Electrical activity of Er and Er-O centers in silicon

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Spin-polarized density functional calculations are carried out on Er and Er-oxygen defects in crystalline Si. We find that the interstitial site is favored but the diffusion barrier of Er_i is only 1.9 eV, and inevitably Er_i forms complexes with impurities and intrinsic defects following postimplantation anneals. Er forms many defects with oxygen, and we argue that optically inactive $Er_2Si_2O_7$ precipitates coexist alongside active Er_i-O_n clusters. The latter are unstable when neutral and possess a range of second donor levels around $E_c - 0.1$ eV. We suggest that those with either deep levels or very shallow ones are inefficient room-temperature optical centers. The Er_i-O_3 defect has a donor level and symmetry consistent with observations of the room-temperature luminescence intensity and low-temperature crystal-field splitting.

I. INTRODUCTION

There has been a continued interest in obtaining efficient room-temperature light emission from Si. Radiative recombination probabilities (internal) in float-zone (FZ)-Si of up to 20% can occur, provided that the material is free from impurities and defects and possesses a properly passivated surface.[1] Alternative routes for room-temperature light emission and especially electroluminescence have involved plastically deformed Si (Ref. 2) or the implantation of rare-earth dopants such as Er into crystalline Si (Ref. 3–5) or nano-Si, where laser action has been demonstrated.[6] However, in none of these cases is there a detailed understanding of the processes leading to light emission.

Studies of the fine structure of the 0.803 eV photoluminescence (PL) due to Er in implanted FZ-Si (Refs. 7–10) have revealed a dominant "cubic" Er-related optical center. In this center, a crystal field of apparent tetrahedral symmetry has split the $^4I_{15/2}$ ground and $^4I_{13/2}$ excited states into five and three states, respectively, leading to five PL lines at low temperature with separation of about 10 meV. This suggests a defect with T_d symmetry with an Er atom located either at a substitutional or T_d interstitial site. Channeling experiments[11] have given support for a tetrahedral interstitial location, although extended x-ray fluorescence spectroscopy (EXAFS) on FZ-Si implanted with Er gives a coordination shell of 12 Si atoms surrounding Er at a distance of 3.00 Å.[12] Whereas the Er-Si distance is as expected for Er defects in Si,[13] the coordination number of 12 is extraordinary. One would have to think in terms of a pentavacancy with Er centrally sited to obtain such a coordination, but then the Er-Si separation would not be correct. However, we believe the EXAFS data actually refers to a precipitate, possibly a microprecipitate, of bulk metallic $ErSi_2$, as this possesses the same coordination of 12 Si atoms surrounding each Er and Er-Si bond lengths of 3.0 Å.[14] Figure 1 shows the Si environment to Er in bulk $ErSi_2$. This precipitate being metallic would degrade the luminescence. However, light emission arising from FZ-Si:Er is not of great interest, as strong temperature quenching effects lead to negligible emission at temperatures higher than 150 K. The main interest has been centered on oxygen-rich Czochralski (Cz)-Si, where the presence of oxygen enables the emission to persist to room temperatures.[8,15]

Many different Er-O related centers are detected optically with two dominant centers, O1 and O2, having axial symmetry.[10] This symmetry is also found in electron paramagnetic resonance (EPR) investigations[16,17] and not inconsistent with EXAFS on both molecular beam epitaxy (MBE)-grown and implanted Si, which show that each Er is surrounded by 5.5–6 oxygen atoms at a distance of 2.24 Å, a well-defined bond angle of 135°, and Er-Si distances ~3.6 Å.[18] The concentration of optical centers is, however,
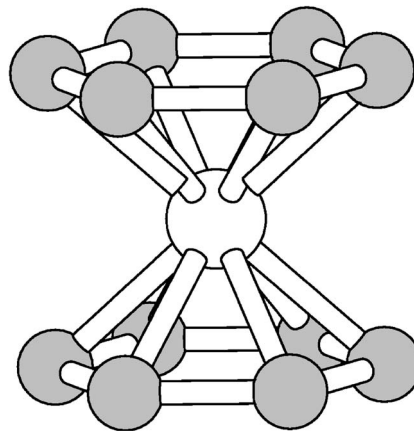

FIG. 1. Environment of Er in $ErSi_2$. Er (white) has 12 Si (gray) neighbors with an Er-Si length of 3 Å consistent with EXAFS measurements.

less than $\sim$1% of the total Er concentration[4], and while EPR and EXAFS have given information about the dominant Er defects, similar microscopic details of the optical centers are lacking.

The PL excitation mechanism of rare-earth (RE) ions in semiconductors is thought to involve several reaction stages where back or branching reactions can limit the light intensity.[19] The first stage is the optical or electrical generation of carriers. This is followed by the capture of an electron in an Er-related donor level at E_d. As we shall see, it is more likely that Er defects in Si possess shallow donors rather than acceptor levels. Then a photogenerated or injected hole at the top of the valence band is captured by the neutral Er donor. This releases an energy $E_d - E_v$ related to the distance of the donor level to the valence band, and this energy is transferred, via an Auger mechanism, to the Er atom exciting it into the $^4I_{13/2}$ state with the difference in energy, $E_b = E_d - E_v - 0.803$ eV, being released as heat. In order for E_b to be positive, E_d must be within 0.33 eV of E_c and defects with deeper levels are optically inactive. Hence, if we can calculate the donor levels of candidate defects, those with levels deeper than 0.33 eV from E_c can be excluded as optical centers. This excitation process is very efficient with a cross section for electron-hole recombination of about 3 $\times 10^{-15}$ cm^2, seven orders of magnitude greater than that for direct photon absorption and two orders of magnitude greater than for impact excitation.[5]

The excited Er atom may relax to the ground state either through radiative emission, or nonradiatively by back transfer, or by other Auger processes. For efficient emission, the nonradiative processes must be suppressed. It appears that in different temperature regimes, different quenching processes operate. Above 100 K, deexcitation of the $^4I_{13/2}$ state occurs by a back reaction where energy is transferred by exciting an electron in the valence band to the empty Er-related donor level, followed by thermalization of the occupied donor level. This would be activated either with an energy E_b or $E_c - E_d$. There is some controversy whether the observed activation energy of 0.15 eV reflects E_b or $E_c - E_d$,[5,19] but since their sum has to be equal to about 0.33 eV, then the donor level is between 0.15 and 0.2 eV below E_c. This is close to levels found by deep-level transient spectroscopy (DLTS) on Er[15,20] and Tb-implanted material.[21] At low temperatures, deexcitation occurs by Auger processes involving free carriers or carriers bound to other impurities or Er-related defects.[5,19,22]

In order to understand in greater detail the electrical levels of Er defects, we have carried out density functional calculations on both Er and Er-O point defects as well as bulk ErSi$_2$ and Er$_2$O$_3$. We have also considered the thermal stability of the defects, bearing in mind that implanted samples are usually annealed at temperatures around 900 °C to eliminate implantation damage.

II. PREVIOUS THEORETICAL WORK

Although there have been several other theoretical investigations of Er defects in Si, none have examined in detail their electrical activities.[13,23–27] Most of the calculations have been made with a local density functional theory where the $4f$ shell of Er^{3+} has been frozen and contains 11 electrons appropriate for the $^4I_{15/2}$ ground and $^4I_{13/2}$ excited states. This seems to be a reasonable assumption given that there is scant evidence for optical spectra arising from Er^{2+} in any semiconductor. One exception seems to be Eu in nanocrystals of ZnS[28]—a strongly ionic II-VI compound where Er^{2+} probably replaces Zn. It does not follow that a calculation that includes the f shell as part of the valence shell is superior to one where the f shell is frozen, as the very strong correlation effects in the f shell may not be treated properly.

The first investigations found that Er prefers to lie at a tetrahedral interstitial (T_i) site.[23] A number of other investigations have supported this[25,26] although some find substitutional Er to be more stable.[13,29] When oxygen is involved, several authors found that Er then lies at a "hexagonal" H_i interstitial site.[13,25] Most work[26] has sought to find structures where six oxygen atoms are arranged around Er, hence determining the defect responsible for the EXAFS data. However, it must be remembered that such defects are probably not responsible for the optical activity, although they must be among the most dominant Er-related centers. In fact, we shall suggest below that these defects are actually precipitates and not point defects at all. As for the electronic structure, only Wan *et al.*[25] report that the effect of oxygen is to move the Er-related gap level closer to the conduction band. This is a finding that we shall discuss below.

III. METHOD

We use an *ab initio* local spin density functional code (AIMPRO) and 64- and 96–atom supercells with MP-2[3] k-point sampling.[30] Dual-space separable pseudopotentials[31] with a frozen-f core are used together with a nonlinear core correction. Thus, irrespective of doping, the f shell of Er contains a fixed number of 11 electrons. This does not imply that there are no Er-related gap levels. The size, location, and electronegativity of Er may lead to gap levels occupied by valence electrons. The basis consists of atom-centered s, p, and d Gaussian orbitals for Si and oxygen, and an additional set of f orbitals for Er. The exponents for the orbitals have been optimized for each element by considering a solid phase with ErN used for Er.[32] Previous studies have been made for rare-earth defects in GaN,[32] SiC,[33] and GaAs.[34] The calculated lattice parameter and bulk modulus of Si were found to be 5.40 Å (exp. 5.43 Å), and 97 GPa (exp. 97.8 GPa), respectively.

The formation energy E_f of a defect in charge state q is defined by

$$E_f = E_{d,q} - \sum_i n_i \mu_i + q E_F,$$

where $E_{d,q}$ is the energy of the defective supercell, with net charge q, containing n_i atoms of i species with chemical potential μ_i. The last term takes into account the effect due to charged defects, and E_F is the Fermi energy relative to the valence-band top (E_v). The chemical potential of Er is taken from the solid ErSi$_2$. The formation energy can be used to estimate the equilibrium solubility of a species but we have

not found it a reliable guide to electrical levels. These are best found by comparing the electron affinities and ionization energies of the defects with those of standard defects with known electrical levels. Such a method can give donor and second donor levels of chalcogen defects in Si to within 0.08 eV.[35] Here, we used substitutional sulfur, having single- and double-donor levels located at $E_c - 0.29$ eV and $E_c - 0.59$ eV, respectively,[36] as a standard defect. To ascertain deep acceptor levels, we used substitutional nickel with a $(-/0)$ level at $E_c - 0.47$ eV.[37]

IV. RESULTS

A. Isolated erbium defects

We investigated the possible locations for an isolated Er atom, namely substitutional (T_s) and interstitial Er (Er_i) located at the tetrahedral (T_i) and "hexagonal" (H_i) sites. We find, in agreement with earlier investigations,[23] the T_i site as the most stable with a formation energy 0.7 eV lower than T_s and 1.9 eV lower than H_i. The formation energy of Er_i with respect to $ErSi_2$ is 3.54 eV, which gives a negligible equilibrium solubility at 900 °C. The electronic structure reveals a gap-related triplet t_2 level close to E_c. The electronic configuration of the neutral defect is t_2^2 and similar to Al_i,[38] except the level is very close to E_c. Indeed, we find the first $(0/+)$ level lying above E_c while the $(+/++)$ level is placed at $E_c - 0.34$ eV. The second donor level can be compared with the $(+/++)$ level of Al at $E_v + 0.17$, which has a similar structure.[39] Thus the neutral state of Er_i is not stable and spontaneously ionizes to Er_i^+ or Er_i^{++}. The donor character of Er is in agreement with experiment.[5] Although a Jahn-Teller distortion might be expected, we find a negligible displacement from the T_d site.

We then investigated the diffusion barrier for Er_i. We find the H_i site to be the saddle point for a diffusion path between two T_i sites. This gives the diffusion barrier to be about 1.9 eV for the neutral defect and 1.81 and 1.85 eV for the singly and doubly positive charged defects, respectively. These imply a relatively easy diffusion of Er through Si, and show that with 900 °C anneals, typically used to remove implantation damage, Er_i will diffuse and form complexes with implantation debris and common impurities such as oxygen. Our conclusion is that Er_i is an unstable defect that has probably escaped detection so far. All observed Er-related defects are then complexes with impurities, although it is also possible that implantation generated defects like vacancies that are also complex with Er_i, creating a substitutional defect.

Substitutional Er has the configuration $a_1^2 t_2^5$, analogous with substitutional Al except that the Er-related t_2 level lies around midgap. We place the $(-/0)$, $(0/+)$, and $(+/++)$ levels at $E_c - 0.59$, $E_c - 0.66$, and $E_c - 1.02$ eV. Several deep Er-related levels are found in DLTS experiments when FZ-Si is implanted with Er (Ref. 15) and are possibly due to Er-vacancy defects. As these levels lie around midgap, they are too deep to excite the f-shell luminescence. Thus our calculations find neither isolated substitutional nor interstitial Er to be candidates for prominent optical centers in FZ-Si.

B. Erbium-oxygen complexes

We now investigate Er-O defects. Interstitial oxygen is known to be located near a bond center position between two
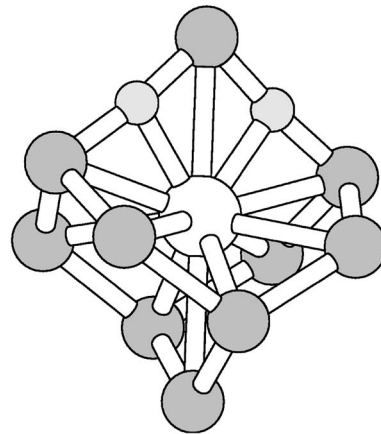

FIG. 2. Structure of Er at a tetrahedral interstitial site surrounded by two oxygen atoms with C_{2v} symmetry. The large white atom is Er, the gray atoms are Si, and the small atoms are oxygen.

Si atoms (BC) and diffuses in the Si lattice at temperatures above about 400 °C with a diffusion barrier of about 2.5 eV.[40] Hence, both Er_i^+ and O are mobile at the temperatures used to eliminate implantation damage, and it is highly likely that Er-O defects can be formed.

With Er at an interstitial tetrahedral site, there are two obvious Er_i-O defects with C_{3v} or C_{1h} symmetry, depending on whether the axial bond center is occupied by oxygen. The latter has a lower energy with an Er_i-O binding energy of 1.13 eV. Assuming equilibrium between Er_i, O, and Er_i-O, the magnitude of the binding energy implies a concentration of Er-O pairs of

$$ N_{\text{Er-O}} = \frac{N_{\text{Er}} N_{\text{O}}}{N_{\text{O}} + \frac{1}{6} N_{\text{Si}} \exp(-E_b/kT)}, $$

when $N_{\text{Er}} \ll N_{\text{O}}$. Here, N_{Si} is the density of Si sites and a factor of 6 arises from the orientational degeneracy of the Er-O pair. For N_{O} between 10^{17} and 10^{19} cm^{-3}, we find, at 900 °C, between about 10% and 90% of Er to be bound as Er-O defects. This shows that the properties of Er in FZ-Si can be expected to be quite different from Cz-Si where Er-O defects are dominant.

The Er_i-Si distances vary between 2.57 and 2.91 Å and the Er_i-O distance is 2.18 Å. These are similar to those given in previous studies.[13,26] The presence of the oxygen displaces the Er-related donor level upwards, and the defect is only stable when charged. We place the $(+/++)$ level at $E_c - 0.29$ eV.

A second oxygen atom can be placed next to the first, making a [110] oxygen chain with approximate C_{2v} symmetry about Er, as shown in Fig. 2. The Er-O bond lengths are still 2.18 Å. A defect with this symmetry has been reported before[41] and also recently has been detected in sublimation-grown Si:Er by Zeeman spectroscopy.[42] The binding energy of the second oxygen atom with Er_i-O is 1.15 eV and the $(+/++)$ level is now found at $E_c - 0.18$ eV.

A third oxygen atom can be placed so that the defect has a trigonal symmetry (Fig. 3). The three Er-O distances are 2.25–2.26 Å and the $(+/++)$ level is now at $E_c - 0.11$ eV.
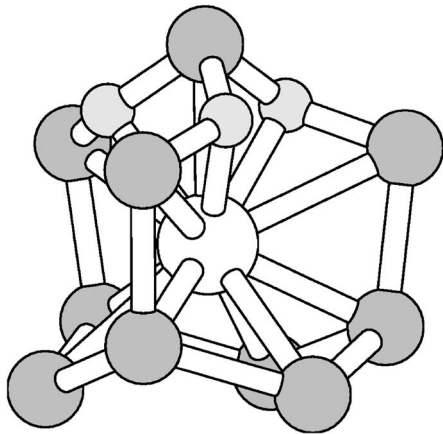
FIG. 3. Structure of Er at a tetrahedral interstitial site surrounded by three oxygen atoms with C_3 symmetry. The large white atom is Er, the gray atoms are Si, and the small atoms are oxygen.

The crystal-field splitting of a dominant PL center in Cz-Si:Er also has this symmetry.[10] Further oxygen atoms can be added with similar binding energies but six oxygen atoms push the $(+/++)$ level into the conduction band.

It appears that defects with many oxygen atoms can be formed. The precise distribution depends on the oxygen and erbium concentrations and the annealing conditions. The larger complexes with one Er atom have shallower donor levels.

We also investigated the stability for Er at a H_i site when surrounded by one to six oxygen neighbors.[25,43] Such complexes were less stable than those with Er at a T_i site. Similarly, Er at the center of an oxygenated hexavacancy[17] leads to unrealistically long Er-O lengths and is unstable with Er moving to form fewer but stronger Er-O bonds. As a consequence, the defect possesses deep levels and would not be optically active.

Although many Er-O_6 point defects can be constructed, it turns out that none of them have Er-Si lengths as long as 3.6 Å: most have Er-Si lengths around 3 Å. Indeed, EXAFS data on Er introduced via the melt into SiO_2 reveals Er surrounded by 5.5–6 O atoms with Er-O distances of 2.28 Å and an Er-Si distance of only 3.11 Å.[4] This shows that the explanation of the EXAFS data on Si:Er requires special defects that are not found in Er-doped SiO_2. This would rule out a pointlike defect where Er is surrounded by six oxygen atoms. We suggest that the defects detected in EXAFS are clusters or microprecipitates of $Er_2Si_2O_7$. In this solid each Er is surrounded by six O atoms at distances of 2.2 Å. Each oxygen sits at a corner of a SiO_2 tetrahedron with four Er-Si lengths of 3.35–3.6 Å and Er-O-Si angles between 125° and 135°.[44] These are close to the Er-O and Er-Si lengths observed in the EXAFS studies.[12,18] The structure of the solid is shown in Fig. 4. Each Er ion is located in channels of SiO_2 tetrahedra. The band gap of this solid[45] is at least 4 eV, and thus the Er can only be excited directly, and not by a carrier-mediated mechanism. Consequently, such precipitates degrade the optical properties of Er in Si.

V. SUMMARY AND DISCUSSION

Our calculations have revealed new results for the structure and electrical activity of Er and Er-O defects in Si. We
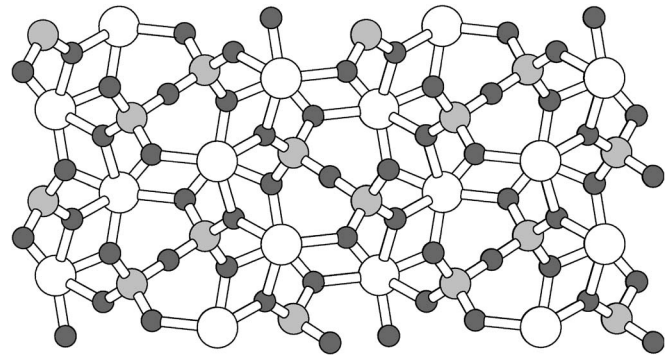

FIG. 4. Structure of $Er_2Si_2O_7$. There are six oxygen (black) neighbors to Er (large white) at 2.2 Å and four Si (gray) neighbors between 3.35 and 3.6 Å, consistent with EXAFS measurements.

find in agreement with several earlier studies that the tetrahedral interstitial site is the most stable site for Er in Si. However, we also find that the diffusion barrier for Er to move to the H site is very low around 1.8 eV, and hence the interstitial defect would not survive postimplantation anneals around 900 °C. We find a $(+/++)$ donor level around $E_c -0.34$ eV. The substitutional defect, which could arise when interstitial Er traps a vacancy, has midgap levels that are too deep to excite the f-shell luminescence. Neither substitutional Er nor interstitial Er can be responsible for the PL in FZ-Si doped with Er, which must be due to a complex of Er with another impurity or intrinsic defect.

The binding energy of Er_i^{++} with oxygen is about 1 eV for each of up to six O atoms around Er. Large Er-O complexes are then to be expected in oxygen-rich material. The formation energy of clusters with three or four oxygen atoms is lower than that of $ErSi_2$, implying that codoping oxidizes $ErSi_2$ precipitates, probably leading to $Er_2Si_2O_7$ precipitates along with Er_iO_n clusters. The precipitates have a structure consistent with EXAFS studies but are optically inactive, and previous studies attempting to link such defects to the optical centers are misguided. If the precipitates were large enough, they could be detected by electron microscopy.

Er_i-O_n clusters are only stable when ionized and have $(+/++)$ levels that become shallower with increasing numbers of oxygen atoms similar to thermal donors. Indeed they are similar to thermal donors found in Al-doped Cz-Si.[46] Families of rare-earth-related donors have been found from Hall effect studies and are associated with levels around $E_c -0.07$ eV.[47] These studies demonstrate the shallow donor nature of Er-O defects. However, it is unclear whether these are single-donor $(0/+)$ or double-donor $(+/++)$ levels. The theory given here suggests they are the latter but single-donor levels cannot be excluded, given the errors in the theoretical estimates of these levels. However, they are too shallow to participate in room-temperature luminescence, bearing in mind that the donor level that appears responsible for the room-temperature luminescence appears to be around $E_c -0.15$ eV.[5]

We can expect that Er_i-O_n defects with donor levels deeper than about $E_c -0.26$ eV will not participate in the

f-shell luminescence since then the back transfer energy E_b is so small and the PL would be quenched at low temperatures. On the other hand, the larger Er-O defects have very shallow donor levels E_d and hence would easily ionize at room temperature before hole capture could occur and before excitation of the f shell. Such defects would also be inefficient optical centers. There is then an optimum Er-O defect that leads to the most efficient luminescence at a particular temperature. This may be the Er$_i$-O$_3$ center as its donor level is close to the observed $E_c - 0.15$ eV level and its trigonal symmetry consistent with low-temperature crystal-field split-

ting data. However, at different temperatures, different Er-O defects could dominate the optical emission.

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