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Hydrogen-related photoluminescent centers in SiC

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Local density functional calculations are used to investigate models of the center responsible for a prominent set of luminescent lines with zero-phonon lines around 3.15 eV in hydrogen rich $4H$-SiC and previously attributed to V_{Si}-H. We find that the electronic structure of this defect and the character of its vibrational modes are inconsistent with this assignment. In contrast, a H_2^* center, bound to a carbon anti-site, is more stable than the isolated molecule and possesses a donor level close to that observed for the H-lines. Moreover, its vibrational modes are in good agreement with experiment. A possible mechanism for the radiation enhanced quenching of the defect is discussed.

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I. INTRODUCTION

The H lines are an extraordinary set of photoluminescent (PL) centers with zero-phonon lines lying within 110–130 meV of the band edge in $4H$-SiC.[2] They have also been detected in $6H$-SiC and $15R$-SiC but not $3C$-SiC.[3] They are formed in H-implanted material or material grown in hydrogen atmosphere, and increase in density on heat treatments up to 800 °C and anneal around 1000 °C.[3] They are the result of a radiative recombination of a hole trapped in a donor level near $E_v+0.1$ eV and a shallow bound electron[4] and have been attributed to V_{Si} centers containing one hydrogen atom[5] but this is not a model we favor. Remarkably, several of the hydrogen, but not the deuterium lines, are quenched by light and this effect is thought to be due to a radiation enhanced dissociation of the C-H bond.[6] It has been suggested that part of the recombination energy is transformed into vibrational energy which is greater for C-H bonds than for C-D and hence is able to disrupt the former but not the latter. The H lines represent the first defect in a semiconductor where recombination enhanced dissociation was seen but the mechanism even now is not understood.

In $4H$-SiC, the four zero-phonon lines observed at low temperature (∼1 K) in hydrogenated material fall into two doublets H_1 and H_2 with H_2 lying about 15 meV lower in energy than H_1. Each doublet consists of two lines with separation ∼0.2 meV attributed to different orientations of an anisotropic defect such as V_{Si}-H.[7] Thus the C-H bond is parallel to the Si-C bond along **c** in the axial form and parallel to the other three Si-C bonds in the nonaxial form. The axial and nonaxial forms have C_{3v} and C_{1h} symmetry, respectively. The two doublets are derived from the two inequivalent Si sites in $4H$-SiC. Zeeman experiments show that the lines are due to recombination of a spin-triplet exciton bound to a neutral center.[7] At higher temperatures, up to 60 K, other more intense doublets H_{1T} and H_{2T} are detected and these involve a bound spin-singlet exciton and are located about 10 meV higher in energy than H_1 and H_2. Their greater intensity reflects their shorter radiative lifetime compared with the spin forbidden H_1 and H_2 transitions. This implies that the center is an isoelectronic one whose electronic structure is a perturbation of the bulk. Local mode replicas are found around 366 and 272 meV for H and D, respectively. These frequencies are typical of C-H and C-D stretch modes. In addition, three modes are found lying in the gap between the acoustic and optic branches in the hydrogen containing centers, but only one gap mode is found in the deuterated case at a position almost the same as one of the gap modes found in the hydrogen isotopic case. This excludes an assignment to a C-H bend mode.[2] The modes are listed in Table I. Such modes place considerable constraints on acceptable models of the centers.

Remarkably for hydrogen, but not deuterium, the H_2 spectral line is quenched by above band gap or resonant radiation but the H_1 line is unaffected. The H_2 line recovers when the quenched sample is warmed up to room temperature. Similar effects are seen in $6H$-SiC and it has been proposed that exciton recombination promotes a dissociation of the C-H bond transforming the defect into a metastable optically inactive form.[4] The metastable form can, however, be transformed back to the active form at low temperatures either by free exciton recombination or by a room temperature anneal. It may be that quenching of H_2 rather than H_1 is observed, as H_2 represents the exciton with the greatest binding energy and is the most localized with an enhanced coupling with the vibronic spectrum. It has also been found recently that above gap radiation stimulates a long range diffusion of hydrogen

TABLE I. Calculated LVM's (meV) and their symmetries for $C_{Si}H_2^*$ and V_{Si}-H and their deuterated counterparts compared with experimental data for the H lines.[2] For each $C_{Si}H_2^*$ gap mode, the corresponding deuterated one is reported while those in brackets fall in the acoustic branch. The previous calculated modes for V_{Si}-H in 3*C*-SiC are also reported. (*m*) denotes the mixing of the *A* and *B* modes for V_{Si}-H as can be seen in Fig. 3(a). The lowest three gap modes of $C_{Si}H_2^*$ also show some mixing in the D case.

	$C_{Si}H_2^*$	V_{Si}-H	V_{Si}-H (1)	Exp. 4*H*-SiC
		Stretch modes		
C-H	371.2 (*A*)	357.3 (*A*)	366.5 (*A*)	366.8
	400.9 (*A*)			
C-D	271.4 (*A*)	261.9 (*A*)	268.6 (*A*)	272.0
	292.3 (*A*)			
		Gap modes		
H	77.5 (*A*)			80.5
	79.7 (*B*)			
	80.5 (*A*)	80.7 (*A*)	78.7 (*A*)	83.9
	90.1 (*A*)			89.6
	94.2 (*B*)			
		95.0 (*A*)		
		95.3 (*B*)	95.8 (*E*)	
D	(74.3)			
	(74.7)			
	76.8 (∼*A*)			
		78.4 (m)	77.5 (*A*)	
		79.5 (m)		
		80.5 (m)	82.3 (*E*)	
	85.6 (*A*)			89.3
	88.8 (*B*)			

leading to the formation of B-H and Al-H defects as well as the H lines.[8]

Although the V_{Si}-H model has been recently investigated theoretically using density functional techniques applied to 64 atom cells,[1,9] there remain considerable difficulties with this assignment. First, the most obvious problem is that the neutral charge state of V_{Si}-H must possess a spin $S=1/2$ and this cannot explain the triplet nature of the H_1 and H_2 lines, and the singlet nature of H_{1T} and H_{2T}. Second, the interpretation of the PL as arising from excitons bound to a neutral isoelectronic center implies an electronic structure of the defect as shown in Fig. 1(b) which requires a fully occupied gap level leading to a donor level around $E_v+0.1$ eV. However, previous calculations showed that V_{Si}-H has several deep dangling bond related gap levels.[9] Its electronic structure, schematically indicated in Fig. 1(a), shows the neutral trigonal defect has a partially filled *e* level which would lead to both *deep* donor and acceptor levels. Indeed, donor and acceptor levels have been calculated to lie at $E_v+0.32$ and $E_v+0.66$ eV.[10] Clearly, these are inconsistent with the experimental electronic structure shown in Fig. 1(b). Third, the previous investigations demonstrated that the C-H bend mode of V_{Si}-H falls into the gap in conflict with experiment. Moreover, the defect possessed only one other gap mode which is insensitive to the H isotopic mass. Although the calculations were performed for 3*C*-SiC it is difficult to see how this would be radically changed in 4*H*-SiC. Fourth, it is unlikely that only V_{Si}-H would be present in proton implanted material and not for example V_{Si} defects with two or more H atoms. These should give additional PL lines but none have been reported.

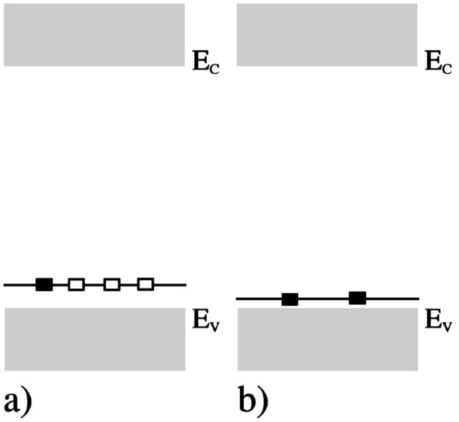

FIG. 1. Gap levels expected for the axial form of V_{Si}-H (a) and the neutral isoelectronic center giving rise to the H lines (b). In (a), a singly occupied *e* level lies in the gap whereas a fully occupied level lies close to the valence band top in (b). In contrast with (b), V_{Si}-H (a) possesses deep acceptor and donor levels.

Because of these difficulties we have investigated additional models. It is clear that defects containing a single H atom will lead to $S=1/2$ centers with deep levels unless chemical donors or acceptors are involved. It seems unlikely that passivated donors or acceptors are responsible for the H lines as B-H related PL centers have distinct transitions.[11] Moreover, the structure of the N_C-H defect excludes a C-H bond.[10] We did investigate a N_C-H-C_{Si} defect which does contain a C-H bond but this did not possess the correct number of gap related modes. Hence, we have looked for defects containing *two* H atoms with the electronic structure shown in Fig. 1(b). These defects are spin singlets when neutral.

The symmetry of the axial form is suggestive of the H_2^* center, shown in Fig. 2(a): a well known trigonal defect in hydrogen treated Si[12,13] where it is electrically inert. It is also believed to be stable in diamond where it is more stable than the molecule[14–16] although it has not yet been detected. There are several possible configurations of this center in 4*H*-SiC but we find that even the lowest energy configuration [Fig. 2(a)] is less stable than an isolated hydrogen molecule by 2.4 eV. However, H_2^* trapped at a carbon-antisite, denoted by $C_{Si}H_2^*$ and shown in Fig. 2(b), is *more* stable than the molecule by 1.2 eV. This is identical to the situation known for Si, where H_2^* trapped by a carbon impurity is more stable than the molecular form. The resulting defects have already been detected in infrared absorption experiments.[17] The presence of carbon antisites in as-grown SiC is to be expected as these defects are known to have low formation energies.[18,19] Moreover, the ubiquitous D_I PL center is also now believed

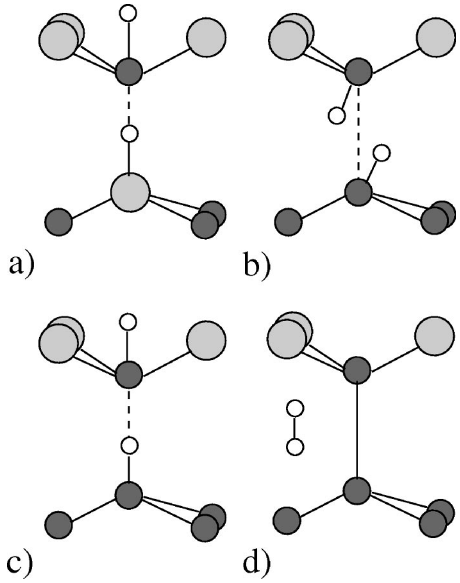

FIG. 2. A schematic representation of the different configurations considered. (a) shows H_2^* while (b) shows $C_{Si}H_2^*$ where a C antisite has trapped a pair of H atoms releasing some of the strain energy; (c) and (d) show metastable centers where a pair of H atoms is trapped at the C antisite. In (d) the two H atoms form an interstitial hydrogen molecule. Small black atoms denote C; larger gray atoms denote Si while small open circles denote H. The most stable defect found is $C_{Si}H_2^*$ (b).

to be a close-by antisite pair.[19,20] We shall show here that the symmetry of $C_{Si}H_2^*$, its electronic structure, the C-H stretch mode as well as three of the gap related vibrational modes, are all consistent with observations on the H-related centers. Moreover, the optical quenching can be explained by a recombination enhanced dissociation of the C-H bonds leading to an optically inactive defect.

II. METHOD

Spin-polarized local density functional (LDF) calculations, using the AIMPRO code,[21] are carried out on large 72 atom supercells of models of these defects in 4*H*-SiC, with a MP-2^3 *k*-point sampling of the Brillouin zone.[22] Dual-space separable pseudopotentials by Hartwigsen, Goedecker, and Hutter[23] are employed. The basis consists of atom centered Gaussian orbitals, with sets of *s*, *p*, and *d* orbitals for all species. The exponents for the orbitals have been optimized for each element (crystalline silicon, diamond and hydrogen molecule). All atoms in the different cells considered are allowed to relax. Details of the method have been described before for defects in SiC and will not be repeated here.[19] The local vibrational modes are obtained by diagonalizing the dynamical matrix whose elements are related to the second derivatives of the energy between the positions of different atoms. The derivatives with respect to the H atoms and their neighbors are computed directly whereas the remaining second derivatives are found from a Musgrave-Pople potential fitted to the energy second derivatives between atoms in the bulk solid.[24]

III. RESULTS

Figure 2 shows the defects containing two H atoms that were investigated. The hydrogen molecule[25] is more stable than H_2^* shown in Fig. 2(a) by 2.4 eV but less stable by 1.2 eV than $C_{Si}H_2^*$. The stable axial form of this is shown in Fig. 2(b) where the H atoms are displaced away from the axial C-C bond making an angle of 30°. However, the reorientation barrier of the H atoms around the C-C bond is about 0.07 eV which suggests a dynamical trigonal symmetry even at low temperatures. Thus we expect two forms of axial centers and two forms of nonaxial centers bound to the different *h* and *k* Si sites in 4*H*-SiC. Among the axial forms, we find the one sited at the *h* site to be lower in energy than the *k* site by 0.11 eV. The *h* and *k* forms would correspond with the H_1 and H_2 doublets although we are unable to say which corresponds with which.

The defect has a shallow donor level whose energy can be estimated by comparing its ionization energy with that of a defect with a known donor level. We use for this purpose the antisite pair whose experimental donor level at $E_v+0.35$ eV is responsible for the D_I-PL line.[19,20] This places the donor level of $C_{Si}H_2^*$ at $E_v+0.15$ eV in excellent agreement with the experimental value of about 0.10 eV required for the H lines in 4*H*-SiC.[2] There are no other energy levels in the gap and hence the electronic structure is as shown in Fig. 1(b) and fully consistent with the optical nature of the H lines. The donor wavefunction is largely localized on the C_{Si}-H pair and not on the other C-H pair. This electronic structure is expected for an isoelectronic center and can be contrasted with that of V_{Si}-H whose axial form possesses a partially occupied deep *e* level as shown in Fig. 1(a).

We now investigate the vibrational modes of the nonaxial form of $C_{Si}H_2^*$. This is because there are three times as many of these as axial ones and consequently they dominate the PL spectrum.[7] This defect has C_{1h} symmetry and consequently only vibrational modes of *A* or *B* symmetry. Only the *A* mode is expected to couple with the PL transition. This follows as the dipole matrix element for a transition between the electronic states *i* and *j*, and the vibrational ground and excited states 0 and *n* is, assuming the Born-Oppenheimer for the wave functions and Condon's approximations for the electronic dipole moment **p**,[26]

$$\begin{aligned}\int \Psi_{i,0}^*(\mathbf{r},\mathbf{R})\mathbf{p}\Psi_{j,n}(\mathbf{r},\mathbf{R})d\mathbf{r}d\mathbf{R} \\ \sim \int \phi_i^*(\mathbf{r},\mathbf{R}_{i0})\mathbf{p}\phi_j(\mathbf{r},\mathbf{R}_{j0})d\mathbf{r} \\ \times \int \chi_{0,i}(\mathbf{R}-\mathbf{R}_{i0})\chi_{n,j}(\mathbf{R}-\mathbf{R}_{j0})d\mathbf{R}.\end{aligned}$$

Here $\mathbf{r},\mathbf{R}$ denote electron and nuclear coordinates respectively. $\mathbf{R}_{i0}$, $\chi_{0,i}$, and $\chi_{n,j}$ denote the equilibrium nuclear sites and vibrational wave functions associated with the electronic ground and excited states *i* and *j*. Since, $\chi_{0,i}(\mathbf{R}-\mathbf{R}_{i0})$ transforms as *A*, then so also must $\chi_{n,j}(\mathbf{R}-\mathbf{R}_{j0})$. This selection rule limits the modes that can be observed in PL and restricts acceptable models of the center.

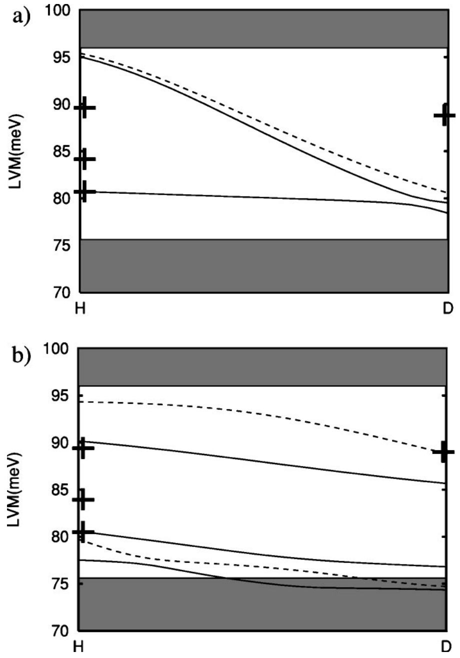

FIG. 3. Gap modes of nonaxial forms of V_{Si}H (a) and $\mathrm{C_{Si}H_2^*}$ (b) when the hydrogen mass is increased from that of H to D. The dashed lines are *B* modes while the solid ones denote *A* modes. Notice that V_{Si}H possesses only two *A* modes while $\mathrm{C_{Si}H_2^*}$ possesses three. The experimental modes of *A* symmetry are shown by crosses.

The $\mathrm{C_{Si}H_2^*}$ defect has several localized vibrational modes given in Table I either falling above the one-phonon spectrum or in the acoustic-optic gap which stretches from 75.6 to 96 meV. We note that the C-H and C-D stretch modes at 371.2 and 271.4 meV are in reasonable agreement with experimental values at ~369 and 273 meV, respectively, for the H lines in 4*H*-SiC.[2] These modes are localized on the C-H pair. We have to suppose that only these modes are detected, and not the ones at 408 and 299 meV.

We now consider the gap modes. These are given along with the experimental ones in Table I and their shift with isotopic mass is shown in Fig. 3(b). There are modes of *A* symmetry at 77.5, 80.5, and 90.1 meV. These agree fairly well with observed modes at 80.5, 83.9, and 89.6 meV. The error is about 3 meV or 4% and typical of the theory. There are two modes of *B* symmetry at 79.7 and 94.2 meV. The 77.5 and 80.5 meV modes involve, respectively, an out-of-phase and in-phase displacement of the two near-by C atoms in the mirror plane. In the 90.1 meV mode, the main displacement is the bending of a $\mathrm{C\text{-}C_{Si}}$ bond lying in the mirror plane accompanied by displacements of the H atoms in the same plane.

It is of interest to follow the variation of the modes with the hydrogen isotopic mass. The dynamical matrix was diagonalized for increasing hydrogen atomic mass and this allowed us to follow the evolution of the modes and relate the hydrogen and deuterium ones. This is shown in Fig. 3(b). Because the gap modes mainly involve displacements of the C atoms in the defect, they are relatively insensitive to the hydrogen isotopic mass in agreement with experiment. The two lowest gap modes drop with increasing H mass. The deuterium *A* mode at 76.8 meV has not been observed perhaps because it falls so close to the top of the acoustic branch. Hence, replacing H by D leads to the elimination of the two lower *A* modes from the gap leaving only one at 85.6 meV of *A* symmetry. This is also in agreement with the experiment.

We have also calculated the vibrational modes due to the nonaxial form of V_{Si}-H having C_{1h} symmetry. These are shown in Fig. 3(a) and Table I. They are in good agreement with values published previously for 3*C*-SiC.[1] The C-H and C-D stretch frequencies are close to the observed stretch frequencies but these are also close to the corresponding frequencies in $\mathrm{C_{Si}H_2^*}$. Thus the stretch modes by themselves do not discriminate between the defects. However, there are only *two* gap modes with *A* symmetry and the upper mode, derived from a split-*E* mode, varies rapidly with isotopic mass in conflict with experiment. This mode is a C-H bend mode. The lower gap mode is insensitive to isotopic mass as it is due to a movement of the C atom in phase with the H atom it is bonded with. This explains the negligible isotopic shift until an attempted crossing with the bend mode occurs. It is clear that the V_{Si}-H model is dynamically too simple to possess a sufficient number of gap modes to explain the experimental data. Moreover, the large shift of the C-H bend mode with hydrogen mass is in conflict with experiment. Indeed, since the experiment rules out the presence of this mode, it can be seen that the V_{Si}-H has only *one* gap mode in relative agreement with experiment.

We must ask whether this result is a consequence of the approximations in the theory. If there were an additional two modes lying in the region covered by the acoustic and optic branches which really should be in the gap, the errors in the calculations would have to be at least 10 meV or about 12%. This is a rather large error.

IV. DISCUSSION

To summarize, $\mathrm{C_{Si}H_2^*}$ is a stable hydrogen dimer having the same symmetry as the centers responsible for the H-line luminescence. It is more stable than the hydrogen molecule. Moreover, its electronic structure is in good agreement with the data and it possessess the correct number of gap *A* modes: three for H and one for D, in the correct location as those observed [Fig. 3(b)]. This is in contrast with an assignment to V_{Si}-H. The presence of the second H atom would, however, be a decisive test of the model. Coimplantation of both D and H would lead to lines arising from the D-H defect whose zero-phonon lines should be shifted slightly from those of H-H or D-D. This might provide evidence for a second hydrogen atom.

We note finally that there are several metastable forms of the defect. For example, where one or both H atoms are rotated to the other side of its neighboring C atom. These defects are at least 0.3 eV higher in energy than that shown in Fig. 2(b). Another metastable form is where both H atoms are moved to form a H_2 molecule. The molecule has no electrical levels and would then be optically inert. The mechanism for the quenching of the H_2 line needs to be addressed. One intriguing possibility is that the metastable optically inactive form responsible for quenching is the hydrogen molecular form [Fig. 2(d)] which is created through the photodissociation of the C-H bonds. The molecule is metastable by 1.2 eV and $C_{Si}H_2^*$ could reform at room temperature. In contrast to the other defects considered, including V_{Si}, the molecular form is inert possessing no gap levels. To confirm the identification of the metastable center with molecular hydrogen, further information on the kinetics of the recovery of the H lines would be useful.

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