

# Magnetic Structure of Mn-doped 6H-SiC

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**Abstract.** We investigated the local magnetic properties of Mn-doped 6H-SiC using ab-initio calculations. The calculation addresses various configurations of Mn single impurity and Mn dimers at substitutional/interstitial sites with and without neighboring Si and C vacancies. The calculations showed that a substitutional Mn atom at either Si or C sites possesses a magnetic moment. The Mn atom at Si site possesses larger magnetic moment than Mn atom at C site. Our calculations show that antiferromagnetically coupled pair of Mn atoms at Si sites with neighboring C vacancy is magnetically more stable. The calculation also showed that the interstitial sites with C neighbors are more favorable than those with Si and the magnetic moment for Mn at interstitial sites is less compared to that at substitutional sites. The results are used to understand the experimental data obtained on Mn- 6H-SiC for various Mn concentrations.

## 1. Introduction

One of the promising classes of materials for application in spintronic are diluted magnetic semiconductors (DMS). Despite much work devoted to the study of DMS, the situation is still controversial from both experimental and theoretical points of view. SiC-based DMSs have attracted considerable interest due to their excellent physical properties due to their extraordinary material properties such as large band gap, high electron saturation velocity, high breakdown field and high thermal conductivity[1]. In addition, SiC is compatible with conventional integrated circuit fabrication. Due to the low solubility of most TM elements in SiC, dopant introduction into SiC is practically limited to ion implantation technique. However, radiation damages such as vacancies, interstitials and extended defects are the undesired effects of ion implantation, which at high ion fluencies can even lead to amorphization of subsurface SiC layers of a few hundred nanometers thickness.

Several reports have been published documenting experimental studies of magnetic properties of SiC with transition metal TM impurities [2-10]. In recent studies, ferromagnetic response was observed in Ni, Mn and Fe implanted 6H-SiC with T<sub>c</sub> of 50, 250, and 270 K, for peak concentration of 5% of substitutional TM atoms [2,3]. In addition, 6H-SiC implanted with various doses of Fe showed the samples with the peak Fe concentration below 3% to exhibit DMS behaviour, with the magnetic ordering disappearing above 20 K [4]. In addition, experimental studies showed that Fe implanted 6H-SiC exhibits a high level of substitutional fraction of Fe atoms on Si-sites but without any ferromagnetic response, even at low temperature under 1 T[6]. SiC doped with Mn has become the most actively studied SiC DMS material and a number of experimental studies testify that Mn can be a suitable impurity for achieving a high-temperature FM ordering in the SiC DMS [7-10].

In addition to experimental work, different computational techniques were used recently to study the magnetic properties of SiC DMS. The Si site substitution was found to be more favorable than the



C site for TM substitution in 3C-SiC [11,12]. Los et al [13] studied the magnetic properties of Fe-doped 4H-SiC using FLAPW method, and they found that Fe can be in either a magnetic or nonmagnetic state and this depends on the TM atom environment in the host matrix. Zhou et al [14] studied the structural and magnetic properties of 3d transition metal doped 3C-SiC using ab initio calculations. They found that the structure of substitutional  $\text{TM}_{\text{Si}}$  is the most stable one for early transition metals like Ti, V, Cr, and Mn, while the clustering of  $\text{TM}_{\text{Si}}\text{-TM}_{\text{I}}$  dimers formed by the neighboring substitutional  $\text{TM}_{\text{Si}}$  and interstitial  $\text{TM}_{\text{I}}$  is energetically favored for late transition metals such as Co, Ni, and Cu. Most of theoretical work done so far concentrated on 3C-SiC with few results relating to TM doped 6H-SiC. We have studied recently the influence of the implantation fluence on the generation of defects and on the Mn fraction at substitutional Si site ( $\text{Mn}_{\text{Si}}$ ) and its effect on the local magnetic moment of Mn [15]. It was shown that as Mn fluence increases, Mn in substitutional sites increases up to certain fluence. Further increase in the fluence leads to an increase in the accumulated damage that suppresses the magnetization. Reduction of magnetization of all samples was observed with heat treatment [16]. It is clear that the defects induced by the implantation play the major role in the magnetic properties of the as-implanted and annealed samples. To have a clear picture about the correlation between structural and magnetic properties, we investigated the structural and magnetic properties of Mn-doped 6H-SiC using ab-initio calculations. In this paper, we report the results of the magnetic properties of Mn doped 6H-SiC. Various configurations of Mn sites have been considered. Magnetic coupling between the Mn atom with and without neighboring vacancy, to Mn at substitutional and/or interstitial sites were explored.

## 2. Methodology

We consider the 6H polytype of SiC, which has a hexagonal structure with 12 bilayers in the unit cell. The layers are stacked in hexagonal (*h*) and cubic (*k*) sequences as  $hk_1k_2hk_1k_2$ . Tetrahedral configurations and the number of nearest neighbors are maintained within all stacking. In this work, we used the FP-LAPW method as implemented in WIEN2k package [17] to study the magnetic properties of Mn-doped 6H-SiC. The embedded impurities in SiC are modeled by a  $2 \times 2 \times 1$  supercell. The muffin-tin radii (RMT) have been chosen as 1.66 au for Si and C and 1.77 au for Mn. An optimum number of k-points was reached by testing the convergence of the total energy and the electric field gradient for the basic unit cell of 6H-SiC with two Mn as substitutional atoms. The supercell calculations were performed with an energy cut-off such that  $\text{RMT}_{\text{Kmax}} = 6.0$  and a k sampling with a  $8 \times 8 \times 2$  Monkhost-Pack mesh. The Kohn-Sham equations were solved using the Perdew-Burke-Ernerhof GGA approximation [18]. The self-consistent cycles were stopped when the set convergence criteria in the total energy and the charge density are reached. Various configurations were studied including a single Mn impurity and Mn dimers at substitutional/interstitial sites with/without neighboring vacancies.

## 3. Results and Discussions:

The main defects introduced by Mn implantation into 6H-SiC are vacancy type defects and interstitials [19]. Consequently, we studied two cases of substitution: (i) Mn at Si/C site without neighboring vacancy, and (ii) Mn at Si/C site with neighboring C/Si vacancy. In addition, Mn at interstitial positions where it can be surrounded by four C/Si atoms with and without C/Si vacancy was also studied. The calculated magnetic moments for each configuration are presented in table 1. The first column represents the substitutional site and the second column is the vacancy site. Here MMI stands for the moment within the muffin tin sphere.

It is clear from the table that the magnetic moment depends on whether the dopant substitutional Mn atom is at C or Si site. In absence of vacancies, the magnetic moment of Mn at C site is smaller as compared to that at Si site in agreement with reported results [20]. In comparison to the corresponding results for Fe in 6H-SiC, it was found that Fe at the substitutional sites without neighbouring vacancy are nonmagnetic [21].

**Table 1.** The dopant site, vacancy site and magnetic moments ( $\mu_B$ ) in 6H-SiC doped with Mn atom. MMI is the magnetic moment per 3d-atom.  $Mn_I(C)$  refers to Mn at interstitial site with C neighbors and  $Mn_I(Si)$  refers to Mn at interstitial site with Si neighbours.

Dopant site	Vacancy site	MMI( $\mu_B$ )
Substitutional site		
Si	-	2.31
C	-	0.68
Si	C	2.68
C	Si	1.44
Interstitial site		
$Mn_I(C)$	-	1.52
$Mn_I(Si)$	-	0.48
$Mn_I(C)$	C	0.45
$Mn_I(Si)$	Si	0.60

In order to simulate the introduction of defects by ion implantation and to be able to compare the energies, vacancies are introduced at neighbouring Si/C sites. In this case it is possible to compare the energies of supercells. We found that Mn at the Si site with a neighbouring C vacancy is far more stable than Mn at the C site with Si. This may be justified by the large differences in atomic radii of Mn and C, on one hand, and their similarities for Mn and Si, on the other hand. The Si site substitution preference is in agreement with previous studies[11-13]. The magnetic moment of Mn increases with introduction of vacancies.

Table 1 shows that Mn interstitial sites has smaller magnetic moment compared to the substitutional sites, which explains the decrease of the magnetic moment by increasing the interstitial defects. We also found that the Mn at interstitial sites with C neighbors are more favorable than those with Si neighbors with an energy difference of about 2.0 eV. On the other hand introduction of vacancies at neighboring sites leads to further reduction in magnetic moment in contrast to the case of substitutional sites. It should be pointed out that these results are consistent with the experimental results for the as-implanted samples. Indeed, we found that the sample with lower fluence, even though most Mn atoms occupy C substitutional site, the relatively low Mn concentration (0.7%) leads to a small magnetic moment. As the fluence increases, the ratio of Mn atoms occupying substitutional sites increases, corresponding to higher Mn concentration (~2%), and the Mn substitute Si site giving relatively higher magnetic moment.

We have also studied the behaviour of Mn dimers in 6H-SiC. We found that antiferromagnetically coupled dimers are more stable than those ferromagnetically coupled. The details of these results will be published elsewhere.

#### 4. Conclusion

The FP-LAPW method is used to study the local magnetic properties of Mn doped 6H-SiC. Substitutional Mn atom at Si atom gives higher magnetic moment compared to the case when Mn substitutes a C atom and at interstitial sites. We found that magnetic moment increases when there is a

neighboring C/Si vacancy of Mn at Si site and Mn at C site respectively. The calculations also showed that the AFM coupled Mn atoms at substitutional sites are more stable than those FM coupled.

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