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Z_1/Z_2 Defects in 4*H*-SiC

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First-principles calculations are carried out on models for the Z_1/Z_2 defects in 4*H*-SiC which are found in as-grown and irradiated *n*-type material. We show that an interstitial-nitrogen–interstitial-carbon defect is exceptionally thermally stable, bistable, and has negative-*U* character with donor and acceptor levels close to those attributed to the defect.

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SiC is a material that seems ideal for high-power, high frequency, and high temperature electronic devices. Recent advances in crystal growth make it possible now to grow epitaxial and bulk SiC material of high quality. However, rapid growth leads to a deterioration in quality with an increase in electrically active grown in defects [1,2]. Among these, the Z_1 and Z_2 defects (denoted by Z_1/Z_2) are dominant in *n*-type 4*H*-SiC, as well as material that has been exposed to radiation [3–6]. They are a pair of defects with closely spaced electrical levels that possess unusual thermal stability—surviving to 1700 °C [7]. In other polytypes such as 6*H*-SiC, the E_1 and E_2 defects have similar properties [8–10]. These four centers are negative-*U* [11] having inverted donor $(0/+)$ and acceptor $(-/0)$ levels. The donor and acceptor levels of Z_1 (Z_2) in 4*H*-SiC occur at $E_c - 0.43(0.46)$ and $E_c - 0.67(0.71)$ eV, respectively, while the corresponding levels of E_1 and E_2 in 6*H*-SiC are shallower by $\sim$0.2–0.3 eV.

There has been much speculation about their origin. They have been linked with the D_I photoluminescence band with zero phonon line at 2.901 eV in 4*H*-SiC which also is thermally stable to high temperatures [3]. However, recent studies [7] show that the luminescence arises from a bound exciton with a deep hole at $E_v + 0.34$ eV probably arising from a complex containing $\mathrm{Si_C}$ [12]. This rules out a connection with Z_1/Z_2 having levels close to E_c. More recently, Z_1/Z_2 has been linked with a silicon vacancy V_{Si} [13]. This connection was suggested when it was shown that the annealing behavior of vacancy centers observed by positron-annihilation is correlated with the annealing of Z_1/Z_2 in 4*H*-SiC [13] and E_1/E_2 in 6*H*-SiC [14]. However, in both cases the maximum in the concentration of deep-level transient spectroscopy (DLTS) centers was not directly linked to that of the positron-annihilation signal. This allows the alternative interpretation that the DLTS centers and vacancies annealed together by mutual annihilation.

Recent work has shown that the Z_1/Z_2 defect in as-grown material increases in concentration both with nitrogen doping and when growth proceeds under carbon rich growth conditions [1]. Evidence was presented that the defect contains a single N atom and possibly a carbon interstitial. The presence of a single N atom in the defect implies that the neutral defect would be paramagnetic in its neutral charge state and that the negative-*U* behavior arises from a different structural form for the positive and negative charged defects. This is similar to many other negative-*U* defects such as interstitial boron [15] and hydrogen [16] in Si, and the *DX* center in AlGaAs [17]. The alternative possibility is a defect with an *even* number of electrons when neutral. There are very few examples of such centers which display negative-*U* properties. One example is the vacancy in Si whose $(+/++)$ level lies above $(0/+)$ [18]. However, the experimental cross sections of the Z_1/Z_2 centers rule out an assignment of Z_1/Z_2 to levels of a double donor, and thus we consider the most likely model for Z_1/Z_2 consists of a complex of a single N atom together with an intrinsic center such as a carbon interstitial or silicon vacancy. The concentrations of both would then be expected to increase in C-rich material.

We investigate candidates for these defects using spin-polarized density functional theory (DFT) as implemented in the AIMPRO code. Gaussian orbitals are used as a basis set together with norm-conserving pseudopotentials. The calculations were carried out in large 128 atom unit cells with a Monkhorst-Pack (MP) 2^3 sampling scheme. Convergence tests were carried out using MP-4^3 sampling for some structures. Differences in total energy between the two schemes were generally less than 0.07 eV. Each Si, C, and N atom has a basis consisting of *s*, *p*, and *d* Gaussian orbitals with 28, 28, and 40 basis functions, respectively. Details of the method have been given previously [19].

The formation energy (E_f) of a defect is defined as

$$E_f = E_{\mathrm{tot}} - n_{\mathrm{C}}\mu_{\mathrm{C}} - n_{\mathrm{Si}}\mu_{\mathrm{Si}} - n_{\mathrm{N}}\mu_{\mathrm{N}} - qE_{\mathrm{F}},$$

where E_{tot} is the total energy of the cell containing n_{C},

n_{Si}, and n_{N} carbon, silicon, and nitrogen 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 and E_{F} is the Fermi energy relative to the valence band top (E_v). The chemical potentials satisfy the condition that $\mu_{\mathrm{C}} + \mu_{\mathrm{Si}}$ 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. In C-rich conditions, therefore, μ_{C} is taken from the energy of a C atom in diamond [20]. Since we are interested in C-rich material, all formation energies quoted are in C-rich material unless stated otherwise. The chemical potential for nitrogen was taken from the energy of an N atom in N_2. Such a choice gives the formation energy of the nitrogen donor, N_{C}, in the neutral charge state to be quite small ~0.3 eV and consistent with its high solubility. The energy levels for defects were found from a comparison of the ionization energies $E(\pm) - E(0)$ with similar quantities found for bulk SiC in the same sized cells where systematic corrections to the energies would be eliminated [21,22]. Here, $E(q)$ is the energy of a charged defect in a supercell. This method when applied to the donor levels of chalcogen centers in Si gave levels too deep, due in part to an underestimate in the band gap found in DFT. However, the *relative* donor levels for S, Se, and Te could be accurately found by comparing their ionization energies. This amounts to an upward rigid shift of about 0.3 eV of the level for each defect. This appears also to be the case for donors with levels in the upper half of the band gap in SiC. Comparing the ionization energies of N_{C} [23] and P_{Si} [24] at hexagonal sites with the ionization energy of bulk 4*H*-SiC gave $(0/+)$ levels at $E_c - 0.52$ eV and $E_c - 0.54$ eV, respectively. These require upward shifts of ~0.5 eV to bring them into agreement with experimental values of ~0.05 eV [25,26]. The donor levels of defects in the upper part of the gap and given below have therefore been shifted upwards by 0.5 eV.

The first candidate for Z_1/Z_2 to be investigated is a nitrogen impurity at a Si site denoted by N_{Si}. Its concentration is expected to be enhanced under carbon rich conditions and the center may be a negative-U one in analogy with the Si donor in AlGaAs which forms the well-known *DX* center. However, we find N_{Si} to be 5.2 eV higher in formation energy than N_{C} and less stable by 3.4 eV when N is interchanged with one of its C neighbors. The resulting N_{C}-C_{Si} pair has a low formation energy of between 2.1 eV (C-rich) and 2.8 eV (Si rich) and $(0/+)$ and $(-/0)$ levels at $E_c - 1.2$ and $E_c - 0.6$ eV, respectively. Thus, this defect is a positive-U one with deep levels and can be excluded as a model for Z_1/Z_2.

We now consider models based on C_i. The lowest energy form of C_i is a split interstitial where two C atoms share a carbon site [12]. The formation energy of the neutral defect is ~6.6 eV. C_i at a Si site also takes the form of a split interstitial but has a slightly higher formation energy of ~7.2 eV. We then investigated the energy barrier, W, to the migration of C_i from a C site to a Si one finding $W \sim 0.6$ eV. There are small variations in these energies due to the two different C and Si lattice sites in 4*H*-SiC. This low barrier suggests that the neutral defect is mobile around room temperature and is similar to the low diffusion barrier of C_i in Si ($W \sim 0.8$ eV [27]) which also anneals at this temperature. The low diffusion barrier is somewhat less than values found for the carbon interstitial in diamond where $W \sim 1.8$ eV [28,29]. Consequently, we expect C_i to diffuse easily until trapped by a majority defect such as nitrogen. The N_{C}-C_i pair, which can also be described as a nitrogen interstitial N_i, is also a split-interstitial pair where both N and C are located at a carbon site. However, the binding energy, E_B, of the pair is only 2.2 eV and the complex would be expected to dissociate at a temperature given by $T \sim (W + E_B)/k_B \ln(\nu_0/\nu)$ or ~850 °C when $\nu_0 \sim 10^{13}\ \mathrm{s}^{-1}$ — a typical atomic jump frequency — and $\nu \sim 1\ \mathrm{s}^{-1}$ the number of diffusion steps per second [30]. It possesses $(0/+)$ and $(-/0)$ levels at $\sim E_c - 1.5$ and $E_c - 1.7$ eV which, together with its low thermal stability, exclude it as a model for Z_1/Z_2. The deep character of these levels prevents easy detection but the defect will compensate N_{C}. The defect should, however, be IR active and it has a calculated local vibrational mode at 1324 cm^{-1}.

Clearly, the Z_1/Z_2 defects are much more stable and there are unlikely to be any dangling bonds. Their presence would not only reduce the stability of the center but lead to deep midgap levels. Now, it is possible to form a defect without dangling bonds when C_i traps a second interstitial. This occurs when two C_i are placed at the centers of adjacent parallel bonds across one of the two types of hexagons found in hexagonal SiC (see Fig. 1). The interstitials can be bonded together not only as σ bonds but their p orbitals, parallel to [0001] in Fig. 1, can form a π bond. The binding energy of the two interstitials is 5.6 eV and such a defect would survive anneals of 2100 °C according to the above equation for the dissociation temperature using $E_b = 5.6$ eV and $W = 0.6$ eV. This defect has a donor level at $E_v + 0.5$ eV and does not possess an acceptor level. This form of the

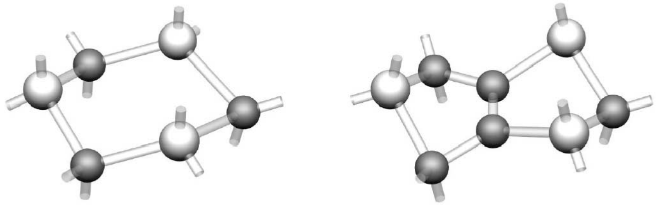

FIG. 1. Left: The chair form of the basal plane hexagon. Right: The C_i-C_i π-bonded pair where two additional C atoms are added to the hexagon and bonded together. C (Si) atoms are shown in black (white). All atoms are fully coordinated.

dicarbon interstitial is also believed to occur in diamond [31].

The defect of interest here is a dimer composed of N_i and C_i. The lowest energy form of the complex is shown in Fig. 2(a) in the positive charge state. The nitrogen atom is not part of the π bond (this structure is $\sim$0.25 eV higher in energy) but one of the neighbors to a π-bonded C atom. Clearly, the defect is thermally stable as these bonds have to be broken in order for it to dissociate.

However, in the negative charge state a π^* orbital is occupied and the defect structure is unstable and changes spontaneously into the one shown in Fig. 2(b). Now the N atom and one of the C_i atoms become threefold coordinated. On an electron counting argument, both of these possess a dangling bond containing *two* electrons. Thus, the structural relaxation can be thought of as turning these into low energy lone pair orbitals which are filled. It is this rearrangement which stabilizes the defect and leads to negative-U behavior. The calculated $(0/+)$ and $(-/0)$ levels lie at $E_c - 0.3$ eV and $E_c - 0.6$ eV, respectively, and are in good agreement with the observed levels of Z_1/Z_2. Thus, the exceptional thermal stability of N_i-C_i, its bistability, electrical levels, and ease of formation, all support the assignment to Z_1/Z_2. We also note that the two different types of hexagons found in 4H-SiC and 6H-SiC, namely the boat and chair configurations, would lead to two types of N_i-C_i defects consistent with the existence of Z_1 and Z_2 in 4H-SiC and E_1 and E_2 in 6H-SiC.

Finally, we investigate whether the Si vacancy, V_{Si}, can be discounted as a candidate for Z_1/Z_2. We restrict our calculation to V_{Si} at a hexagonal site since previous theory has shown that the different lattice sites give quite similar energies and level positions in the gap. In agreement with this theory [32], we find V_{Si} to be stable with spin $S = 1$ when neutral, consistent with experiment [33], and $S = 3/2$ when negatively charged. The $S = 0$ neutral defect and the $S = 1/2$ negatively charged centers are 0.13 and 0.22 eV, respectively, higher in energy. A Mulliken bond-population analysis shows that the spin density of the neutral defect is mainly composed of p orbitals on the four C atoms forming the vacancy cage with little s contamination. Each nearest neighbor C atom is found to have 13% of the total spin density compared with an experimental estimate of 12.8% ± 4% [34]. Its formation energy is 8.1 eV. We find, also in agreement with previous work [35], that it possesses a deep $(-/0)$ level at $E_v + 1.1$ eV. The defect is in fact less stable than interchanging the vacancy and a C neighbor to form V_C-C_{Si} [36]. The resulting center is 1.6 eV lower in energy and possesses shallower $(-/0)$ and $(0/+)$ levels at $E_c - 0.7$ and $E_c - 1.0$ eV, respectively. The instability of V_{Si} may be connected with disappearance of the EPR signal attributed to it above 750 °C [37]. N_C binds to V_{Si} with an energy of 3.3 eV, and the resulting defect possesses $(-/0)$ and $(0/+)$ levels at $E_v + 1.5$ eV and around E_v. The structure with the N atom along the c axis is slightly lower in energy (≤ 0.1 eV) than the structure with the N atom and the vacancy in the basal plane. The N atom stabilizes V_{Si} suppressing the transformation of the latter into V_C-C_{Si} as this defect, with a neighboring N_C, is 0.3 eV higher in energy than V_{Si}-N_C. The defect where N_C neighbors V_C-C_{Si} has acceptor and donor levels at $E_c - 0.9$ and $E_c - 1.4$ eV. None of these levels are close to those of Z_1/Z_2, and we can rule out a connection between the centers.

In summary, we have investigated candidates for the commonly observed Z_1/Z_2 defects in 4H-SiC. We find that the most likely model involves a thermally stable π-bonded dicarbon interstitial complex next to a nitrogen atom. The di-interstitial does not possess any unpaired electrons. The π bond is unstable in the negative charge state but the presence of a single N atom in the defect allows the formation of two atoms with lone pairs. The calculated energy levels and thermal stability are in good agreement with observations. Finally, it is to be noted that the defect would disappear when trapping a mobile vacancy which offers an explanation for the simultaneous disappearance of a positron-annihilation signal due to vacancies and Z_1/Z_2 defects.

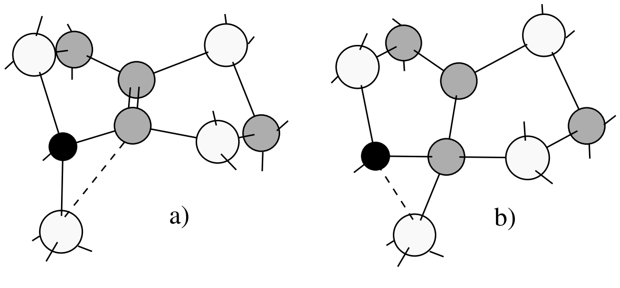

FIG. 2. (a) The N_i-C_i defect in the positive charge state and (b) in the negative charge state. N, Si, C atoms are shown in black, white, and gray. Note the π bond in (a) is broken in (b) and N and one carbon atom possess a dangling bond. The dashed line shows the bond which is switched between (a) and (b).

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[1] I. Pintilie, L. Pintilie, K. Irmscher, and B. Thomas, Appl. Phys. Lett. **81**, 4841 (2002).

[2] K. Fujihira, T. Kimoto, and H. Matsunami, Appl. Phys. Lett. **80**, 1586 (2002).

[3] T. Dalibor, C. Peppermüller, G. Pensl, S. Sridhara, R. P. Devaty, W. J. Choyke, A. Itoh, T. Kimoto, and H. Matsunami, in *Proceedings of the 6th International Conference on Silicon Carbide and Related Materials*, edited by S. Nakashima, H. Matsunami, S. Yoshida, and H. Harima, IOP Conf. Proc. No. 142 (Institute of Physics and Physical Society, London, 1996), p. 517.

[4] T. Dalibor, G. Pensl, T. Kimoto, H. Matsunami, S. Sridhara, R. P. Devaty, and W. J. Choyke, Diam. Relat. Mater. **6**, 1333 (1997).
[5] C. G. Hemmingsson, N. T. Son, A. Ellison, J. Zhang, and E. Janzén, Phys. Rev. B **58**, R10 119 (1998).
[6] C. G. Hemmingsson, N. T. Son, O. Kordina, J. P. Bergman, J. L. Lindström, S. Savage, N. Nordell, and E. Janzén, J. Appl. Phys. **81**, 6155 (1997).
[7] L. Storasta, F. H. C. Carlsson, S. G. Sridhara, J. P. Bergman, A. Henry, T. Egisson, A. Hallén, and E. Janzén, Appl. Phys. Lett. **78**, 46 (2001).
[8] M. O. Aboelfotoh and J. P. Doyle, Phys. Rev. B **59**, 10 823 (1999).
[9] M. Gong, S. Fung, C. D. Beling, and Z. You, J. Appl. Phys. **85**, 7604 (1999).
[10] C. G. Hemmingsson, N. T. Son, and E. Janzén, Appl. Phys. Lett. **74**, 839 (1999).
[11] P. W. Anderson, Phys. Rev. Lett. **34**, 953 (1975).
[12] T. A. G. Eberlein, C. J. Fall, R. Jones, P. R. Briddon, and S. Öberg, Phys. Rev. B **65**, 184108 (2002).
[13] A. Kawasuso, F. Redmann, R. Krause-Rehberg, M. Weidner, T. Frank, G. Pensl, P. Sperr, W. Trifthäuser, and H. Itoh, Appl. Phys. Lett. **79**, 3950 (2001).
[14] A. Kawasuso, F. Redmann, R. Krause-Rehberg, T. Frank, M. Weidner, G. Pensl, P. Sperr, and H. Itoh, J. Appl. Phys. **90**, 3377 (2001).
[15] J. R. Troxell and G. D. Watkins, Phys. Rev. B **22**, 921 (1980).
[16] C. Herring, N. M. Johnson, and C. G. Van de Walle, Phys. Rev. B **64**, 125209 (2001).
[17] D. J. Chadi and K. J. Chang, Phys. Rev. Lett. **61**, 873 (1988).
[18] G. D. Watkins and J. R. Troxell, Phys. Rev. Lett. **44**, 593 (1980).
[19] J. Coutinho, R. Jones, P. R. Briddon, and S. Öberg, Phys. Rev. B **62**, 10 824 (2000).
[20] S. B. Zhang and J. E. Northrup, Phys. Rev. Lett. **67**, 2339 (1991).
[21] S. M. Jeong, H. W. Shim, H. S. Yoon, M. G. Cheong, R. J. Choi, E.-K. Suh, and H. J. Lee, J. Appl. Phys. **91**, 9711 (2002).
[22] J. Coutinho, R. Jones, P. R. Briddon, and S. Öberg, Phys. Rev. B **67**, 35205 (2003).
[23] H. H. Woodbury and G. W. Ludwig, Phys. Rev. **124**, 1083 (1961).
[24] S. Greulich-Weber, M. Feege, J.-M. Spaeth, E. N. Kalabukhova, S. N. Lukin, and E. N. Mokhov, Solid State Commun. **93**, 393 (1995).
[25] W. Götz, A. Schöner, G. Pensl, W. Suttrop, W. J. Choyke, R. Stein, and S. Leibenzeder, J. Appl. Phys. **73**, 3332 (1993).
[26] M. A. Capano, J. A. Cooper, M. R. Melloch, A. Saxler, and W. C. Mitchel, J. Appl. Phys. **87**, 8773 (2000).
[27] G. D. Watkins and K. L. Brower, Phys. Rev. Lett. **36**, 1329 (1976).
[28] S. J. Breuer and P. R. Briddon, Phys. Rev. B **51**, 6984 (1995).
[29] D. C. Hunt, D. J. Twitchen, M. E. Newton, J. M. Baker, T. R. Anthony, W. F. Banholzer, and S. S. Vagarali, Phys. Rev. B **61**, 3863 (2000).
[30] It might disappear at a lower temperature by trapping another mobile center.
[31] J. P. Goss, B. J. Coomer, R. Jones, T. D. Shaw, P. R. Briddon, M. Rayson, and S. Öberg, Phys. Rev. B **63**, 195208 (2001).
[32] L. Torpo, M. Marlo, T. E. M. Staab, and R. M. Nieminen, J. Phys. Condens. Matter **13**, 6203 (2001).
[33] H. J. von Bardeleben, J. L. Cantin, I. Vickridge, and G. Battistig, Phys. Rev. B **62**, 10 126 (2000).
[34] M. Wagner, N. Q. Thinh, N. . Son, W. M. Chen, E. Janzén, P. G. Baranow, E. N. Mokhov, C. Hallin, and J. L. Lindström, Phys. Rev. B **66**, 155214 (2002).
[35] A. Zywietz, J. Furthmüller, and F. Bechstedt, Phys. Rev. B **59**, 15 166 (1999).
[36] E. Rauls, T. Lingner, Z. Hajnal, S. Greulich-Weber, T. Frauenheim, and J.-M. Späth, Phys. Status Solidi B **217**, R1 (2000).
[37] T. Lingner, S. Greulich-Weber, J.-M. Spaeth, U. Gerstmann, E. Rauls, and H. Overhof, Physica (Amsterdam) **308B–310B**, 625 (2001).