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Density functional calculations for manganese impurity in bulk silicon material

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ABSTRACT

Using the density functional theory within the spin generalised gradient approximation (σGGA), we systematically investigate the structural, magnetic, and electronic properties of silicon crystal upon the influence of doping manganese atoms. We have also presented detailed results and comparison for the substitutional and interstitial Mn-doped structures. It is found that the tetrahedral interstitial site is the energetically most stable structure for the Mn-doped Si with a little energy preferency over the substitutional site. To account the effect of the electron correlation on the Mn 3d orbitals, we have carried out similar calculations by employing the Hubbard potential U within the standard GGA method (*viz.* σGGA+U method). Finally we have compared the results obtained within these computational approaches, σGGA and σGGA+U, with the available theoretical and experimental findings.

1. Introduction

Dilute magnetic semiconductor (DMS) materials have received great interest in recent years due to their use in enormous technological and industrial applications [1,2], such as spintronics. In spintronics, the combination of the spin of electrons and their charges provides an opportunity to fabricating a remarkable new generation of microelectronic and multi-functional devices which could be used for improving the performance of computers, data processing, and information storage [3–5]. Various studies have investigated the possibility of generating spintronics using half-metals and semiconductor environment [6]. It has been found that these materials are particular ferromagnets which can be considered as hybrids between metals and semiconductors. Moreover, the analysis of the density of states (DOS) shows that the majority is metallic and the minority is semiconducting leading the system to be half metallic. However, there are many experiments to achieve the half-metallicity, such as the use silicon with transition metals [6,7] or transition metal oxides like CrO_2 and Fe_2O_3 [8].

Doping of III–V semiconductors by Mn atoms has been recognised as attractive materials for DMSs and hence received much attention. For instant, (Ga,Mn)As have gained much more interest due to its relatively high Curie temperature (about 110 K) and compatibility with the well-characterised GaAs environment [1,9]. It has been reported that the substitution of the Mn atom for the Ga site in GaAs results in a local spin $\frac{5}{2}$ magnetic moment, and gives rise to an acceptor state at about 113 meV above the valence band [10]. Although these materials are quite important and interesting for different technological applications, group-IV based DMS materials would be extremely useful, given that group-IV semiconductors are the keystones of most of electronic devices. However, ferromagnetic (IV,Mn) has attracted remarkable attention and provided valuable test ground DMS properties [2]. Among these ferromagnetic materials, Mn_xGe_{1-x} DMS's have received great deal and been studied by different experimental techniques [11,12]. Despite that many experimental results are available for Ge-based DMS, fewer experimental and theoretical studies have been devoted to investigate progressive changes in the atomic and electronic structures of the Si upon the incorporation of Mn atoms. Detailed calculations of the electronic properties and magnetic moments of Mn adatoms have indicated the possibility of achieving ferromagnetic semiconductor Si(0 0 1) surfaces [13–16]. Experimental studies have demonstrated that the deposition of Mn atoms on clean Si(0 0 1) surfaces leads to the possibility of growing super doped Si:Mn thin films [17]. Recently, Liu and Reinke [18] have studied the formation of Mn nanostructures on the Si(0 0 1)-(2 × 1) surface using scanning tunnelling microscope (STM) as a function of Mn coverage. They have concluded that Mn wire formation dominates at low coverages. It has been also reported that some Heusler alloys, such as Co_2MnX (X=Si, Ge or Sn) are ferromagnets [19] and would have the capability of providing spin polarised carriers for spintronics usage [20]. In Heusler half metals, the DOS near Fermi level is finite only for one spin channel. This is in marked contrast to usual ferromagnetic metals for which both spin channels contribute at the Fermi level. Dalpian et al. [21] have studied the stability of Mn impurity in Si. They have reported that the formation energy of Mn in Si is high and the most stable site is the

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interstitially tetrahedral. In other study, Miura et al. [22] have reported that Mn cluster is more stable than isolated Mn impurity in bulk Si. Yabuuchi et al. [23] have shown, using first-principles calculations, that tensile strain stabilises substitutional Mn and retains the magnetic moment. Very recently, Küwen et al. [24] have presented *ab initio* density functional calculation for the incorporation of Mn and Fe impurities in Si crystals. They found remarkable differences between Fe and Mn on substitutional sites while interstitial doping leads to similar effects. Even though the recently reported results for Mn impurity in the bulk Si are informative, there is still issues to be resolved. Some of these are the relaxation mechanism and the lateral movement of the Si atoms around the Mn impurity. Moreover, the effect of including the potential correction 'U' within the calculations in the case of highly concentration doping. Additionally the location of acceptor states and their dispersions are, to the best of our knowledge, not investigated yet by means of the electronic band structure.

Upon the above considerations, theoretical understanding of the fundamental properties of the Mn-doped Si materials is quite useful and extremely demanding due to their fascinating ferromagnetic properties. In the present work, we present first-principles total energy calculations to report on the structural, electronic, and magnetic properties of the (Si,Mn) structure. Details of the equilibrium geometry are described within the generalised gradient approximation of the density functional theory. The magnetic properties of the systems have been determined in terms of the magnetic moment. Furthermore, we have investigated the electronic properties by examining the electronic band structure and density of states. We further compare the results of the standard GGA with the corrected potential GGA methods and then compare our findings with the available data.

2. Computational method

We have carried out our first-principles calculations within the density functional theory [26] using the spin generalised gradient approximation (DFT-σGGA). The Perdew–Burke–Ernzerhof exchange-correlation scheme [27] was considered to treat the electron–electron interaction. The electron–ion interactions were treated by using the ultrasoft pseudopotentials [28]. The single-particle Kohn–Sham [29] wave functions were expanded in the framework of a plane wave basis set. Test calculations have shown that a kinetic energy cutoff for the wave functions equal to 25 Ryd is sufficient to obtain well converged results. Self-consistent solutions of the Kohn–Sham equations were obtained by employing $4\times4\times4$ **k**-points Monkhorst–Pack set [30] within the bulk Brillouin zones. Throughout the calculations we use the calculated Si equilibrium lattice constant of 5.43 Å which is very comparable with the reported experimental value. A cubic unit cell containing 64 Si atoms was considered. Increasing the cell to a bigger one (216 atoms) does not affect much on the stability of the structures and hence the properties of each structure. The relaxed internal atomic positions have been obtained by total-energy and atomic-force minimisation using the Hellman–Feynmann theorem. The equilibrium atomic positions were determined by relaxing all atoms in the unit cell except the Mn atom which was frozen into its bulk position.

In order to account the effect of the electron correlation on the Mn 3d shells, we apply the σGGA+U method within the calculations. The value of Hubbard correlation (U) is chosen to be 4.0 eV, which corresponds to the experimental value [31] and also many other groups [32–34] have used a similar value in their calculations. Unlike previous suggestions of the value of U, it has been found that a smaller value of U (approximately 3–4 eV) will give rise the correct ordering of the occupied and unoccupied states.

3. Results and discussion

We have considered two doping sites for the Mn impurity in the bulk Si crystal: interstitial (hexagonal and tetrahedral) and substitutional. Since there is one more Si atom for the structure with the Mn atom in the interstitial site than that for the structure with the Mn atom substituting for Si, we consider the chemical potential argument to compare the total energies of the two structures. Using the equation

$$\Delta E = E_{\mathrm{int}} - E_{\mathrm{sub}} - \mu_{\mathrm{Si}}, \tag{1}$$

where E_{int} and E_{sub} are the total energies of the interstitial and substitutional site structures, respectively, and μ_{Si} is the chemical potential of the Si atom. Our total energy calculations indicate that the tetrahedral impurity in Si crystal is more favourable for the interstitial site than the hexagonal site by an approximate energy of 0.42 eV/cell. However, the substitutional site for the Mn impurity is found to be more stable than the hexagonal site with energy gain of 0.25 eV/cell and less preferable than the tetrahedral site by an energy of 0.17 eV/cell. These values are quite consistent with the formation energy results obtained by Dalpian et al. [21]. In the following we will compare the structural, magnetic, and electronic properties of tetrahedral interstitial and substitutional sites within the σGGA and σGGA+U methods.

3.1. Substitutional site

Having replaced the central Si atom by the Mn atom, we relaxed all atoms with respect to the Mn atom. The optimised structure, shown in Fig. 1(a), indicates that the bond lengths between the impurity and the nearest neighbour Si atoms are longer than the that of bulk Si. The calculated σGGA Si–Mn bond length of 2.38 Å is larger than the bulk Si bond length of 2.34 Å, indicating strain relief under the relaxation process. This value is in excellent agreement with the value obtained by Yabuuchi et al. [23] of 2.39 Å. The next nearest neighbour Si atoms are located at 3.84 Å from the Mn atom. From these values we find that the nearest neighbour Si atoms move away from the impurity whereas the next nearest neighbour Si atoms move towards the impurity. These observations are quite different from those obtained for the Mn doped in bulk GaAs. In a previous work for the substitutional Mn in GaAs [25] we have found that the nearest neighbour As atoms are contracted (move towards) to the Mn atom. Having included the Hubbard correction in the calculation (σGGA+U), we observe substantial change in the bond lengths of the impurity and its nearest neighbour atoms. The nearest neighbour Mn–Si bond lengths have increased by 3.8% to 2.47 Å compared to Mn–Si bond lengths obtained by σGGA method. This indicates that considering of U in the calculation will come over the effect of the strong interaction between the Mn 3d electrons and Si *p* electrons, resulting in longer bond lengths. Moreover, the distance between the impurity and the next nearest neighbours is approximately 3.84 Å which is slightly larger than that without U. The average Si–Si bond lengths around the impurity of 2.33 Å are quite identical in both calculation schemes and slightly smaller than the bulk Si–Si bond length. From both σGGA and σGGA+U calculations we clearly observe longer bond lengths for Mn–Si compared to the bulk Si–Si bond length. This increase suggests that the substitutional Mn structure becomes more stable as the lattice constant of MnSi crystal decreases. In other words it indicates that, since the Mn atom is seven-fold coordinated, the substitutional Mn atom seems to break its bonds with the