Electronic structure and magnetic properties of (Cu, N)-codoped 3C-SiC studied by first-principles calculations*

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(Received 22 March 2016; revised manuscript received 12 May 2016; published online 19 July 2016)

The electronic structures and magnetic properties of the Cu and N codoped 3C-SiC system have been investigated by the first-principles calculation. The results show that the Cu doped SiC system prefers the anti-ferromagnetic (AFM) state. Compared to the Cu doped system, the ionicities of C–Cu and C–Si in Cu and N codoped SiC are respectively enhanced and weakened. Especially, the Cu and N codoped SiC systems favor the ferromagnetic (FM) coupling. The FM interactions can be explained by virtual hopping. However, higher N concentration will weaken the ferromagnetism. In order to keep the FM interaction, the N concentration should be restricted within 9.3% according to our analysis.

Keywords: ferromagnetism, 3C-SiC, codoped system

PACS: 61.72.–y, 71.15.Pd, 71.20.–b **DOI:** 10.1088/1674-1056/25/9/096108

1. Introduction

Compared with the conventional semiconductors, the diluted magnetic semiconductors (DMSs), in which the cations are substituted by transition metal (TM) ions, have attracted a great deal of attention due to their promising applications in spintronics.[1,2] The DMSs with high Curie temperature and inherent ferromagnetism are preferred for applications. Among those systems, SiC-based DMSs have been frequently studied in the last few decades due to the outstanding properties of SiC. Although many researchers have reported the magnetic behaviors of SiC-based DMSs, the results are not completely consistent with each other. For instance, Azri *et al.*[3] pointed out theoretically that Mn-doped SiC has different moments at different Mn sites. Applying the *ab initio* method, Elzain *et al.*[4] found that the Fe doped SiC is magnetic when the Fe atoms are at the interstitial sites. Syväjärvi *et al.*[5] fabricated ferromagnetic Mn doped 4H-SiC by the chemical vapor deposition method. Theodoropoulou *et al.*[6] also prepared Mn and Fe doped 6H-SiC with high Curie temperature and without secondary phase. However, Stromberg *et al.*[7] prepared Fe doped 6H-SiC by the pulsed laser deposition (PLD) method and found super-paramagnetic cluster Fe_3Si. In order to exclude the FM TM-based second phases, the doping with non-TMs in SiC may be a good choice. In fact, Lin *et al.*[8] have explored the magnetic properties of Al doped 4H-SiC by the first-principles calculation. Liu *et al.*[9] revealed that local surface magnetism can be induced in SiC by nonmetal dopants, and the magnetism diminishes gradually and finally disappears with doping depth. Both theoretical and experimental reports[10–12] have revealed that irradiation can induce magnetism in SiC. The defects induced ferromagnetism also has been observed in SiC,[13–15] which puzzles the understanding of ferromagnetism. Moreover, the co-doping with TM and non-metal elements may be an effective method making the DMSs FM.[16] All possible Cu-based second phases are nonmagnetic,[17] and thus Cu may be a good dopant candidate for SiC.[18–20] In this paper, we performed the first-principles calculations to study the electronic structures and magnetic properties of the (Cu, N) co-doped 3C-SiC system and provided a feasible method to make the SiC-based DMSs FM.

2. Computational details

The calculations were performed by using the CASTEP package with a plane-wave basis set and ultrasoft pseudopotentials.[21] A plane-wave cutoff energy of 500 eV was used throughout, and the convergence criterion was 10^{-6} eV for self-consistent calculations. The Brillouin zone integrations were performed with a Γ-centered $6\times6\times6$ Monkhorst–Pack k-points mesh[22] for the primitive cell and a $2\times2\times2$ mesh for the $2\times2\times2$ (64-atom) supercell. The atomic coordinates for all the doped configurations have been optimized until the atomic forces are smaller than 0.01 eV/Å. The exchange–correlation functional was treated with the Perdew–Burke–Ernzerhof (PBE) formulation of the generalized gradient approximation (GGA).[23] With these choices, the relaxed 3C-SiC crystal structure parameter of $a = 4.308$ Å is in good agreement with the experimental value.

*Project supported by the Higher School Science Research Outstanding Youth Fund Project of Ningxia, China (Grant No. NGY2015049).
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3. Results and discussion

First, we studied the optimal doped sites for Cu and N. In thermodynamic equilibrium, the concentration of impurities, defects, or complexes is given by the expression[24]

$$C = N_{\text{sites}} N_{\text{config}} \exp(-E^{\text{f}}/k_{\text{B}}T),$$

where N_{sites} is the number of sites in the lattice to which the defect can be incorporated, N_{config} is the number of equivalent configurations in which the defect can be incorporated, E^{f} stands for the formation energy, k_{B} is the Boltzmann constant, and T is the temperature. As summarized in Table 1, C is substituted by N (N@C) and Si by Cu (Cu@Si) with lower formation energies, which may be attributed to the optimal doped sites and are in good agreement with other reports.[25,26]

Table 1. Formation energies at different doping sites for N and Cu.

Doped site	N@Si	N@C	Cu@Si	Cu@C
Formation energy/eV	–1.37	–7.20	4.46	4.88

Next, we investigated the electronic structure of Cu doped SiC at Si site. In 3C-SiC, the four C atoms near the Cu atom have a regular tetrahedron structure with T_d symmetry. From the point view of group theory, the degenerated defect state splits into the a-singlet with lower energy and the t-triplet with higher energy due to the polarity crystal field.[27] The Mulliken population as shown in Table 2 reveals that the C–Cu length is increased, and the ionicity is enhanced compared with that of C–Si. The five electrons come from the Cu, and four neighboring C atoms occupy the defect states. The a-singlet is fully occupied by two electrons, while the t-triplet is partially occupied by the other three electrons. Such electron configuration of $a^2t_+^3t_-^0$ leads to a net local moment of 3 μ_{B}, where "+" and "−" mean spin-up and spin-down, respectively. The calculated results imply that the defect states introduced by Cu are in the band gap of SiC, as shown in the band structure of $Si_{31}CuC_{32}$ (Fig. 1). Figure 1 indicates that the t_+ states are non-degenerated and all occupied; and the t_- states are also non-degenerated but unoccupied. The electron occupation calculated is in accordance with that analyzed by the group theory. Figure 2 gives the total density of states (DOS) and projected DOS (PDOS). It shows that the introduced defect states mainly come from the Cu-d electrons.

Table 2. The Mulliken population of different configurations.

Configuration	Atom	Charge	Bond	Population	Length/Å
$Si_{32}C_{32}$	Si	1.26	C–Si	0.75	1.896
	C	–1.26			
$Si_{31}CuC_{32}$	Cu	0.82	C–Cu	0.36	2.037
	Si	1.26	C–Si	0.75	1.896
	C	–1.26			
$Si_{31}CuC_{31}N$	Cu	0.76	C–Cu	0.30	2.034
	N	–1.11	N–Si	0.50	1.921
	Si	1.26	C–Si	0.76	1.898
	C	–1.26			

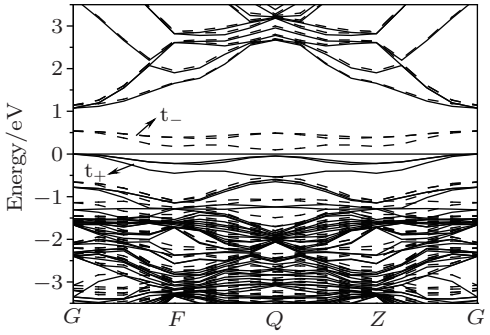


Fig. 1. The band structure of $Si_{31}CuC_{32}$, the horizontal line at 0 eV is the Fermi level.

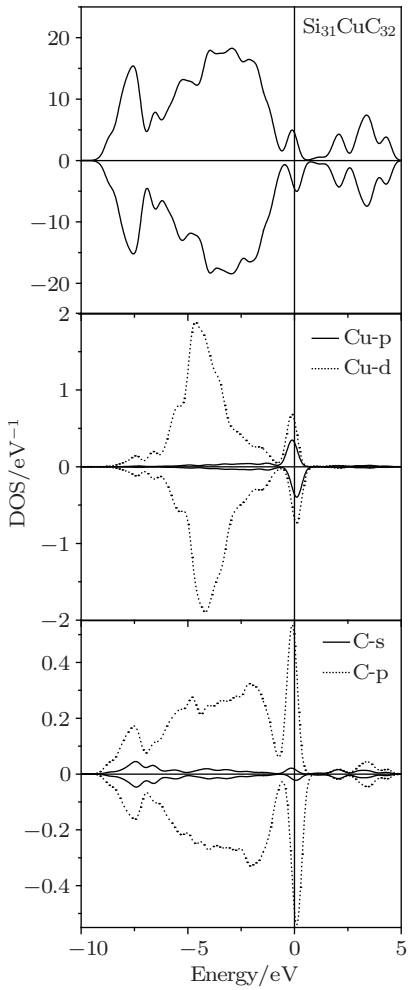


Fig. 2. The total DOS of $Si_{31}CuC_{32}$ and PDOS of Cu and C. The vertical line at 0 eV is the Fermi level.

The magnetic interactions between the Cu@Si defects were then investigated. We calculated the total energies of SiC supercell containing two Cu@Si in FM and AFM states. The total energy difference $\Delta E = E_{\text{FM}} - E_{\text{AFM}}$ is 239 meV, meaning that the magnetic coupling of the Cu@Si defects is AFM. For Cu@Si, the defect state occupation is $a^2t_+^3t_-^0$. The t_+ states are all occupied, and thus cannot accommodate other electrons with spin-up; while the t_- states are un-occupied, and thus can hold other electrons with spin-down. Therefore,

the AFM interaction is allowed as shown in Fig. 3(a), which is similar to the mechanism revealed in other reports.[28,29]

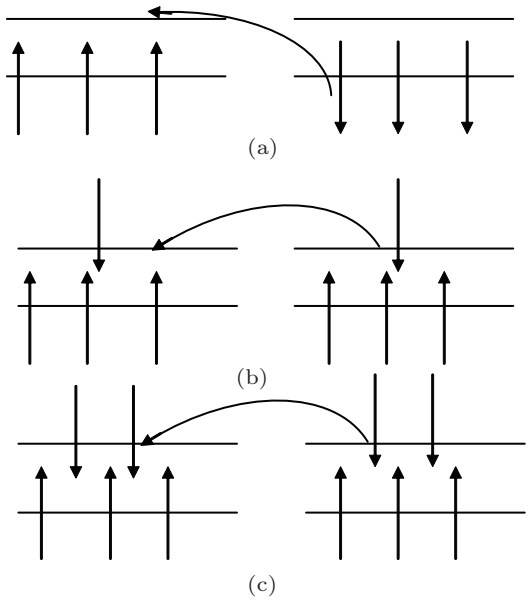


Fig. 3. The electron configurations and schematic exchange mechanisms of defect states in (a) $Si_{31}CuC_{32}$, (b) $Si_{31}CuC_{31}N$, and (c) $Si_{31}CuC_{30}N_2$.

To make the Cu doped SiC DMSs FM, another defect should be introduced. We studied the electron structure of one Cu and one N codoped SiC ($Si_{31}CuC_{31}N$). The structure model is shown in Fig. 4 (for this doped system, Cu is at site 1, N is at site 2). As shown in Fig. 5(a), the codoped system is spin-polarized near the Fermi level, and the calculated magnetic moment is 2 μ_B. Figures 5(b) and 5(c) indicate that the magnetic moment is mainly contributed by Cu-p, Cu-d, and C-p states. The doped N offers one more electron than C, but it has no contribution to the moment as shown in Fig. 5(d). When the N is doped into the system, we found that the ionicities of Cu–C and C–Si are respectively enhanced and weakened, while the covalency of C–Si becomes stronger compared with that of the undoped system, as shown in Table 2. In addition, the N atom has one more electron than the C atom and favors the C sites. The electron configuration of defect states of Cu and N codoped SiC should be $a^2t_+^3t_-^1$, resulting in a local moment of 2 μ_B from the viewpoint of group theory. Figure 6 gives the band structure of the Cu and N co-doped system. It shows that three t_+ orbits are below the Fermi level

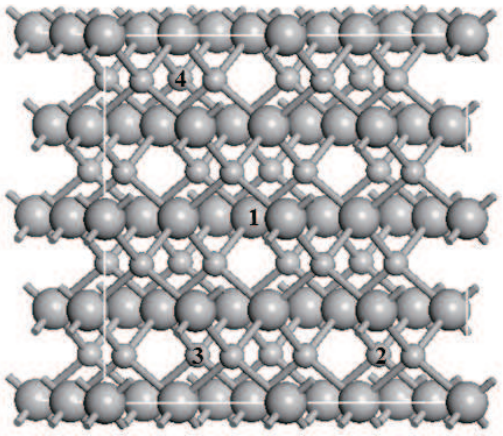


Fig. 4. The structural model used in calculations. Big balls denote Si atoms, and little balls denote C atoms. The doped Cu is at site 1, and the doped N is at sites 2, 3, and 4.

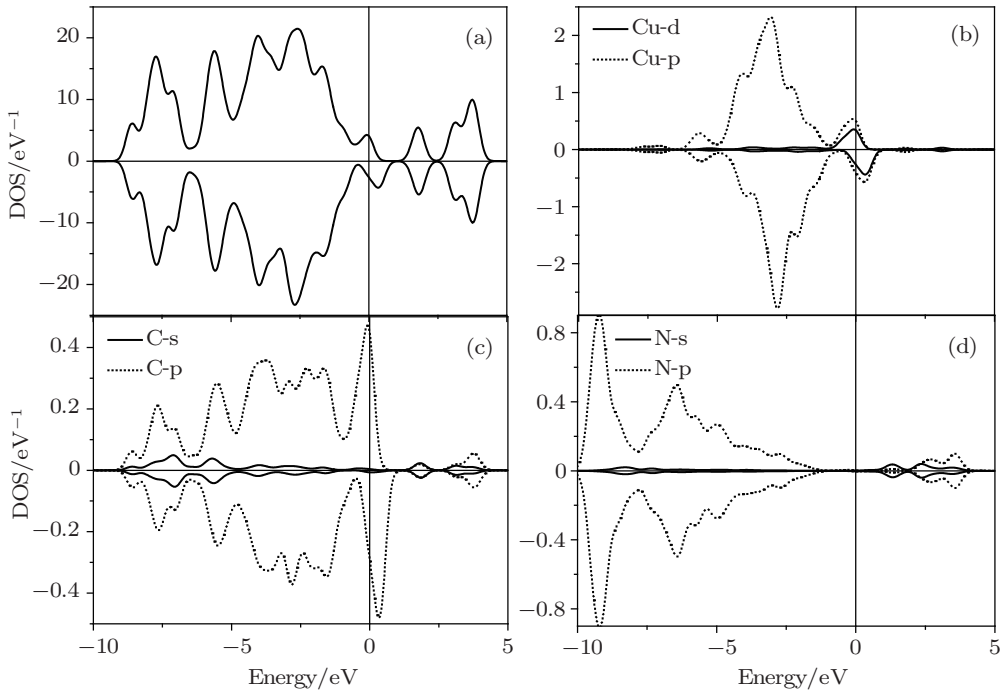


Fig. 5. (a) The total DOS of Cu and N co-doped SiC ($Si_{31}CuC_{31}N$), (b) PDOS of Cu, (c) PDOS of C near Cu, and (d) PDOS of N. The vertical line at 0 eV is the Fermi level.

and all occupied, one t_- orbit is occupied, while the other two t_- orbits are unoccupied above the Fermi level. Such electron occupation of defect states will lead to a local moment of 2 μ_B. The calculated results consist with the analysis from the group theory. The magnetic interactions between such local moments are also investigated. The FM ordering is 185 meV more stable than the AFM ordering. On the other hand, for the electron configuration $a^2t_+^3t_-^1$, the t_- states are partially occupied by one electron, and can hold other electrons with the same spin orientation. Therefore, the FM coupling is allowed. The FM interactions can be explained by the virtual hopping model as shown in Fig. 3(b). In order to evaluate the FM magnetic coupling strength, we used the simple and powerful Heisenberg model.[27,30,31] According to the Heisenberg model, the nearest-neighbor magnetic coupling parameter J_0 is evaluated by the equation $\Delta E = E_{FM} - E_{AFM} = -4J_0S^2$, where S is the net spin. For the Curie temperature, we used the equation $|\Delta E| = |E_{FM} - E_{AFM}| = \frac{n}{2}k_BT_C$[30] based on the mean field theory, where n is the degree of freedom in the system ($n = 6$ for a polyatomic system), k_B is the Boltzmann constant, and T_C is the Curie temperature. From Table 3, it is found that the ferromagnetism is favorable even at room temperature for the co-doped system.

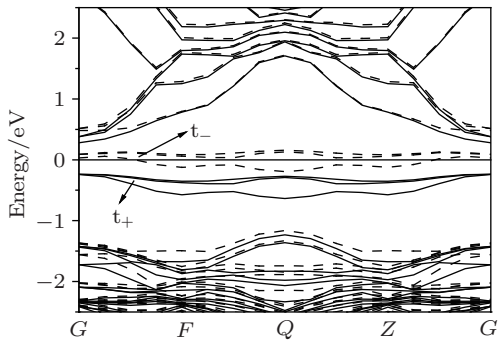


Fig. 6. The band structure of $Si_{31}CuC_{31}N$, the horizontal line at 0 eV is the Fermi level.

In order to clarify the effect of N content on the FM interactions between local moments, we studied the electron structures and magnetic properties of the two N atoms and one Cu codoped system in the 64-ion supercell corresponding to the N concentration of 6.2% ($Si_{31}CuC_{30}N_2$). For this doped system, the Cu atom is at site 1, and the N atoms are at sites 2 and 3, as shown in Fig. 4. As shown in Fig. 7, the DOS of $Si_{31}CuC_{30}N_2$ is similar to that of $Si_{31}CuC_{31}N$, except that the Fermi level shifts up compared to that of $Si_{31}CuC_{31}N$. Moreover, the electron occupation near the Fermi level is unsymmetrical, which means that the system has a moment, and the calculated moment is 1 μ_B. The N atom has one more electron than the C atom, the electron configuration of the defect states of the Cu and two N atoms codoped SiC should be $a^2t_+^3t_-^2$, resulting in a local moment of 1 μ_B, which is consistent with our calculated results. The FM coupling is 151 meV more stable than the AFM one. On the other hand, for the electron configuration $a^2t_+^3t_-^2$, the t_- states are partially occupied by two electrons, which can hold another electron with the same spin orientation. Therefore, the FM coupling is also allowed as shown in Fig. 3(c). To evaluate the FM magnetic coupling strength, the coupling parameter J_0 is also evaluated. As listed in Table 3, $J_0 = 151$, suggests that the FM ordering is stable even at room temperature.

If we continued to increase the N concentration, the electron occupation of defect states would be $a^2t_+^3t_-^3$ for $Si_{31}CuC_{29}N_3$, as shown in Fig. 8. The t_+ and t_- states are

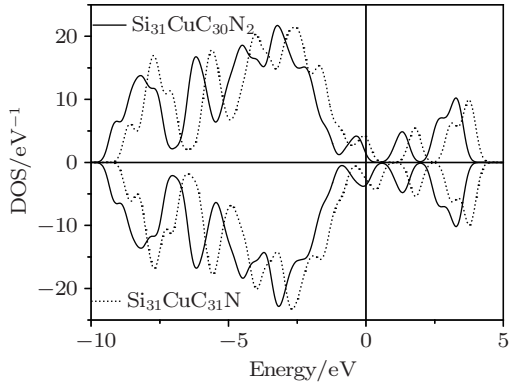


Fig. 7. The total DOS of $Si_{31}CuC_{30}N_2$ and $Si_{31}CuC_{31}N$, the vertical line at 0 eV is the Fermi level.

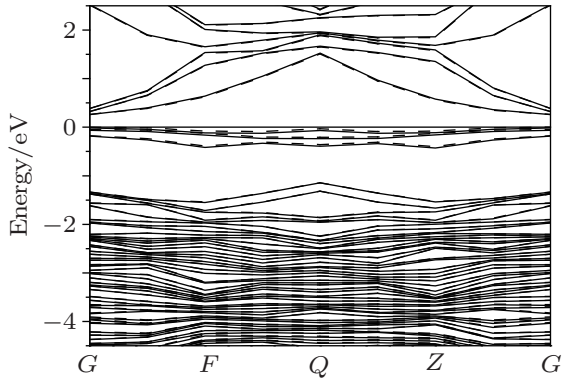


Fig. 8. The band structure of $Si_{31}CuC_{29}N_3$, the horizontal line at 0 eV is the Fermi level.

Table 3. The electron structures, $\Delta E = E_{FM} - E_{AFM}$, J_0, and magnetic coupling of different systems.

System	Electron structure	ΔE/meV	J_0/meV	Curie temperature/K	Coupling
$Si_{31}CuC_{32}$	$a^2t_+^3t_-^0$	239	–26.56	–	AFM
$Si_{31}CuC_{31}N$	$a^2t_+^3t_-^1$	–185	46.25	704	FM
$Si_{31}CuC_{30}N_2$	$a^2t_+^3t_-^2$	–151	151	583	FM

fully occupied, which cannot result in moments, and therefore there is no magnetic coupling. Therefore, in order to keep the FM coupling, the N concentration should be restricted within 9.3%. Our results could provide a vital clue for making the SiC FM with higher Curie temperature by the Cu and N co-doping.

4. Conclusion

We have investigated the electronic structures and magnetic properties of the Cu and N codoped SiC system by using the first-principles calculation. Our results show that the Cu doped SiC system prefers the AFM interaction. After doping with N, the ionicities of C–Cu and C–Si are respectively enhanced and weakened. More importantly, the Cu and N codoped SiC systems tend to be ferromagnetic. The FM interactions can be explained by the virtual hopping model. However, higher N concentration will weaken the ferromagnetism. Actually, in order to keep the FM coupling, the N concentration should be restricted within 9.3% according to our analysis.

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