PHYSICAL REVIEW B **77**, 121203(R) (2008)

Soft modes at the stacking faults in SiC crystals: First-principles calculations

Tiju Thomas,[1] Dhananjai Pandey,[2] and Umesh V. Waghmare[1,*]
[1]*T.S.U., Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur Campus, Bangalore 560 064, India*
[2]*School of Materials Science and Technology, Banaras Hindu University, Varanasi-221 005, India*

(Received 9 January 2008; published 17 March 2008)

We use first-principles calculations based on density functional theory to determine and understand the driving force of the observed stacking fault expansion in SiC. We verify the suggestion based on recent experiments that the free energy difference between the faulted and the perfect structures is responsible for this expansion and show that its origin lies in a large entropy associated with soft vibrational modes of the faulted SiC structure that involve shearing of SiC on a long length scale. As a consequence, velocity of sound is expected to reduce noticeably in SiC with stacking faults, measurement of which should validate the soft-mode mechanism. Such mode-softening is absent in related group IV semiconductors, such as Si, Ge, and C.

DOI: 10.1103/PhysRevB.77.121203 PACS number(s): 61.72.Nn

Among the group IV semiconductors (Si, Ge, C, and SiC), SiC is unique in exhibiting hundreds of polytypes that differ only in the stacking sequence of Si-C double layers.[1] Due to its excellent physical properties such as high hardness, low density, and thermal expansion, it has found numerous applications in automotive components, seal faces, armour, mechanical seals, bearings, heat exchanger tubes, etc.[2] As it is available in large single crystal wafer form,[3] SiC is also interesting as a wide band-gap semiconductor for electronic applications: it is a promising material for the next generation power diodes owing to its low on-resistance, high breakdown voltage, radiation stability, and low switching losses.[4] Recently, there have been efforts aimed at developing dilute magnetic semiconductors (DMS)[5] based on SiC for use in spintronic devices.

However, formation of line defects[6,7] and expansion of stacking faults[8] in SiC crystals are known to be possible causes of degradation of the performance of SiC-based power diodes. Understanding the mechanism of stacking fault expansion in SiC is important to its use in electronic devices, and it will shed light on a related fundamental question of the stability of polytypes of SiC.[9] It is also interesting to find out if this mechanism operates in other group IV semiconductors.

In a power electronic device current densities as high as $50-100\ \mathrm{A/cm^2}$ lead to an enormous amount of heating and operational temperatures are higher than the normal ones. Optical emission microscopy (OEM) based experiments on 4*H*-SiC used in high current density conditions revealed stacking fault expansion in the basal plane of the system, establishing that 4*H* polytype of SiC is unstable at high temperatures with respect to formation and expansion of stacking faults.[8] Based on this work, free energy differences were *suggested* to be the driving force of stacking fault expansion. However, the microscopic origin or the degrees of freedom responsible for this are unknown.

Many groups have carried out first-principles investigation of the stability of various polytypes of SiC and their stacking faults.[10–12] With very small energy differences involved, the exact ordering energies of polytypes is a bit scattered in these studies. However, they all estimated very small but positive stacking fault energies. It is not clear yet what drives the stacking fault expansion in SiC at high temperature.

In this work, we use first-principles calculations to determine free energy differences between different polytypes and stacking-faulted structures of SiC through determination of configurational and vibrational entropies. Configurational and vibrational contributions to free energy are determined from the knowledge of the full stacking fault energy surface[13] and of the vibrational spectrum, respectively. We show that soft shear modes developed in the faulted structures drive their stability at finite temperature.

Along the (111) direction of the diamond (or zinc blende, labeled here as 3*C* polytype) structure, triangular lattices of atoms described with high symmetry positions *A*, *B*, and *C* are stacked periodically as (*AaBbCc*), where upper and lower case letters label the two fcc sublattices occupied by Si and C atoms, respectively. The polytypical structures obtained with a variation in this stacking sequence (studied in this work) are all tetrahedrally coordinated. 4*H* and 6*H* structures are made with *AaBbAaCc* and *AaBbCcAaCcBb* stacking sequences, respectively. The structure with a deformation stacking fault results when this stacking sequence is altered at a specific plane. There are two types of $(111)/(000l)$ planes where a deformation type stacking fault can form: (a) $A|a$ called as "shuffle," and (b) $a|B$ called as "glide."

Our calculations are based on first-principles pseudopotentials within density functional theory as implemented in the plane wave self-consistent field (PWSCF)[14] code. We employ a local density approximation (LDA) to exchange the correlation energy functional and use ultrasoft pseudopotentials[15] to represent interaction between ionic cores and valence electrons, and a plane wave basis with an energy cutoff of 30 Ry (180 Ry) in the representation of the Kohn-Sham wave functions (density). Supercells with 12 atomic planes for elemental semiconductors and 24 atomic planes for SiC are used in the calculations of configurations with stacking faults. Corresponding Brillouin zones are rather small in the *z* direction (perpendicular to the plane of the fault) and integrals over them were sampled with a uniform $5\times5\times1$ mesh. Positions of atoms inside the supercell were relaxed to attain a minimum energy structure using Hellman-Feynman forces in the Broyden, Fletcher, Goldfarb,

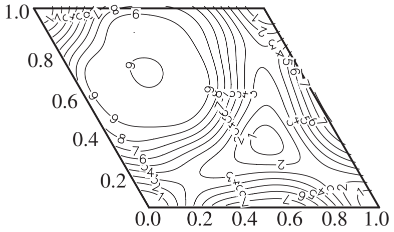

FIG. 1. Contour plot of generalized stacking fault energy(γ) surface for slip on the glide plane of 4*H*-SiC. For isovalues of energies equispaced between the minimum and maximum, contours are labeled with integers from 1 (lowest energy) to 10 (highest energy).

and Shanno (BFGS)-based method.[16] Structural parameters for Si, Ge, and C in diamond structure and 3*C*, 4*H*, and 6*H* polytypes of SiC agree with the experimental values within the typical LDA errors. We find the cohesive energies of all the SiC polytypes are rather close to each other and both 6*H* and 4*H* structures are almost equal within the calculational errors and the lowest in energy.

We first determined generalized stacking fault energy (γ) surfaces[13] for the (111) or basal planes of all the crystals studied here. It corresponds to the energy required to displace one-half of the crystal on one side of the given plane relative to the other and exhibits periodicity of the crystal plane. For a given displacement path going from the origin to a burgers vector **b**, a maximum in the γ surface gives the the energy barrier for slip along that path. The lowest of these barriers among the family of various paths joining origin and **b** is called the unstable stacking fault energy[17] γ_{us}. A local minimum of the γ surface defines an intrinsic [also called deformation(10)] stacking fault. We used Fourier transform to analyze the γ surface by sampling it on a uniform 5×5 mesh in the planar unit cell.

In all the tetrahedral systems considered here, our results rule out the possible slip on the shuffle plane as it is energetically 25–36 times more expensive than the slip on the glide plane. The γ surfaces of the glide plane of all tetrahedral semiconductors are topologically similar (see Fig. 1 for the γ surface of SiC). We find γ_{us} is about the same for the three polytypes of SiC, which is about half the γ_{us} of diamond and larger by 80% than that of Si and Ge (see Table I). The trend in our estimates of γ_{us} suggests that nucleation of dislocations on (111) planes is much easier in Si and Ge than in SiC and diamond.[17] The energy of the intrinsic stacking fault located at (2/3,1/3) in the γ surface (γ_{isf}) bears a rather different trend: it is smallest for the polytypes of SiC and five times larger for Si and even larger for diamond. These values generally agree well with experimental estimates and other calculations[18] wherever available. Significantly lower values of γ_{isf} (and somewhat large γ_{us}) of SiC support large areas of stacking faults which sometimes extend right up to the crystal boundaries with partials disappearing at the surface.

TABLE I. Calculated and experimental estimates of intrinsic (γ_{isf}) and unstable (γ_{us}) stacking fault energies for the slip in glide plane.

System	γ_{isf} (calculated) ($\mathrm{mJ/m^2}$)	γ_{isf} (experimental) ($\mathrm{mJ/m^2}$)	γ_{us} ($\mathrm{J/m^2}$)
Si	46.9	69 (Refs. 26 and 27)	1.7
C	250	279 (Refs. 27 and 28)	5.5
Ge	48.5		1.6
3*C*-SiC	10.1		2.8
4*H*-SiC	9.1	14.7 ± 2.5 (Ref. 11)	2.9
6*H*-SiC	2.6	2.5 ± 0.9 (Ref. 12)	2.9

We estimated the free energies of perfect and faulted SiC with $F=E+F_{config}+F_{vib}$, where E is the total energy obtained with DFT calculations, F_{config} and F_{vib} are the configurational and vibrational contributions to free energy, respectively.

F_{config} is obtained from the detailed structure of basins of the γ surface centered at (0,0) and (2/3,1/3) corresponding to perfect and faulted structures. We approximated the γ surface in the neighborhood of the centers (x_0,y_0) of these basins (sampled by the system at finite temperature T) with a symmetry invariant parabolic form: $E(x,y)=E_o+K[(x-x_o)^2+(y-y_o)^2]$, to determine configurational contribution to free energy[19]

$$F_{conf}=-k_BT\log\left(\frac{K}{2\pi k_BT}\right), \qquad (1)$$

where x and y are the components of displacements for which the GSF has been obtained, the parameter K was determined from DFT calculations carried out on a fine uniform 3×3 mesh over an area of $0.174\ \mathrm{bohr}^2$ centered in each basin. Similarly, vibrational free energy is determined with

$$F_{vib}=-k_BT\sum_{iq}\log\left[2\sinh\left(\frac{\hbar\omega_{iq}}{2k_bT}\right)\right], \qquad (2)$$

ω_{iq} being the frequency of a phonon i with wave vector q, obtained with DFT linear response calculations.[21] Such formalism has been used earlier with great success in the description of thermal properties of Si.[20] We sampled q at Γ and K points with weights of $\frac{1}{3}$ and $\frac{2}{3}$, respectively, omitting acoustic modes at the Γ. While this is an approximate description of phonons, our estimates of specific heat, a related thermal property, are within 8% of experimental values up to temperatures of 800 K (see inset in Fig. 2).

The stacking fault energy as a function of temperature is obtained using $\gamma_s(T)=\gamma_s(0)+\Delta F_{conf}(T)+\Delta F_{vib}(T)$, where $\gamma_s(0)$ is the stacking fault energy at zero temperature, and ΔF is the difference in free energy of the perfect and the faulted structures. For 4*H*-SiC, we find the vibrational contribution to $\Delta F/T$ ($-2.4\times10^{-5}\ \mathrm{J/m^2\,K}$) dominating over the configurational contribution ($0.27\times10^{-5}\ \mathrm{J/m^2\,K}$). While the same is true in 6*H*-SiC, both vibrational and configurational contributions (of -1.8×10^{-5} and $-3.14\times10^{-6}\ \mathrm{J/m^2\,K}$) to free energy favor its faulted structure. Evidently, vibrational entropy plays a crucial role in stabilizing the faulted structure in both 4*H*-SiC and 6*H*-SiC structures at high temperatures. The estimated stacking fault energy of both 4*H* and 6*H* poly-

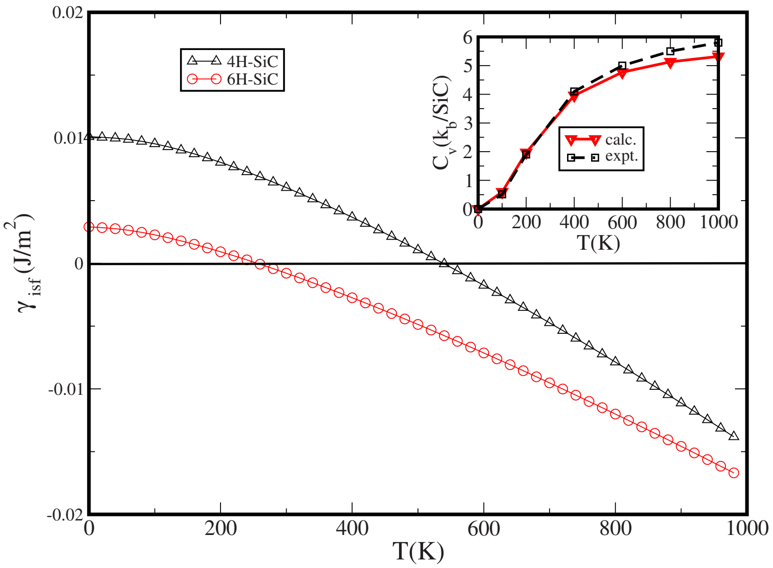

FIG. 2. (Color online) Stacking fault energy (γ_{isf}) of 4H and 6H polytypes of SiC as a function of temperature. Inset shows a comparison of our calculated estimate of specific heat with experimental values as a function of temperature.

types becomes negative (see Fig. 2) above a certain temperature (530 K for 4H-SiC and 250 K for 6H-SiC). If there are perfect dislocations already present or introduced by external stresses during plastic deformation, they will split spontaneously because of the low stacking fault energy. The split partials repel each other and usually a positive SFE holds them together at an equilibrium separation. The main consequence of the negative stacking fault energy would be that the partials would move out to the surface in the absence of any obstacle on the slip plane and the stacking fault would spread over the slip plane. However, there may always be other dislocations on the slip plane which would stop the partials from moving out to the surface.

We now determine the precise microscopic mechanism that stabilizes the faulted structure by examining mode-by-mode contribution to the vibrational free energies. In comparison with the perfect structure, there emerge four soft phonon modes (see Fig. 3) in the faulted 4H structure with frequencies 107, 107, 110, and 110 cm^{-1} (80, 80, 82, and 82 cm^{-1} in the 6H-SiC), which lowers its free energy through its contribution to the entropy. We note that most of these soft modes involve shear straining of the structure over a longer length scale in a direction perpendicular to the plane of the fault [see Fig. 3(b)]. These soft modes couple with shear strain and can drastically reduce shear elastic moduli, which in this case is C_{44}. Thus large shear strains can be induced even with small shear stresses in the system. While the same modes would respond strongly to applied stresses and stabilize the faults, our work supports that faults will be stabilized thermally even in the *absence of external stresses*.

We note that the crossover temperatures determined here are expected to have some errors due to the small size of the supercell and high density of stacking faults used in our calculations. However, the mechanism of soft modes identified here is expected to be reliable. In contrast to the 4H structure, we find the configurational contribution to free energy alone is adequate in stabilizing faults in the 6H structure. We now suggest a simple experiment to validate the microscopic mechanism proposed here: we predict that the velocity of sound (transverse acoustic waves) will be reduced noticeably upon formation of stacking faults (possibly thermally) in both 4H and 6H structures. Similar calculations of phonons in Si, C, and GaAs show no softening of phonons due to the presence of stacking faults, indicating the unique properties of SiC among group IV and related semiconductors.

Finally, we would like to comment on the relative stability of 4H and 6H structures of SiC. Many groups[22–25] have reported energies of these structures within a couple of meV per atom of each other. However, these are very small energies and we think both structures are equally stable at $T=0$ K within our calculational errors. By including vibrational contribution to free energy at nonzero temperature, we

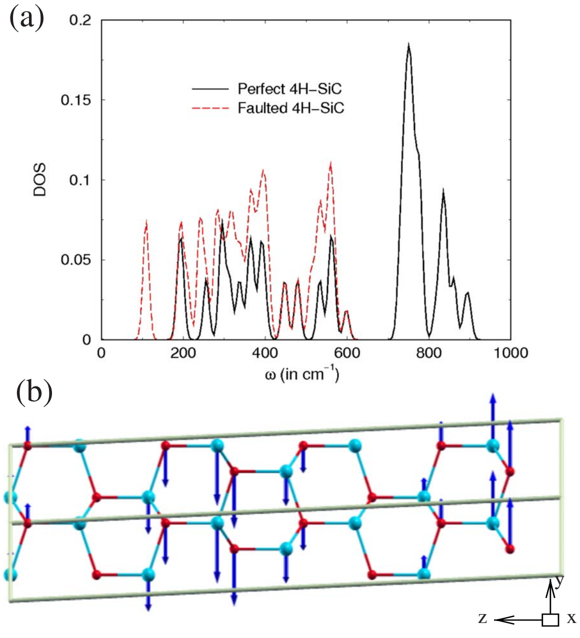

FIG. 3. (Color online) (a) Phonon density of states of perfect and faulted 4H-SiC (top) and 6H-SiC (bottom); arrows indicate the soft modes in faulted structures. (b) Soft phonon mode of frequency 107 cm^{-1} in faulted 4H-SiC.

find that the 6*H* structure is more stable than the 4*H* structure by a sizeable difference in free energy (with a rate of 6×10^{-5} eV/atom/K). Along with our earlier conclusion that the 6*H* structure would also tend to form faults at finite temperature, we conclude that both 4*H* and 6*H* structures of SiC are metastable at finite temperature.

In summary, we have verified the speculation based on experimental work[8] that free energy difference is the driving force of stacking fault expansion in SiC. The stability of the faults has been shown to arise from the vibrational entropy and particularly soft phonon modes that involve atomic displacements that shear the faulted structure on long length scale. As a result, stacking faults are expected to grow at finite temperature in both 4*H* and 6*H* polytypes of SiC and this is a fundamental limitation of SiC for use in devices. Our work should stimulate further theoretical and experimental work that focuses on destabilizing stacking faults in SiC through suitable doping or other means.[29]

The authors thank the late F. R. N. Nabarro for stimulating discussions. T.T. acknowledges useful suggestions from S. Aarti, J. Bhattacharjee, N. Ellegard, M. Upadhyay Kahali, and G. Dutta. We are grateful to the CCMS and the central computer Lab at JNCASR for the use of computational facilities.

---

*waghmare@jncasr.ac.in

[1] A. R. Verma and P. Krishna, *Polymorphism and Polytypism in Crystals* (Wiley, New York, 1966).

[2] P. Melinon, B. Masenelli, F. Tournus, and A. Perez, Nat. Mater. **6**, 479 (2007).

[3] D. Nakamura, I. Gunjishima, S. Yamaguchi, T. Ito, A. Okamoto, H. Kondo, S. Onda, and K. Takatori, Nature (London) **430**, 1009 (2004).

[4] B. Ozpinecci, Ph.D. dissertation, The University of Tennessee, Knoxville, 2002.

[5] V. L. Shaposhnikov and N. A. Sobolev, J. Phys.: Condens. Matter **16**, 1761 (2004).

[6] A. O. Konstantinov and H. Bleichner, Appl. Phys. Lett. **71**, 3700 (1997).

[7] H. Lendenmann, F. Dahlquist, N. Johansson, R. SÃderholm, P. A. Nilsson, J. P. Bergman, and P. Skytt, Mater. Sci. Forum **727**, 353 (2001).

[8] S. Ha, M. Skowronski, J. J. Sumakeris, M. J. Paisley, and M. K. Das, Phys. Rev. Lett. **92**, 175504 (2004).

[9] D. Pandey and P. Krishna, in *Current Topics in Materials Science*, edited by E. Kaldis (North-Holland, Amsterdam, 1982) pp. 9,415; Prog. Cryst. Growth Charact. **7**, 213 (1983).

[10] U. Lindefelt, H. Iwata, S. Oberg, and P. R. Briddon, Phys. Rev. B **67**, 155204 (2003).

[11] M. H. Hong, A. V. Samant, and P. Pirouz, Philos. Mag. A **80**, 919 (2000).

[12] K. Maeda, K. Suzuki, S. Fujita, M. Ichihara, and S. Hyodo, Philos. Mag. A **57**, 573 (1988).

[13] V. Vitek, Philos. Mag. **18**, 773 (1968).

[14] S. Baroni, A. D. Corso, S. de Gironcoli, and P. Giannnozzi, http://www.pwscf.org

[15] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).

[16] http://www.library.cornell.edu/nr/bookcpdf/c10-7.pdf

[17] J. R. Rice, J. Mech. Phys. Solids **40**, 239 (1992).

[18] E. Kaxiras and M. S. Duesbery, Phys. Rev. Lett. **70**, 3752 (1993).

[19] R. LeSar, R. Najafabadi, and D. J. Srolovitz, Phys. Rev. Lett. **63**, 624 (1989).

[20] G.-M. Rignanese, J.-P. Michenaud, and X. Gonze, Phys. Rev. B **53**, 4488 (1996).

[21] S. Baroni, S. Gironcoli, A. D. Corso, and P. Giannozi, Rev. Mod. Phys. **73**, 515 (2001).

[22] S. Limpijumnong and Walter R. L. Lambrecht, Phys. Rev. B **57**, 12017 (1998).

[23] C. H. Park, B. H. Cheong, K. H. Lee, and K. J. Chang, Phys. Rev. B **49**, 4485 (1994).

[24] P. P. Kackell, B. Wenzien, and F. Bechstedt, Phys. Rev. B **50**, 17037 (1994).

[25] C. Cheng, R. J. Needs, and V. Heine, J. Phys. C **21**, 1049 (1988).

[26] H. Foll and C. Carter, Philos. Mag. A **40**, 497 (1979).

[27] P. Kackell, J. Furthmuller, and F. Bechstedt, Phys. Rev. B **58**, 1326 (1998).

[28] P. Pirouz, D. J. H. Cockayne, N. Sumida, P. Hirsch, and A. R. Lang, Proc. R. Soc. London, Ser. A **386**, 241 (1983).

[29] M. S. Miao and W. R. L. Lambrecht, Phys. Rev. B **68**, 125204 (2003).