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Optical and electrical properties of vanadium and erbium in 4*H*-SiC

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Local-density-functional calculations are carried out on vanadium and erbium centers in 4*H*-SiC. Particular attention is paid to their electrical and optical properties. We find that both V and Er lie at Si sites and can exist in three charge states with deep donor and acceptor levels. While isolated V_{Si} possesses intra-*d* and ionization induced optical transitions around 0.94 and 2.9 eV respectively, the intense and temperature stable intra-*f* optical transitions due to Er are unlikely to be due to an *isolated* Er defect. It is suggested that both impurities can trap H and N forming complexes which may limit the electrical efficiency of V and act as Er related exciton traps.

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I. INTRODUCTION

Transition-metal impurities in semiconductors are important because they can possess multiple charge states and are efficient carrier traps. Moreover, they often give rise to internal intra-*d* optical transitions. Rare-earth dopants on the other hand are of increasing interest because their intra-*f* luminescence is stable to high temperatures in wide bandgap materials.[1] They are not noted for introducing deep levels. Recently, however, it has been reported that the intra-*f* luminescence of Er in SiC is stable to around ~180 °C and that the defect has a deep donor level.[2–5] It is then of interest to compare the properties of a transition metal such as vanadium, whose internal transition is also stable at room temperature,[6] with the rare-earth Er impurity. We shall argue below that both possess three charge states and although their optical properties derive from internal transitions, it is unlikely that isolated Er, in contrast with V, is the optical center that is observed. While the *d* orbitals on V are known to interact strongly with surrounding atoms, the *f* shell is almost decoupled. Russel-Saunders L-S coupling within the *f* shell leads to a $^4I_{15/2}$ ground state separated from an $^4I_{13/2}$ excited state by ~0.803 eV. The surrounding crystal field splits the ground state into a number of levels with separation ~4 meV (Ref. 7) as well as introducing parity breaking terms leading to dipole allowed intra-*f* transitions.

Similarly, crystal field and covalent effects split the d^1 manifold of V into a singly occupied e level lying ~0.94 eV below empty t_2 levels. The latter are further split in hexagonal SiC into e and a_1 levels. Optical transitions seen in both absorption and luminescence occur between the e levels which are further split by ~1 meV mainly by spin-orbit coupling.[8] The transition energy differs by ~20 meV in different polytypes[9] and when V occupies different types of Si sites. The occupancy of the *d* manifold can be changed by doping. Donor levels are reported at $E_v+1.3$ and $E_v+1.5$ eV for different sites in 6*H*-SiC (Refs. 10,11) and average values of $E_v+1.53$ (Ref. 12) or $E_v+1.66$ eV (Ref. 9) have been reported for 4*H*-SiC. There is a continuing debate over the position of the acceptor level. In 4*H*-SiC, values at $E_c-0.860$ and $E_c-0.895$ eV have been assigned to V at the two Si sites,[11] but other values, $E_c-0.80$ eV (Ref. 13) and even $E_c-0.97$ eV (Ref. 14) have been reported although the last may be a V complex. Early optical absorption investigations attributed a threshold at ~2.8 eV to the V acceptor level[15] but we shall reassign this transition below.

In contrast, the strong Coulomb potential in Er prevents a change in the occupancy of the *f* shell whatever the Fermi level be. However, recent deep level transient spectroscopy (DLTS) experiments on *p*-type 4*H*-SiC implanted with Er reveal a level at $E_v+0.75$ eV (Ref. 4) or $E_v+0.68$ eV.[16] The identification was aided using both stable and radioactive ^{160}Er implants while the absence of a Poole-Frenkel effect suggests a donor level. Only about 10% of the implanted Er is electrically active and no Er related levels in the upper third of the gap were found from implants in *n*-type material. Although there have been reports of several electron paramagnetic resonancce (EPR) centers related to Er in as-grown *n*-type 6*H*-SiC,[17] no detailed atomistic models were given.

Er related photoluminescence has been reported for several polytypes.[2,3,16,18] The observation of the 2.36 eV^{2}H$_{11/2}$ $\rightarrow{}^4$I$_{15/2}$ as well as the 0.803 eV (1.54 μm)^{4}I$_{13/2}\rightarrow{}^4$I$_{15/2}$ transitions in *n*-type SiC (Ref. 7) imply an Er^{3+}($4f^{11}$) electronic configuration. It might then be thought that substitutional Er can only behave as an acceptor just as the isoelectronic Al substitutional defect. This, however, as we shall show below, is not correct.

II. METHOD

Spin-polarized local-density-functional (LDF) calculations, using the AIMPRO code,[19] are carried out on V and Er defects in 72 atom supercells. Previously, the method has been used to investigate the alphabet PL lines[20] and the Z_1/Z_2 negative-U centers[21] in 4*H*-SiC. Hartwigsen, Goedecker, and Hutter[22] pseudopotentials with frozen nonpolarized $2p^6$ and $4f^{11}$ cores were used for V and Er, respectively. Following earlier calculations of Er in Si and GaN (Ref. 23) a nonlinear core correction was included. The basis consisted of atom centered Cartesian Gaussian orbitals. Centered on each C, Si and the V atom were sets of *s*, *p*, and *d* orbitals, while in addition *f* orbitals were sited on Er. The exponents for the orbitals for each element were optimized for bulk diamond, Si, V, and ErN, respectively. Calculations were carried out using MP-2^3 *k*-point sampling[24] and the charge density was Fourier transformed with a maximum cutoff of 300 Ry. All atoms in the cell were allowed to relax.

The formation energy E_f of a defect is defined as

$$E_f=E_{tot}-n_C\mu_C-n_{Si}\mu_{Si}-n_X\mu_X-qE_F,$$

where E_{tot} is the total energy of the cell containing a number of atoms n_C, n_{Si}, and n_X for carbon, silicon and type *X*, respectively, and a defect with a net charge of *q* electrons; μ_C and μ_{Si} are the chemical potentials of C and Si; E_F is the Fermi energy relative to the valence band top (E_v). The chemical potentials satisfy the condition that $\mu_C+\mu_{Si}$ is equal to the energy of a Si-C pair in bulk 4*H*-SiC and that they are bounded above by the energies of a C or Si atom in standard thermodynamic forms such as pure diamond or Si. If $E(\mathrm{C})$, $E(\mathrm{Si})$, and $E(\mathrm{SiC})$ are the energies of a C, Si, and SiC unit in diamond, silicon, and SiC, then we write $\mu_C=E(\mathrm{C})-\chi\Delta H$ and $\mu_{Si}=E(\mathrm{Si})-(1-\chi)\Delta H$ where $0<\chi<1$ and ΔH is the cohesive energy of SiC, i.e., $E(\mathrm{Si})+E(C)-E(\mathrm{SiC})$. This is found to be 0.49 eV, compared with an experimental value of 0.72 eV. We choose here the stoichiometric case where $\chi=\frac{1}{2}$ (Ref. 25) although our results are not qualitatively affected if we used C-rich or Si-rich growth conditions. The chemical potentials of Er is taken from bulk $\mathrm{ErSi_2}$ in equilibrium with SiC. For V it is set to zero as we are not interested in its absolute solubility.

The formation energy enables us to find the most stable site for V or Er, i.e., whether the impurity lies at a Si or C site. However, we have found that it is not a reliable guide to the energy levels[26] especially as the LDF energy gap in 4*H*-SiC is 2.53 eV compared with an experimental value of 3.26 eV. The energy levels are best found by comparing the ionization energies and electron affinities—calculated from self-consistent total energies—with known defects having close-by levels. This is called the marker method and gives errors of around 0.2 eV in Si.[26] It is then natural to use the calculated and observed donor levels of V to improve the estimate of the Er level.

The calculated *a* and *c* lattice parameters for 4*H*-SiC are found to be 3.061 and 10.030 Å, and in good agreement with experimental values of 3.078 and 10.086 Å, respectively.[27] The bulk modulus was found to be 224.2 GPa for 4*H*-SiC in agreement with an experimental value of 224 GPa, reported for 3*C*-SiC.[27]

III. VANADIUM IN 4*H*-SIC

The formation energy for substitutional $\mathrm{V_{Si}}$ at a cubic site is 4.3 eV lower than at a corresponding C site and 4.7 eV lower than at a pseudo-T_d interstitial site near C. For the substitutional impurity $\mathrm{V_{Si}}$ three of the V-C bonds are 1.94 Å while the fourth along [0001] is 1.96 Å. The Kohn-Sham levels show a gap related *e* level occupied by a single electron and unoccupied *e* and a_1 levels in agreement with the configuration required to explain the 0.94 eV intra-*d* absorption band.[8] In the negative-charge state, an additional electron occupies the lower *e* level leading to $S=1$ or $S=0$ spin states. We find the latter is higher in energy by 0.5 eV. Thus $\mathrm{V_{Si}^-}$ has $S=1$ in agreement with EPR investigations.[10]

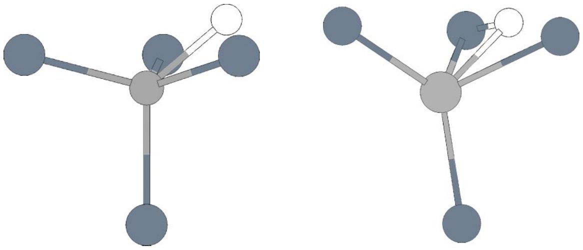

FIG. 1. Hydrogen bound to $\mathrm{V_{Si}}$ (left) and $\mathrm{Er_{Si}}$ (right). The figure shows the configurations of the neutral charge state. The dark balls represent C and the white hydrogen.

The donor level of $\mathrm{V_{Si}}$ is $E_v+1.39$ eV and found from the comparison of the ionization energies of V and of bulk material in the 72 atom cell. This is in good agreement with the reported values $E_v+1.53$ (Ref. 12) and $E_v+1.66$ eV.[9] Turning to the acceptor level. Here, we compare the electron affinity of $\mathrm{V_{Si}}$ with that of bulk and place the level at $E_c-0.57$ eV. This is in fair agreement with the observed levels around $E_c-0.8$ to $E_c-0.9$ eV discussed above.

Previous radio-tracer investigations into the $(-/0)$ level of V found an erratic activation efficiency which varied inexplicably between samples.[14] We considered this may be due to complexes with hydrogen. Hydrogen introduced during growth or by processing is known in the case of Si to strongly interact with transition metals and perturb their levels.[28] We find that H bonds to $\mathrm{V_{Si}}$ with a binding energy of 2.2 eV. The H atom lies in the plane defined by V and two of its C neighbors (see Fig. 1). The neutral center has $S=0$ and would not be paramagnetic. Its acceptor level is deeper than that of isolated V by 0.13 eV while the donor level is shallower by 0.2 eV. This might mean that its acceptor level is not detected in the radio-tracing experiments[14] which would then explain the low and sample dependent activation efficiency of V noted there. It would, however, be necessary to assume that Cr and Ti are not affected by hydrogen in the same way as no such erratic behavior was observed for these impurities.

Finally, we look at the intra-$d\,{}^2E\rightarrow{}^2E$ transition. This can be found from the energies of the two configurations found by promoting a electron from the lower to the upper *e* level. Similar calculations have been carried out for defects in diamond.[29] This gives an excitation energy of 0.87 eV in good agreement with the observed value of ~0.94 eV reported for 4*H*-SiC.[9]

IV. ERBIUM IN 4*H*-SIC

The formation energy for substitutional $\mathrm{Er_{Si}}$ at a cubic site is 4.9 eV. This demonstrates a very low equilibrium solubility for Er in SiC and the need for ion implantation to grow suitably doped material. This energy is 5.8 eV lower than Er residing at a C site and 8.3 eV lower than at the same interstitial site described above for V. Thus it is likely that Er only occupies the Si sublattice. In this case, three of the Er-C bonds are 2.16Å and the unique one is 2.21 Å. The Kohn-Sham energy levels of the cell containing Er revealed an unexpected result. The gap contained a t_2 level occupied with a single hole and lying in the lower half of the gap. This was split into e lying below a_1 levels localized on the C *neighbors* of Er. This demonstrates that the electrical activity of Er is to be understood in terms of a vacancy model where Er ''donates'' its three valence electrons to the states formed by the dangling bonds on its four C neighbors similar to transition metal impurities such as Pt in Si. This suggests that, unlike other group-III dopants such as Al, $\mathrm{Er_{Si}}$ can act as both a donor and as an acceptor. The donor and acceptor levels of $\mathrm{Er_{Si}}$ are found to be $E_v+0.53$ eV and $E_c-1.90$ eV, respectively. If we correct the levels using the errors in the V donor level as described above, we place the donor level of Er between $E_v+0.67$ and $E_v+0.74$ eV and in excellent agreement with experimental values around $E_v+0.7$ eV. There are no reports of the acceptor level. In fact, this is to be expected because it is so deep. DLTS experiments in $3C$-SiC might reveal the $(-/0)$ level, shifted by the 0.9 eV conduction band offset with $4H$-SiC, to around E_c-1 eV.

Clearly, the electropositive character of Er suggests an attraction with nitrogen or hydrogen. We have investigated the trigonal form of the complexes found by placing N at a C neighbor to Er and H directly bonded to a C neighbor and to the metal (see Fig. 1). The binding energy of the pairs is found to be 3.24 and 3.1 eV, respectively, and their donor levels lie 0.04 and 0.23 eV higher than the donor level of $\mathrm{Er_{Si}}$. The former is also close to the observed level. As expected from the vacancy model, the t_2 shell is now filled and there are no acceptor levels in the gap for both of these defects. Thus these impurities have passivated the acceptor activity of Er.

V. CONCLUSIONS

We have found that both Er and V possess three charge states, with deep donor and acceptor levels. The calculated levels are in fair agreement with experimental values with errors about 0.2–0.3 eV. However, the mid-gap acceptor level of Er is too deep to be detected by DLTS, although the trivalent character of Er strongly implies that a deep acceptor level should exist. In contrast with V, its electrical activity arises from the dangling bonds on the four C neighbors and not from the $4f$ (Ref. 11) core which has been frozen in the calculation.

Hydrogen and nitrogen bind strongly to both V and Er and perturb the donor levels. H deepens the acceptor level of V but both H and N passivate the acceptor activity of Er. The presence of H may explain the erratic activation efficiency of implanted V which varies dramatically between samples,[14] while its impact on the excitation efficiency of Er is unknown. In Si, hydrogen increases the luminescence intensity.[30]

The calculated intra-d optical transition at 0.87 eV of V confirms the assignment of the ~ 0.94 eV luminescence. Negatively charged V^{3+} has a $S=1$ ground state, in agreement with EPR studies, but can exist in an $S=0$ state which we place 0.5 eV higher in energy. This state leads then to a trap whose $(-/0)$ level lies around $E_c-0.3$ to $E_c-0.4$ eV. This is in excellent agreement with the observed threshold at $\sim E_c-0.4$ eV but previously attributed to the *ground state* V acceptor level.[15] As a consequence of our calculations, we attribute this acceptor level to the $S=0$ excited $\mathrm{V}^{3+}/\mathrm{V}^{4+}$ transition.

The EPR results show that more than one Er defect exists and the question arises whether isolated $\mathrm{Er_{Si}}$ or complexes, such as Er-N and Er-H, dominate the intra-f luminescence. The 1.54 μm transition has only been detected in nitrogen doped material where $\mathrm{Er_{Si}^-}$ or $\mathrm{Er_{Si}}$-$\mathrm{N_C}$ can exist. It seems unlikely that isolated $\mathrm{Er_{Si}}$ is the optical center. This is because a photogenerated hole would be captured by the negatively charged acceptor and the subsequent capture of an electron would release only ~ 1.90 eV which is insufficient to excite the 2.36 eV$^2\mathrm{H}_{11/2}\rightarrow{}^4\mathrm{F}_{15/2}$ intra-f transition.[3] Thus, according to our results, it is unlikely that isolated Er is responsible for the observed internal transition in contrast with V. However, Er-N or possibly Er-H complexes, having only donor levels below $E_v+0.9$ eV in $4H$-SiC remain candidates for the optical centers.

Note added in proof. Recently,[31] it has been shown that *N* doping increases considerably the 1540 nm PL intensity in SiC doped with Er at low temperatures consistent with an increased fraction of Er-N defects. The PL intensity falls at room temperature possibly because of an increased free electron Auger de-excitation.

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