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Alphabet luminescence lines in 4H-SiC

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First-principles density functional calculations are used to investigate antisite pairs in 4H-SiC. We show that they are likely to be formed in close proximity under ionizing conditions, and they possess a donor level and thermal stability consistent with the series of 40 photoluminescent lines called the alphabet lines. Moreover, the gap vibrational mode of the silicon antisite defect is close to a phonon replica of the b_1 line and possesses a weak isotopic shift with ^{13}C in agreement with observation.

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Room-temperature electron-irradiation of 4H-SiC creates a series of around 40 sharp photoluminescent lines in a 0.1-eV interval around 2.8 eV.[1] These are labeled $a_k, b_k, c_k, \ldots, l_k$, $k \leqslant 4$, with increasing energy. Photoexcitation spectroscopy demonstrates that the lines with different k are linked to excitations of the same defect and the whole set seems to come from about 12 centers. The lines are detected immediately after room-temperature irradiation and disappear and/or transform among themselves or into a new band labeled $D_{\rm I}$ around 1000–1300°C. A phonon replica of the b_1 no-phonon line shows a gap vibrational mode at 629 cm^{-1} (78 meV) between the top of the acoustic branch at 610 cm^{-1} (75.6 meV) and bottom of the TO optic branch at 774 cm^{-1} (96 meV).

We argue here that the lines are due to the recombination of a delocalized electron with a localized hole bound to a Si antisite defect, $\mathrm{Si_C}$, in proximity with a C antisite, $\mathrm{C_{Si}}$, although the defects are not necessarily nearest-neighbor pairs.

Recent work has indicated that the defects result from damage to the carbon sublattice as the lines are produced when the electron-irradiation energy lies below the threshold, $\sim$250 keV, for damage on the Si sublattice.[2] Moreover, some of the spectral lines are observed well outside the damaged region, implying rapid defect mobility at room temperature under ionizing conditions. This suggests that interstitials are involved in the formation of the defects.

The carbon interstitial (C_i) in both bulk Si (Refs. 3 and 4) and diamond[5,6] takes the form of a [100] split interstitial where a pair of atoms share a substitutional site and are aligned along a cube edge. The self-interstitial in both materials is known to be mobile under ionizing conditions.[7,8] We shall show below that the carbon interstitial in SiC at a Si site has a similar structure involving a C and Si atom sharing a silicon site. In this case, instead of the C atom diffusing away, a Si atom can sometimes be ejected, leading to the formation of a carbon antisite. This reaction is, however, endothermic by $\sim$6 eV in the neutral-charge state. If one takes into account that during irradiation the crystal contains many electron-hole pairs, it is possible that different charge states are involved in the kick-out reaction (*Bourgoin* mechanism).[21] We shall show below that the enthalpy is lowered to 0.6 eV if the interstitial traps two holes before the Si atom is ejected. This reaction could then occur at room temperature. The result is the creation of a Si interstitial Si_i together with $\mathrm{C_{Si}}$.

We shall also show that the neutral Si_i forms a split interstitial at a C site. Thus a similar reaction can take place leading to the production of $\mathrm{Si_C}$ and C_i. The reaction $\mathrm{Si}_i \rightarrow \mathrm{Si_C} + \mathrm{C}_i$ is endothermic by 1.8 eV in the neutral-charge state. If Si_i traps a hole, then the reaction is endothermic by only 0.17 eV and has a high probability of occurring.

The net effect is the catalytic creation of an antisite pair via a carbon interstitial. This process can be repeated so that starting from a single carbon interstitial, many antisite pairs can be made. If the reaction has high probability, then the antisites are likely to be in close proximity.

There are two inequivalent C and Si substitutional sites in 4H-SiC. These are labeled k or h sites referring to the cubic or hexagonal layers they inhabit, respectively. There are thus four possible antisite pairs separated by a single bond and a further four pairs at second-neighbor separation although these involve the same atomic species such as $\mathrm{Si_C}$-$\mathrm{Si_C}$. Third-neighbor defects involve $\mathrm{C_{Si}}$ and $\mathrm{Si_C}$ pairs. There are 6 of these and 6 at fifth-neighbor separation. Hence the number of distinct pairs at third, and fifth-neighbor separation is sufficient to explain the 12 defects seen in 4H-SiC. Early calculations[9] found $\mathrm{Si_C}$ to be electrically inactive in 3C-SiC but later work[10] suggests electrical activity and places the donor level at $E_v + 0.21$ eV in 4H-SiC. Recently, electron paramagnetic resonance (EPR) has identified Si_C^+ in 4H as the $E16$ center detected after room-temperature electron-irradiation.[11] The center exhibits trigonal symmetry. The defect is only found in p-type material implying that $\mathrm{Si_C}$ has a deep donor level. A hyperfine interaction with a single ^{29}Si atom is resolved with 34% of spin density in a p orbital and 6% in an s orbital on the unique atom. The defect is stable up to 1625 °C.

To investigate these defects, first-principles local density

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TABLE I. Formation energies (eV) of defects in stoichiometric 4*H*-SiC. The Fermi energy is taken to lie at the valence-band top for the charged defects.

Defect	Neutral	+1	+2
$(C_i)_{C_k}$	6.70	5.04	3.34
$(C_i)_{Si_k}$	7.33	5.21	4.42
$(Si_i)_h$	9.02	6.62	3.71
C_{Si}	3.60	3.61	
Si_C	4.15	3.43	
C_{Si}-Si_C	5.33	4.73	
C_{Si}-$Si_C \| c$	5.68		

functional pseudopotential[12] calculations were carried out with the AIMPRO (Ref. 17) supercell code using 72-atom supercells for 4*H*-SiC and 2^3 *k*-point sampling.[13] The wave-function basis consists of *s*- and *p*-atom-centered Gaussian orbitals with four different exponents. In addition, *d* orbitals were associated with the two smallest exponents. The charge density was Fourier transformed using reciprocal lattice vectors corresponding to an energy cutoff of 240 Ry. The calculated *a* and *c* cell dimensions of 4*H*-SiC are 3.054 and 9.999 Å compared with experimental values of 3.078 and 10.086 Å respectively.[14] The bulk modulus was found to be 227 GPa for 4*H*-SiC in agreement with an experimental value of 224 GPa for 3*C*-SiC.[14] When the basis for both Si and C was increased to *d* orbitals associated with each of the four exponents, the Si-C bond length decreased by only 0.5% and the bulk modulus increases by 0.4%.

To investigate reaction energies, we calculate the differences in formation energies of the isolated defects in 72-atom supercells. The formation energy (E_f) of a defect is defined as

$$E_f = E_{tot} - n_C \mu_C - n_{Si} \mu_{Si} - q E_F ,$$

where E_{tot} is the total energy of the cell containing n_C and n_{Si} carbon and silicon atoms, respectively, and a defect with a net charge of q electrons. μ_C and μ_{Si} are the chemical potentials of C and Si in SiC and E_F is the Fermi energy relative to the valence-band top (E_v). The chemical potentials satisfy the conditions that they are bounded above by the energies of a C or Si atom in standard thermodynamic forms like pure diamond or Si, and $\mu_C + \mu_{Si}$ is the energy of a Si-C pair in bulk 4*H*-SiC. The heat of formation is the difference between the energies of a Si and a C atom, in their standard states, and a Si-C pair in 4*H*-SiC. We find this to be 0.54 eV in good agreement with earlier studies[10,15] and an experimental value of 0.72 eV.[16] We take in the following $\mu_{Si} - \mu_C$ to be given by the standard values. E_F is taken to be zero for positively charged defects formed during the e^- irradiation. We investigated the antisite defects C_{Si}, Si_C, close-by antisite pairs and the interstitial defects C_i and Si_i.

The two inequivalent C in 4*H*-SiC lead to two possible C_{Si} and likewise two possible Si_C all of which possess trigonal symmetry. We found each pair of antisites to be degenerate in energy and Table I gives their formation energies. These are sufficiently high that the defects would not normally be present in equilibrium. Similar energies were also found with a larger basis of four *d* orbitals on each atom. The energy of Si_C dropped by only 0.13 eV while that of C_{Si} increased by 0.25 eV. These changes are quite small, less than 7% of the formation energies, and we therefore believe the calculations to be converged with respect to the basis.

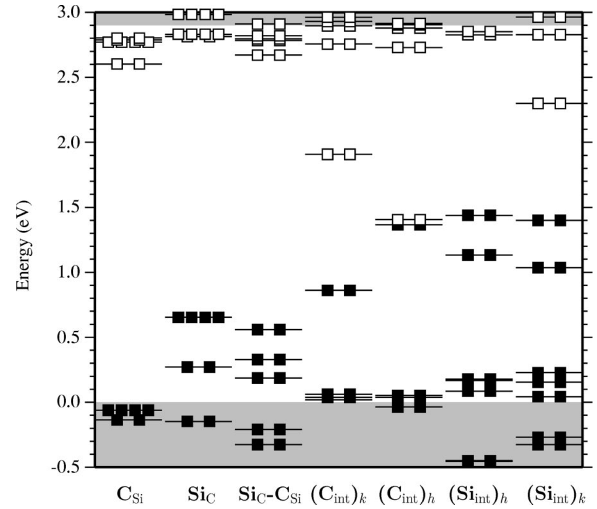

FIG. 1. The Kohn-Sham levels at Γ of antisite and neutral interstitial defects in 4*H*-SiC evaluated in 72-atom supercells. Occupied (empty) levels are denoted by solid (open) boxes. Gray regions correspond to bulk band positions at the zone center. The calculated band gap for 4*H*-SiC in this cell at Γ is 2.9 eV. Note that C_{Si} has no gap levels whereas Si_C has a deep donor level which becomes shallower for the Si_C-C_{Si} pair. C_i and Si_i refer to split-interstitial structures at carbon sites.

Figure 1 shows the Kohn-Sham levels at Γ in a 72-atom supercell containing antisite defects. The electron bands of the bulk 4*H*-SiC were calculated in a supercell of the same size as the defect cells and are shown in gray. The calculated band gap in 4*H*-SiC is 2.18 eV compared with an experimental value of 3.26 eV. The underestimate in the gap is a well-known failing of density functional theory and should not affect the energies of defects. C_{Si} is an electrically inert defect with C-C bond lengths of 1.660 and 1.664 Å (|| to **c**) at a *h* site or 1.659 and 1.645 Å (|| to **c**) at a *k* site, compared with 1.54 Å in diamond. Si_C at a *k* site has Si-Si bond lengths of 2.120 and 2.131 Å (|| to **c**) compared with 2.33 Å in bulk Si. At a *h* site the bond lengths are 2.116 and 2.143 Å (|| to **c**). For the neutral Si_C defect, the Kohn-Sham levels at the zone center indicate a fully occupied doublet ~0.65 eV above E_v or using the experimental value for the band gap, 2.61 eV below the conduction-band minimum (E_c). An alternative way of estimating the (0/+) level is to compare the formation energies of the defect in the neutral and positive-charge states with the energies of the neutral and charged host.[20] This gives a level 2.54 eV below E_c for $(Si_C)_k$ and 2.53 eV for $(Si_C)_h$. It is not possible to find accurate energy levels using density functional theory with periodic boundary conditions but the calculated ones are qualitatively consistent with a deep donor level around $E_c - 2.9$ eV associated with the alphabet series if we assume an

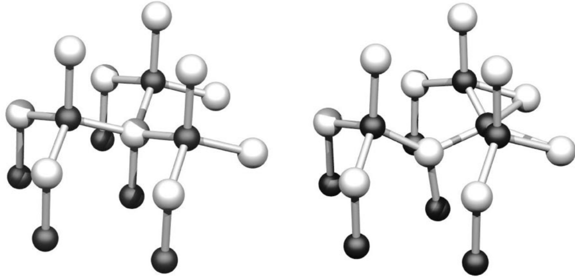

FIG. 2. The neutral C_i defect trapped near a k-Si site. The C atoms are shown in black and the Si atoms in white. The left figure shows bulk 4H-SiC for comparison.

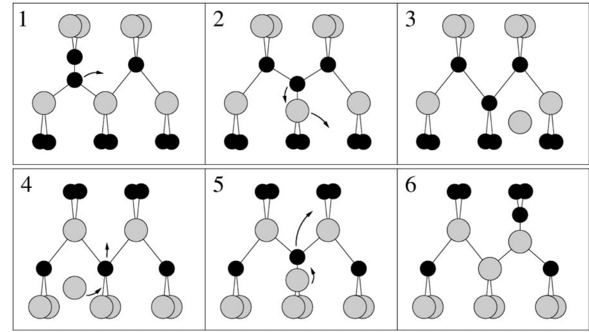

FIG. 3. Schematic diagram of the processes leading to antisite pair formation. A carbon interstitial at a C site (1) moves to a neighboring Si site (2) whereupon a Si interstitial defect (Si_i^{++}) is created along with C_{Si} (3). The cage sited Si interstitial (4) neutralises and forms a Si split-interstitial (5). A carbon atom is then ejected leading to the formation of a carbon interstitial and Si_C (6).

exciton binding energy of ~ 0.1 eV. This suggest that a perturbed form of Si_C is responsible for the alphabet series.

The wave function of the Si_C donor level is composed of p orbitals with Mulliken bond populations giving 28% localization on the unique Si atom. This result is in agreement with the hyperfine tensor for $E16$ with the small spin density on the unique atom arising from spin-polarization effects.

The vibrational modes of C_{Si} and Si_C were found by computing the energy second derivatives with respect to the displacement of the antisite atoms and their neighbors. The dynamical matrix of the supercell is then found using these values together with those found from a Musgrave-Pople potential for the other atoms in the supercell.[17] The computed phonon gap is between 625 cm^{-1} (77.5 meV) and 765 cm^{-1} (94.8 meV) compared with experimental values of 610 and 774 cm^{-1}.

The highest vibrational mode of Si_C lying in the gap between the acoustic and optic branches occurs at 748.4 cm^{-1} while that of C_{Si} lies at 758.6 cm^{-1}. The Si_C defect has almost tetrahedral symmetry and is associated with a triplet mode which is split into a doublet 657.0 (E symmetry) and singlet 655.4 cm^{-1} (A_1 symmetry). Only the latter mode would be expected to accompany a photoluminesence (PL) transition and is in good agreement with the observed replica at 629 cm^{-1} (78 meV). The mode shifts by only 0.8 cm^{-1} with ^{13}C consistent with its origin as a compressed Si-Si bond and agrees with recent investigations showing that the phonon replica of b_1 hardly shifts in ^{13}C material.[18]

We now turn to the interstitials whose structure is charge state dependent. Neutral C_i at the k-carbon site is around 0.2 eV lower in energy than at the h-carbon site. The interstitial at the k- and h-silicon sites (see Fig. 2) is about 0.6 eV higher in energy than at the corresponding carbon sites (Table I). The defects have a split form similar to the defects in Si or diamond. They possess deep midgap donor levels and possibly an acceptor level in the upper half of the gap (Fig. 1).

The silicon interstitial is bistable. The lowest-energy configuration for the neutral defect is one where Si_i lies near a carbon atom in a dumbbell configuration. The two atoms in the dumbbell are 2.14 Å apart and replace a C atom at a h site. The angle between the **c** axis and the dumbbell is 37.9°. At the k site we find this angle to be 41.4° and a separation of the two dumbbell atoms of 2.06 Å. Surprisingly, Si_i at the k site is almost 1 eV higher in energy than at the h site. We attribute this to the fact that there are different nearest neighbors for the interstitial in the two different sites. In the positive charge state, Si_i at the h site is located at a cage site surrounded by three C atoms at a distance ~ 1.85 Å. At the k site the Si_i has four C neighbors. The Si-C separation is ~ 1.81 Å along the c axes and 1.83 Å in the plane. The k site is also around 1 eV higher in energy than the h site in the $+2$ charge state.

We now discuss a mechanism for the production of antisites during irradiation. The first stage involves the creation of a C vacancy and C_i pair. If C_i moves to a Si site, as shown in Fig. 3, then the reaction $(C_i)_{Si} \rightarrow C_{Si} + (Si_i)_C$ is endothermic by 5.9 eV (Table I) and will not occur. However, if the defect now traps two holes, then the reaction $(C_i)_{Si}^{++} \rightarrow C_{Si} + Si_i^{++}$ is endothermic by only 0.6 eV. This reaction results in the formation of C_{Si} and a silicon interstitial. We then suppose that Si_i^{++} rapidly neutralizes by trapping two electrons and is then able to move to a dumbbell configuration at a C site. In turn, the resulting $(Si_i)_C$ defect can itself lead to the production of an antisite. $(Si_i)_C \rightarrow Si_C + (C_i)_{Si}$ is endothermic by 1.8 eV (see Table I) but $Si_i + h \rightarrow Si_C + (C_i^+)_{Si}$ is endothermic by only 0.17 eV. This strongly suggests that a supply of holes and electrons makes the formation of antisite pairs highly likely. We have, however, assumed that the barriers to the reactions and the preexponential factors in the rates are not important. Thus we assign the alphabet bands to antisite pairs with the zero-phonon line of the exciton bound to Si_C being perturbed by a nearby C_{Si}. These pairs are expected to be thermally stable and survive anneals to 1300 °C. Nevertheless, the widely different annealing behavior and the energy threshold for the creation of the individual lines suggests that some may be Si_C perturbed by other defects.

Among the antisite pairs, the nearest-neighbor pair is unique as it alone has one Si-C bond within the core. There are four inequivalent versions. Two are trigonal centers and two possess C_{1h} symmetry. The energies of the trigonal defects are about 0.3 eV higher than the C_{1h} ones which differ by only 0.07 eV. The binding energy of the pair is ~ 2.3 eV. The $(0/+)$ level of the antisite pair at the h site is calculated to be 2.66 eV below the conduction band and deeper than Si_C, which suggests that the pair may be responsible for the

most energetic transition (the l band at 2.8998 eV) or possibly the 2.901 eV (427.26 nm) D_{I} band. The antisite pair gives a large number of gap vibrational modes but a Si-related one at 624.9 cm^{-1} lies close to the observed replica at 669.4 cm^{-1} (83 meV) of D_{I}. Consistent with experiment,[19] where a shift with ^{13}C is not detected, we find a shift of only 0.4 cm^{-1}.

In conclusion, we have shown that antisite pairs possess properties in common with the centers giving rise to the alphabet series of luminescent lines. The transition energy, local vibrational mode and its isotopic shift, thermal stability, and the large number of defects are all consistent with experiment. We have also suggested a novel mechanism for their formation in irradiated material. The most stable antisite pair may be responsible for the most energetic alphabet line or the D_{I} band, which survives to higher temperatures.

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