  $\Gamma_6$  for  $-0.46 < x < 0.58$ , and  $\Gamma_8$  for  $x > 0.58$ . The  $g$  values in cubic symmetry<sup>18</sup> for  $\Gamma_7$  and  $\Gamma_6$  are 6.0 and 6.8, respectively. If a lower symmetry crystal field compared to the parent cubic field is present, then the trace of the  $g$  tensor will be conserved<sup>19–22</sup> such that

$$g_{\text{cubic}} = 1/3(g_1 + g_2 + g_3). \quad (2)$$

Using the values previously obtained in the fitting gives, via Eq. (2), a cubic  $g$  value of 6.28. This suggests that the parent cubic ground state may have a  $\Gamma_7$  representation, which would imply that  $x$  is negative. Lea *et al.*<sup>23</sup> have shown that for  $\text{Er}^{3+}$  a negative value of  $x$  can arise if the ion is tetrahedrally coordinated (or cubically coordinated) but that  $x$  is positive only if the coordination is octahedral. The observed monoclinic symmetry may therefore arise from the distortion of a tetrahedrally coordinated  $\text{Er}^{3+}$  complex.

A further indication about the nature of the environment of the erbium center may be obtained by a comparison with the EPR results<sup>22</sup> of  $\text{Er}^{3+}$  in  $\text{Y}_2\text{O}_3$  which possesses the same crystal structure as  $\text{Er}_2\text{O}_3$ . There are two sites occupied by

the trivalent ion, one of which exhibits trigonal symmetry and the other orthorhombic symmetry. In both sites the trivalent ion is surrounded by six O atoms approximately at the corners of a cube. In the case of the trigonal site, the principal  $g$  values are  $g_{\parallel}=12.176$  and  $g_{\perp}=3.319$ . In the case of the orthorhombic site the principal  $g$  values are  $g_z=12.314$ ,  $g_x=1.645$ , and  $g_y=4.892$ . It is interesting to note that not only is the average  $g$  value in both cases the same as the value we obtain, but also the principal  $g$  values for the orthorhombic site are similar to those obtained. Furthermore, both of these sites may be regarded as originating from a distorted tetrahedral structure so it is reasonable for the parent cubic field to have a  $\Gamma_7$  ground state as suggested earlier.

The implication of the similarities noted above is that the dominant  $\text{Er}^{3+}$  signal seen by EPR arises from the  $\text{Er}^{3+}$  surrounded by six O atoms in a configuration similar to that in the orthorhombic site in  $\text{Er}_2\text{O}_3$ . This is consistent with our findings that the center is only observed when the Er is coimplanted with O. It is also consistent with the preliminary EXAFS analysis<sup>24</sup> on our samples which indicate that Er has oxygen atoms as nearest neighbors, in a fashion similar to what was observed by Adler *et al.*<sup>6</sup> Hence the spectrum that we observe may arise from an erbium/oxygen complex with a structure similar to that of the orthorhombic site of  $\text{Er}_2\text{O}_3$  embedded with well defined orientations within the Si lattice. The results given so far do not indicate whether the Er resides on a Si substitutional or interstitial site. We have therefore performed Rutherford backscattering spectrometry/channeling measurements on these samples and we can exclude the possibility that Er is residing on a substitutional site. It is interesting to note that theoretical calculations by Needels *et al.*<sup>25</sup> have identified the tetrahedral interstitial site for Er in Si as the most energetically favorable position (apart from the erbium silicide). These calculations, however, were performed for Er incorporated into pure silicon with no extra impurity. On the basis of our data, we suggest that the structure may consist of an Er atom residing in an interstitial site within the Si lattice with six O atoms surrounding the Er in a fashion similar to that of the orthorhombic site in  $\text{Er}_2\text{O}_3$ . It can therefore be proposed that one of the consequences of the interaction with O is the stabilization of Er atoms into the tetrahedral site by avoiding precipitation and silicide formation. This enhances the effective solubility and produces more defined Er sites.

In conclusion, EPR measurements have shown that Er incorporation in Si with a concomitant O codoping produces paramagnetic  $\text{Er}^{3+}$  ions sitting in well defined lattice sites

exhibiting monoclinic symmetry. We believe that one of the roles of the codopant is that of stabilizing this configuration and preventing precipitation.

Work in Catania was partially supported by the Esprit Project SCOOP.

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