First-principle calculation on the defect energy level of carbon vacancy in 4H–SiC*

Jia Ren-Xu(贾仁需)†, Zhang Yu-Ming(张玉明), and Zhang Yi-Men(张义门)

School of Microelectronics, Key Laboratory of Wide Band-Gap Semiconductor Materials and Devices, Xidian University, Xi'an 710071, *China*

(Received 4 February 2010; revised manuscript received 17 May 2010)

First, electronic structures of perfect wurtzite 4H–SiC were calculated by using first-principle ultra-soft pseudopotential approach of the plane wave based on the density functional theory; and the structure changes, band structures, and density of states were studied. Then the defect energy level of carbon vacancy in band gap was examined by substituting the carbon in 4H–SiC with carbon vacancy. The calculated results indicate the new defect energy level generated by the carbon vacancy, and its location in the band gap in 4H–SiC, which has the character of deep acceptor. A proper explanation for green luminescence in 4H–SiC is given according to the calculated results which are in good agreement with our measurement results.

Keywords: 4H–SiC, energy band structure, carbon vacancy

PACC: 7155E, 7855C

1. Introduction

4H–SiC is an attractive semiconductor material with a wide band gap, high breakdown field, and high heat conductivity, which realizes high-power, high-temperature, and high-frequency devices.[1−3] Deep levels in 4H–SiC can compound the ntype carriers to form the semi-insulated 4H–SiC, however they also have several harmful effects such as carrier trapping, the increase in leakage current, and a reduction in the minority carrier lifetime. For example, to realize SiC bipolar devices for high-voltage power switches, control of the carrier lifetime is an important issue which determines the on-state resistance as well as the switching speed.[4−6] Therefore, deep levels should be controlled and reduced in the fabrication of high-performance SiC devices.

Through fundamental studies on SiC growth and characterization in recent years, deep levels in 4H–SiC have been mostly elucidated using deep level transient spectroscopy (DLTS) and electron spin resonance (ESR) spectroscopy,[7−11] although the microscopic structures of almost all the deep levels are still an open question, and few reports are on the theoretical calculation and analysis.

In this report, electronic structures of perfect wurtzite 4H–SiC and 4H–SiC with carbon vacancy are calculated by a first-principle ultra-soft pseudopotential approach of the plane wave based on the density functional theory. The structural change, band structure, and density of states are studied. The relationship of carbon vacancy and band gap has been analysed based on the test results of ESR.

2. Model, detail of calculation and measurement

2.1. Model

Perfect 4H–SiC is of a wurtzite structure, which belongs to $P63mc$, with a symmetry of $C6v-4$ and lattice parameters $a = b = 3.073$ nm, $c = 10.53$ nm. The unit cell is of hexagonal close packing, which contains sixteen silicon (Si) atoms and carbon (C) atoms. The 2×2×2 supercell with 128 Si and C atoms is selected in this model, and the model of carbon vacancy is based on the 2×2×2 supercell by replacing the carbon atom with vacancy, as shown in Fig. 1.

*Project supported by the National Natural Science Foundation of China (Grant No. 60876061) and the Fundamental Research Funds for the Central Universities.

†Corresponding author. E-mail: rxjia@mail.xidian.edu.cn

© 2010 Chinese Physical Society and IOP Publishing Ltd

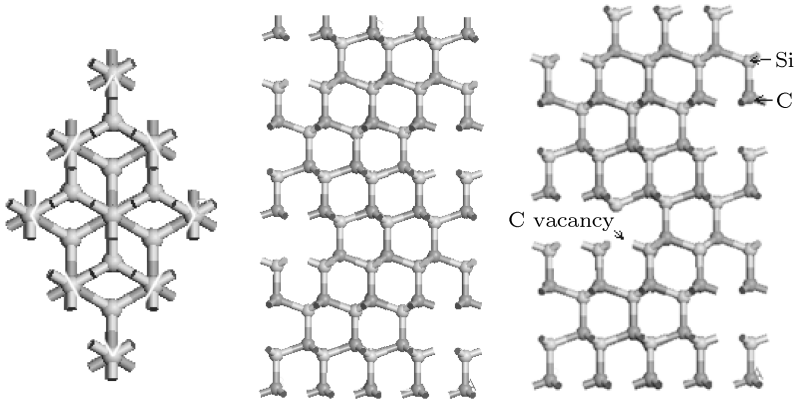


Fig. 1. Supercell of 4H–SiC (2×2×2): (a) top view of 4H–SiC supercell, (b) perspective view of 4H–SiC supercell, and (c) perspective view of 4H–SiC supercell with carbon vacancy.

2.2. Detail of calculation

The calculation in this study is based on the quantum mechanical program Castep.[12−14] Tridimensional cyclic boundary condition is adopted to change the electric system to the function of plane wave in the cyclic potential field of crystal. The interaction of ion and valence electron is approached by ultra-soft pseudo-potential to reduce the number of plane waves. Valence electron configurations of Si and C are selected as $3s^2 3p^2$ and $2s^2 2p^2$, respectively. In this calculation, the accuracy of convergence is 2×10^{-5} eV/atom in the iterative program and the stress accuracy of convergence in crystal is 0.1 GPa with cut-off energy ($E_{\rm cut}$) of plane wave 310 eV in the reciprocal space k. The total energy calculations are in the reciprocal space k, and Monkrs–Park method is used to selected k points during the integral calculation in the Brillouin zone.

2.3. Measurement

The defects in unintentionally doped homoepitaxial 4H–SiC have been studied using electron spin resonance (ESR) spectroscopy with 9.07 GHz frequency spectrograph. The temperature is 110 K and the direction of magnetic field (B) is parallel to c axis of 4H–SiC.

3. Results and discussion

3.1. Structure of crystal lattice

The structures of perfect 4H–SiC and 4H–SiC with carbon vacancy are optimized firstly, and the optimized crystal lattices are shown in Table 1.

Table 1. The crystal lattices of perfect 4H–SiC and 4H–SiC with carbon vacancy optimized (in unit of nm).

name	this report	experimental value	Ref. [16]	error
4H–SiC	$a = 0.3081$	$a = 0.3073$	$a = 0.3038(1)$;	0.26%
	$c = 1.0102$		$a = 0.3051(2)$	0.49%
4H–SiC:	$a = 0.3091$	$c = 1.0053$	$c = 0.994(1)$;	0.59%
with carbon vacancy	$c = 1.0121$		$c = 0.9984(2)$	0.68%

The parameters of crystal lattice are in good agreement with the experimental values[15] and those in Ref. [16] shown in Table 1. The a and c parameters of 4H–SiC with carbon vacancy have a slight increment. It is believed that the crystal lattices are distorted and the stress appears in the crystallization due to the absence of carbon atoms, which causes the increase of crystal volume less than that of the perfect 4H–SiC.

3.2. Band structures and density of states

The band structures of perfect 4H–SiC calculated by ultra-soft pseudo-potential approach of the plane wave are shown in Fig. 2.

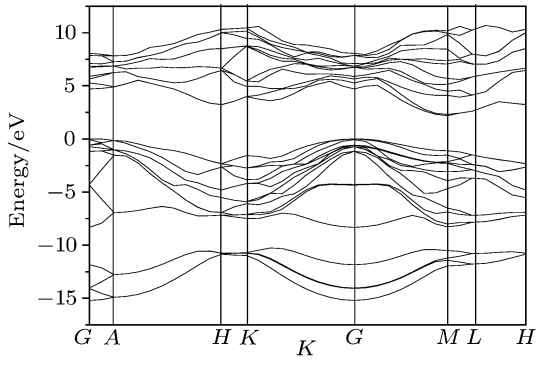


Fig. 2. Band structure of the perfect 4H–SiC.

It is found that the bottom of 4H–SiC conduction band is at the point M, and the top of valence band is at the point G, indicating that the 4H–SiC is an indirect band-gap semiconductor. The energy band is dual-degenerate on the line A/H and L/H in the Brillouin zone, which is caused by inverse symmetry in the c axis.[17]

The perfect 4H–SiC total density of states and partial-wave density of states are shown in Fig. 3.

The energy band of perfect 4H–SiC can be divided into three parts, band 1 (−15 eV∼10 eV), band 2 (−8 eV∼0 eV), and band 3 (2.3 eV∼11 eV), as shown in Fig. 3(a). According to the partial-wave density of states for Si atom (b) and for C atom (c), the band 1 has strong independence, and it is not related to the other bands. The states of Si2p2 and C3p2 are distributed in the band 2, and the top of valence band is determined by the states of C3p2. The state of Si3p2, a few states of Si3s2 and C2p2 are distributed in the band 3, and the bottom of conduction band is determined by the state of Si3p2.

The deep level energy caused by carbon vacancy is calculated and analysed with the reasonable results of perfect 4H–SiC. The calculations also follow the process (a) crystal cell optimized, (b) atomic parameters optimized to obtain crystal lattices, (c) calculations of electronic characterizations. The parameters of crystal lattices optimized are given in Table 1.

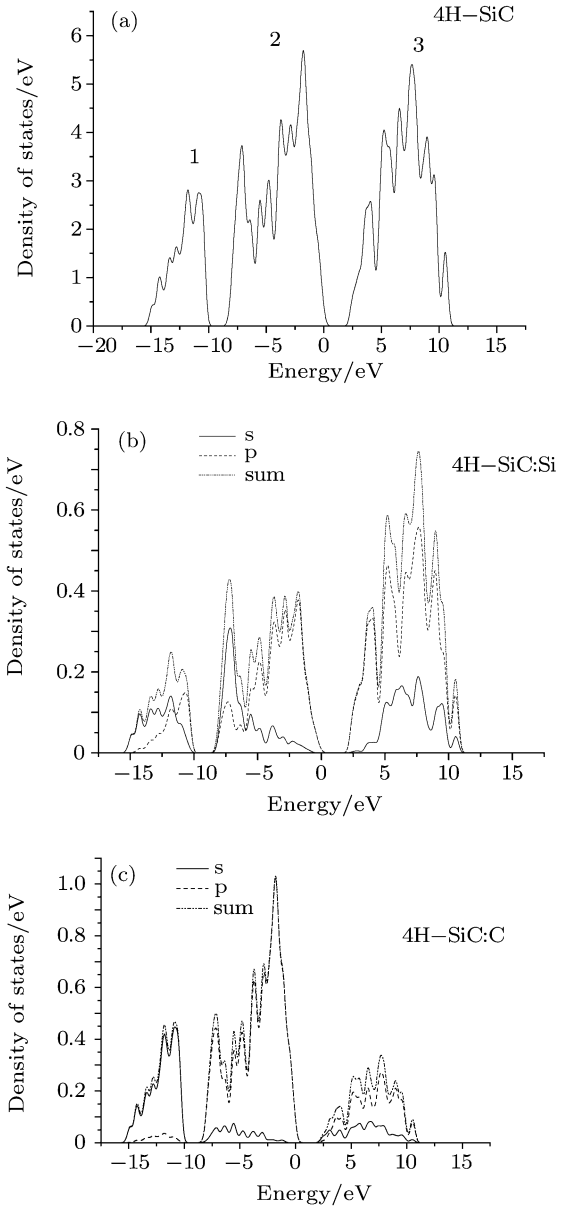


Fig. 3. The perfect 4H–SiC total density of states (a) and partial-wave Si atom (b), and C atom (c).

The total density of states of 4H–SiC with carbon vacancy is shown in Fig. 4(a), and the variations of density of states caused by carbon vacancy in the band gap are amplified in Fig. 4(b) in details.

The results of calculation indicate that some new density of states appears in the band gap due to the carbon vacancy, and the new energy band is at almost the middle of the band gap with the characterizations of deep level acceptors.

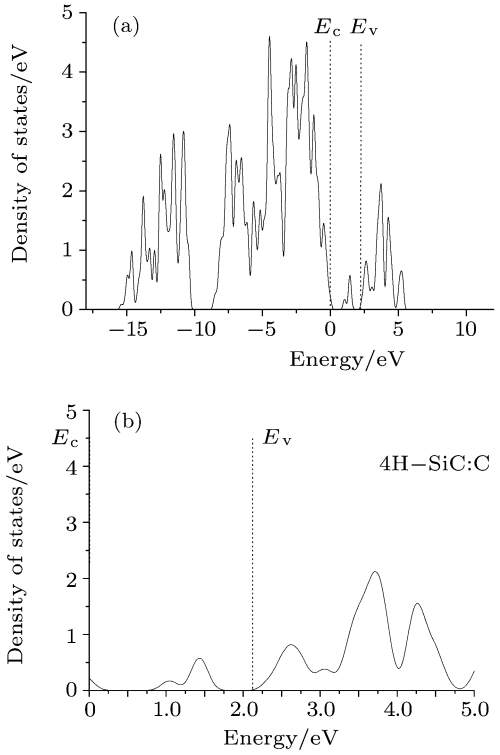


Fig. 4. The total density of states in 4H–SiC with carbon vacancy (a), and enlarged part showing the variation of density of states caused by carbon vacancy in the band gap (b).

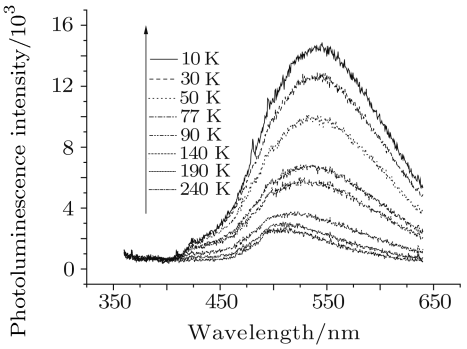


Fig. 5. The Photoluminescence versus wavelength for different temperatures.

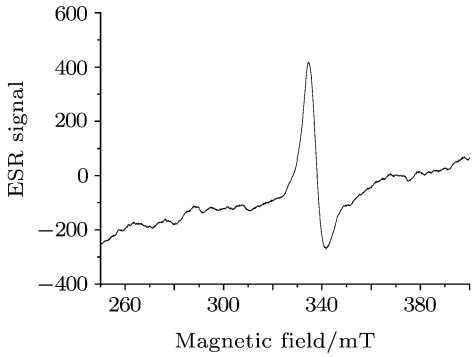


Fig. 6. Electron spin resonance (ESR) of the sample as a function of B with $B \parallel c$.

To verify the analysis above, the unintentionally doped 4H–SiC prepared by low pressure chemical vapour deposition (LPCVD) is studied by electron spin resonance (ESR) and low-temperature photoluminescence (LTPL), as shown in Figs. 5 and 6.[18] The deep energy level was found in the band gap with the green light exciting in the sample; and lots of carbon vacancies existed in the sample according to the ESR results, which induced deep acceptor level based on our theoretical calculation. It is believed that the deep acceptor levels in the middle of 4H–SiC band gap are mainly caused by carbon vacancy according to the agreement of experiment results and calculation.

4. Conclusion

In this report the electronic structures of perfect wurtzite 4H–SiC and 4H–SiC with carbon vacancy were calculated by a first-principle ultra-soft pseudopotential approach of the plane wave. The structural changes, band structures and density of states were studied. The results of calculation and experiments indicated that some new density of states appeared in the band gap due to the carbon vacancy, and the new energy band was almost in the middle of the band gap with the character of deep level acceptors.

References

[1] Itoh A and Matsunami H 1997 *Crit. Rev. Solid State Mater. Sci.* **22** 111

[2] Jia R X, Zhang Y M and Zhang Y M 2008 *Acta Phys. Sin.* **57** 4456 (in Chinese)

[3] Chelnokov V E, Syrkin A L and Dmitriev V A 1997 *Diamond Relat. Mater.* **6** 1480

[4] Zvanut M E and Konovalov V V 2002 *Appl. Phys. Lett.* **80** 410

[5] Carlos W E, Glaser E R and Shanabrook B V 2003 *Physica* B **151** 340

[6] Son N T, Magnusson B, Zolnai Z, Ellison A and Janzén E 2004 *Mater. Sci. Forum.* **437** 457

[7] Dalibor T, Pensl G and Matsunami H 1997 *Phys. Status Solidi* A **162** 199
[8] Hemmingsson C, Son N T and Kordina O 1997 *J. Appl. Phys.* **81** 6155
[9] Storasta L, Bergman J P and Janzén E 2004 *J. Appl. Phys.* **96** 4909
[10] Danno K and Kimoto T 2006 *J. Appl. Phys.* **100** 113728
[11] Danno K and Kimoto T 2007 *J. Appl. Phys.* **101** 103704
[12] Payne M C, Teter M P and Allan D C 1992 *Rev. Mod. Phys.* **64** 1045
[13] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865
[14] Keiji W, Masatoshi S and Hideaki T 1999 *J. Electron. Chem.* **473** 250
[15] Jiang Z Y, Xu X H and Wu H S 2002 *Acta Phys. Sin.* **51** 1586 (in Chinese)
[16] Michael E L, Sergay L R and Michael S S 2001 *Properties of Advanced Semiconductor Materials* (New York: John Wiley & Sons) p. 129
[17] Bechstedt F 1998 *Mater. Sci. Forum.* **264–268** 265
[18] Jia R X, Zhang Y M and Zhang Y M 2009 *Chin. J. Semicond.* **30** 033003-3