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The electronic structure and magnetic properties of transition metal-doped silicon carbide

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Abstract

The band structure and magnetic properties of cubic (3C) and hexagonal (6H) polytypes of silicon carbide doped with 3d transition metals have been studied by *ab initio* calculations. We demonstrate that for 3C-SiC Cr and Mn produce half-metallic ferromagnetic solutions at both (Si and C) substitution sites, but with different magnetic moments, while SiC:Fe remains paramagnetic. A similar situation has been observed for 6H-SiC; however, Fe on the Si site at low concentrations leads to a ferromagnetic ordering.

1. Introduction

The introduction of magnetic or spin-related functions into semiconductor materials has become a new challenge for researchers in the fields of solid-state physics [1–3]. One of the most important issues is the development of ferromagnet/semiconductor hybrid structures, in which the spin degree of freedom can be used. This problem may be solved with the help of diluted magnetic semiconductors (DMSs), i.e. semiconductor compounds in which a fraction of the constituent ions is replaced by magnetic ones [4, 5]. The main interest in these compounds is caused by the fact that, in contrast to usual magnetic semiconductors with complex structure, the DMSs offer a possibility of studying the magnetic phenomena in crystals with a simple, well-known band structure and excellent magneto-optical and transport properties. Several types of DMSs based on III–V and II–VI semiconductors are already being studied both theoretically and experimentally. Among them, Mn-doped InAs and GaAs are the most investigated [6–11]. However, existing data show a rather low T_c , being 30 and 110 K for (In, Mn)As and (Ga, Mn)As, respectively, due to a limited solubility of Mn in the host materials. ZnO and ZnS doped with transition metals were predicted to be candidates for high- T_c ferromagnetic DMSs [8]. Some results were also obtained on Mn-doped GaP and GaN as well as on other DMSs [12]. Hence, the search for semiconducting materials exhibiting room temperature ferromagnetism is still continuing.

Very little attention has been paid so far to the DMS behaviour of doped SiC despite the potential of SiC for high-power and high-temperature electronics. With its wide bandgap (3.0 eV for the 6H polytype), excellent transport properties and dopability, it might be a good candidate for spintronic applications. Recently, some promising experiments have been done on Fe- and Mn-implanted SiC, for which T_c of 270 and 250 K, respectively, were obtained [13, 14]. However, there is a lack of theoretical data; only cubic 3C-SiC doped with 3d-metals has been partially studied [15, 16].

In the present paper we report a theoretical study of the electronic and magnetic properties of 3C and 6H polytypes of SiC doped with Cr, Mn and Fe.

2. Computational details

SiC crystallizes in more than 200 different structures, so-called polytypes. The most widely used are 3C, 4H and 6H. In this paper we will study cubic 3C and hexagonal 6H. All SiC polytypes can be built by tetrahedra where one C atom is surrounded by four Si atoms. Because of the symmetry, each Si atom is also surrounded by four C atoms.

3C-SiC has the zinc-blende structure, described by the face-centred cubic (fcc) lattice (space group T_d^2) with two atoms in the unit cell. The lattice parameter obtained from the experiment is 0.436 nm [17]. 6H-SiC polytype possess hexagonal close-packed symmetry (space group C_{6v}^4). Its unit cell consists of six double layers or 12 atoms. The experimental lattice constants are $a = 0.3081$ nm, $c = 1.512$ nm [17]. The main difference between the polytypes is the stacking sequence of the Si–C double layers. The cubic 3C-phase can also be present by a hexagonal lattice with stacking sequence ABC, while the 6H-phase has stacking sequence ABCACB, where A, B, C denote different double layers [23, 24].

Embedding impurity to SiC has been modelled by a $2 \times 2 \times 2$ supercell formed by stacking 8 cubic (for 3C-) or hexagonal (6H-) SiC unit cells. Thus, the resulting system contains 64 or 96 atoms, respectively. The replacement of one or more silicon or carbon sites with a 3d metal atom allows one to obtain different dopant concentrations. In the case of large impurity concentration we consider dopant atoms to be placed periodically at the most distant positions in the supercell, while one 3d metal atom gives the minimum concentration of about 3 at.% for 3C- and 2 at.% for 6H-SiC.

The electronic band structure and magnetic properties of silicon carbide have been calculated by means of the self-consistent full-potential linearized augmented-plane-wave method (FLAPW) in its scalar-relativistic version [18] using the WIEN2K package [19]. The local spin density approximation (LSDA) of Ceperly and Alder in the parameterization of Perdew and Wang [20] has been applied in the calculations of the exchange–correlation potential. Local orbitals were added in order to improve convergence and relax the remaining linearization errors. The Brillouin zone (BZ) integration for the self-consistent procedure and the calculations of the total and projected densities of states (DOS) have been carried out by the modified tetrahedron method [21]. Within the muffin-tin spheres, lattice harmonics with angular momentum l up to 10 are used to expand the charge density, the potential and the wavefunctions. The muffin-tin radii R_{MT} have been chosen as 1.9 au for Si and metallic dopants and 1.6 au for C. The calculations were performed with the energy cut-off constant $R_{MT}K_{max} = 8.0$. The self-consistent procedure has been done using 10 sampling \mathbf{k} -points in the irreducible BZ. A further increase in the cut-off value, basis set and \mathbf{k} -points number did not lead to any noticeable changes in the eigenvalues. Moreover, the increase of these parameters does not influence the equilibrium volume of the unit cell obtained within the approach applied. The self-consistent iterations were considered to be converged when both the total energy and the total charge in the atomic spheres were stable within 10^{-4} eV/unit cell and 10^{-4} electron charges/atom, respectively.

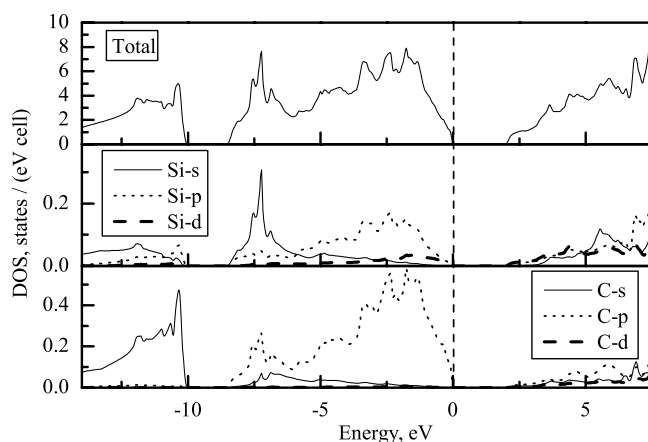


Figure 1. The total (upper panel) and partial densities of states of undoped hexagonal 6H-SiC. Solid curves correspond to s, dotted curves to p, and thick-dashed curves to d states.

3. Results and discussion

The lattice constants of undoped silicon carbide, used in our calculations, were obtained by minimizing the total energy with respect to changes in the size of the unit cell, using the LDA exchange–correlation potential. For the cubic phase a lattice constant of 0.437 nm and bulk modulus of 209 GPa were found, which correlates well with the experimental data (0.436 nm and 224 GPa [17]). For the hexagonal structure, the minimization was carried out by varying the parameters a and c with one and the same volume, whereupon the volume was varied, keeping the ratio a/c fixed. The atomic positions were kept ideal, whereas the lattice parameters were found to be $a = 0.308$ and $c = 1.511$ nm.

Cubic SiC is an indirect-gap semiconductor with an experimental gap width of about 2.4 eV [26]. Our calculated values are much smaller (about 1.3 eV). It is well known that LDA usually underestimates band gaps in s–p bonding semiconductors such as Si or SiC. When the generalized gradient approximation (GGA) of Engel and Vosko [22] was applied, the resulting band structure remained practically the same except for a constant energy shift of the band gaps. The indirect gap value became 2.1 eV, which correlates well with the results of experimental measurements and other theoretical calculations [24, 25]. However, this Engel–Vosko potential does not properly describe the total energy, and overestimates the magnetic moment. Spin-polarized calculations of bulk base-centred cubic Fe showed it to be $2.31 \mu_B$ compared to $2.19 \mu_B$ obtained by LDA. The experimental value is $2.21 \mu_B$ [27]. Thus, all calculations presented in this paper are done with the LDA of Ceperly–Alder.

The total and projected DOSs of undoped 6H-SiC are shown in figure 1. In general, the DOSs of the two different polytypes look similar and contain all the main features. Therefore, we have presented them only for 6H-SiC. The valence band can be divided into two subbands, separated by a gap of about 1.5 eV below -8.5 eV. The first part, starting from the bottom of the valence band to -10 eV, is composed mainly of the localized atomic C-s states with a small admixture of Si-s and Si-p states. The second wide region can also be divided into two parts, one of which is located between -8.5 and -5.5 eV and mainly consists of C-p and Si-s states. The other part extends from -5.5 eV to the Fermi energy. The bonding p states of silicon and carbon dominate there. A mixture of Si-sp and C-sp states characterizes the

Table 1. Magnetic moments (μ_B) in 3C-SiC for two boundary concentrations of dopants (25 and 3 at.%). MMT is the total magnetic moment of the supercell, while MMI is the magnetic moment per 3d-atom.

Impurity concentration (%)	Cr		Mn		Fe	
	MMI	MMT	MMI	MMT	MMI	MMT
Dopant at the C site						
25	0.89	1.47	0.68	1.00	0.00	0.00
3	0.96	2.00	0.59	1.00	0.00	0.00
Dopant at the Si site						
25	1.62	2.00	2.04	2.56	0.00	0.00
3	1.56	2.00	2.10	3.00	0.00	0.00

bottom of the conduction band. Our results agree well with previous *ab initio* calculations and with photoemission measurements of undoped SiC [15, 16, 25].

The magnetic properties of doped SiC are defined by the magnetic moment of the unit cell. The resulting values calculated for the 3C polytype are presented in table 1. The large difference between the total magnetic moment of the unit cell and the magnetic moment per 3d-atom in some cases can be explained by the fact that in FLAPW calculations not all the charge is located at the atomic sites but a part of it is situated in the interstitial region.

The analysis of table 1 shows that the calculations of 3C-SiC doped with light magnetic atoms (Cr, Mn) converge at a ferromagnetic solution. However, the magnetic moment differs depending on whether a dopant atom substitutes the C or Si sites. When an Fe atom is used as a dopant, a nonmagnetic solution occurs for both substitutional sites. This is confirmed by the similar DOSs, calculated for the spin-up and spin-down configurations (which are equal to the DOS in the non-magnetic state). The situation for Fe-doped SiC can also be proved by the application of the Stoner criterion. It states that a compound will be magnetic if $D_\sigma(E_F)I \geq 1$, where $D_\sigma(E_F)$ is the DOS at the Fermi level in the nonmagnetic case and I is the Stoner exchange integral [28]. Thus SiC:Fe must be paramagnetic due to the zero DOS at the Fermi level. The results obtained for 3C-SiC are comparable with other theoretical data [15, 16], according to which heavy group VIII metals (Fe, Co, Ni) form a paramagnetic solution, whereas light metals (Cr, Mn) form ferromagnetic ones. The magnetic moment of Cr at the C site is practically equal to that at the Si site, while for Mn this difference is about three times. The values obtained for the two boundary concentrations (25 and 3 at.%) differ from each other. This can be caused by an increased interaction between impurities at higher concentrations, whereas at lower concentrations the dopant atoms can only interact with their neighbours due to the high distance between dopants in the supercell.

The calculated total and projected DOSs of doped 3C-SiC do not differ much from those obtained for 6H-SiC. Thus in figures 2 and 3 we have presented only the DOSs of doped 6H-SiC when Cr, Mn and Fe substitutes Si or C sites, respectively.

More detailed analysis of the spin-decomposed DOSs show that upon doping SiC by transition metals the valence band gets a significant 3d-character due to the hybridization of d states of the impurity with the s and p states of its neighbours. The impurity d-electrons also add some contribution to the lowest conduction band near the Fermi level. The substitution of the Si site leads to the formation of narrow bands in the gap region, consisting mainly of localized d states of the metal. The Cr spin-up states form a high-energy structure in the gap region, which is occupied and predominantly determines the magnetic moment. The spin unpolarized 3d states of Fe also form narrow occupied bands below the Fermi level. The 3d-electrons of

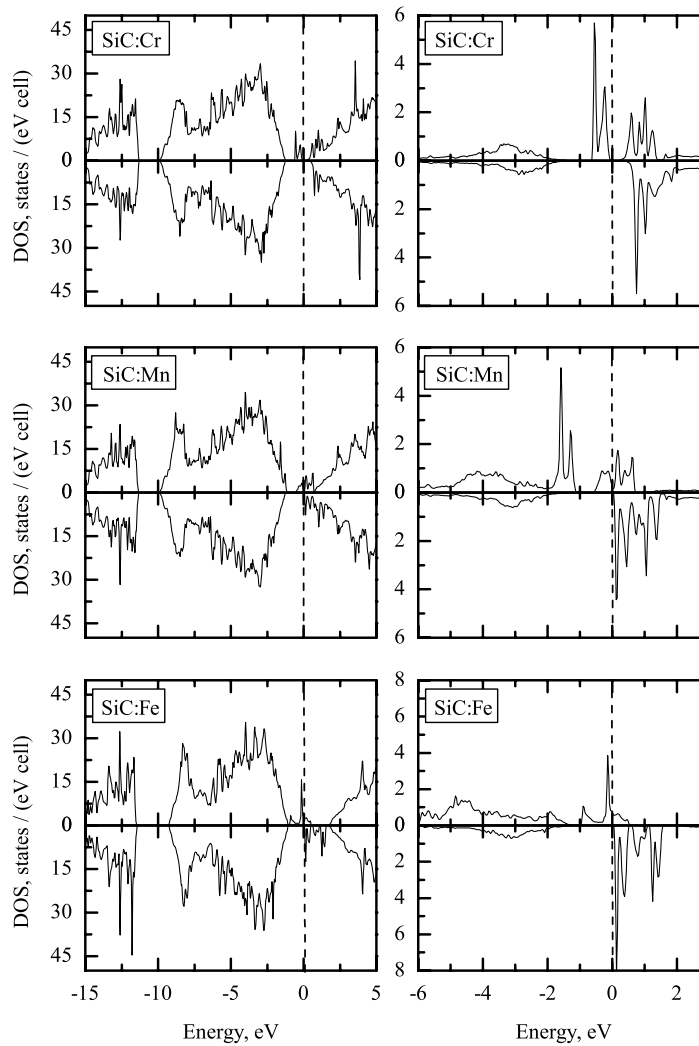


Figure 2. The total (left panel) and 3d-metal (right panel) densities of states of Cr-, Mn-, Fe-doped 6H-SiC. The dopant is at the Si site. The Fermi level corresponds to zero energy.

Mn at the Si site contribute to the conduction band of SiC by partially (spin-up) or totally (spin-down) unoccupied states.

The DOSs of the 3C-SiC structures with a dopant at the C site differ from those mentioned above by the location of the Fermi level. So, Cr 3d states with spin-down polarization form completely occupied bands, while for Mn these are only half-occupied, resulting in a reduction of the magnetic moment. Moreover, SiC doped with Cr and Mn at the C site can be classified as a so-called half-metallic ferromagnet. This term was introduced by de Groot *et al* [29]. Due to the ferromagnetic decoupling, one of the spin subbands (generally the majority-spin or up-spin subband) is metallic while the other is gapped (insulating).

The magnetic moment values calculated for 6H-SiC are presented in table 2. They do not differ much from the values obtained for the cubic structure. The major differences are found for Cr at the C site, which gives a non-magnetic solution at high concentrations, and for Fe

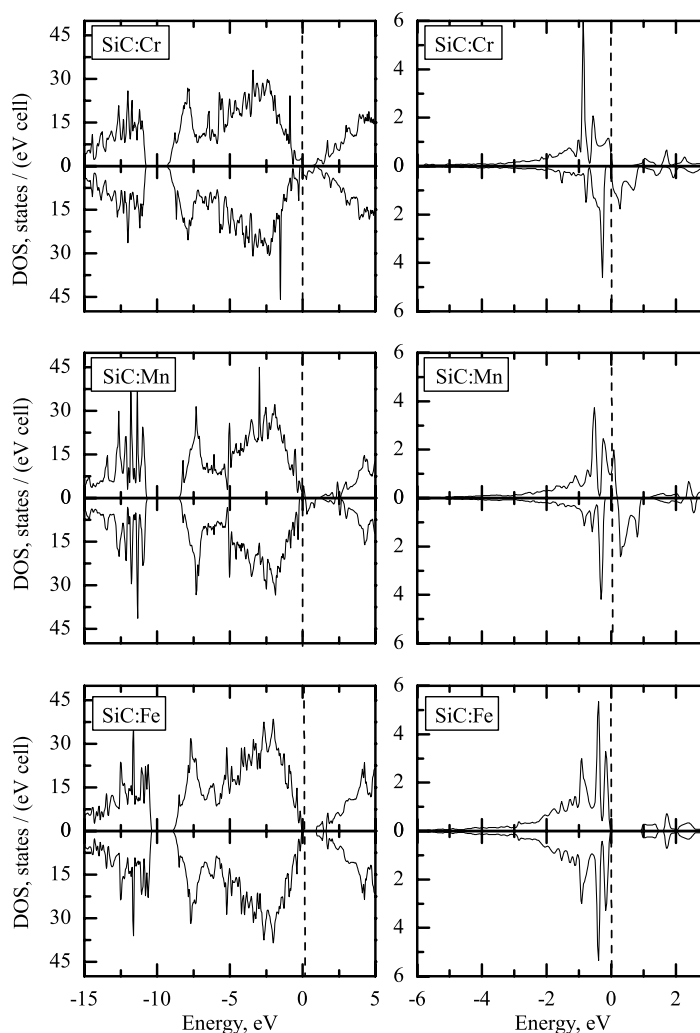


Figure 3. The total (left panel) and 3d-metal (right panel) densities of states of Cr-, Mn-, Fe-doped 6H-SiC. The dopant is at the C site. The Fermi level corresponds to zero energy.

at the Si site causing a ferromagnetic behaviour at low concentrations. Manganese provides a ferromagnetic solution for both types of substitution. However, replacement of a Si atom leads to a higher magnetic moment of the system than that of a C atom. These results practically do not depend on the location of the dopant site (at one of three double layers) in the crystal. The calculated total and projected DOSs of 6H-SiC in general look similar to those obtained for the cubic SiC phase due to the similar DOSs of host polytypes, except for the features related to different magnetic properties of the doped compounds. So, for the substitution of the Si site the metal 3d states hybridized with the s and p states of their neighbours give wider bands in the gap region as compared to 3C-SiC. The most distinctive features are the different up and down spin-polarized DOSs of Fe-doped SiC giving the resulting non-zero magnetic moment.

Table 2. Magnetic moments (μ_B) in 6H-SiC for two boundary concentrations of dopants (16 and 2 at.%). MMT is the total magnetic moment of the supercell, while MMI is the magnetic moment per 3d-atom.

Impurity concentration (%)	Cr		Mn		Fe	
	MMI	MMT	MMI	MMT	MMI	MMT
Dopant at the C site						
16	0.00	0.00	0.81	1.00	0.00	0.00
2	1.02	2.00	0.67	1.00	0.00	0.00
Dopant at the Si site						
16	1.54	1.89	1.48	1.57	0.00	0.00
2	1.50	2.00	2.17	3.00	2.76	4.00

4. Conclusions

The electronic and magnetic properties of the 3C- and 6H-polytypes of silicon carbide doped with Cr, Mn and Fe were studied by the *ab initio* FLAPW technique. The former two metals were found to produce a ferromagnetic solution at the Si and C substitutional sites for both polytypes considered. Non-magnetic phases were obtained for Fe in 3C-SiC, while the replacement of Si by Fe in 6H-SiC at low concentrations transformed the crystal into a ferromagnet.

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