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First-principles design of ferromagnetic nanostructures based on group-IV semiconductors

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Abstract

We perform first-principles density functional calculations for Mn doped group-IV (Ge, Si) based diluted magnetic semiconductors. It is found that the ferromagnetic spin configuration is stabilized when two Mn atoms are located along the [110] direction in Ge and Si hosts due to the strong ferromagnetic exchange interaction between Mn impurities. Furthermore, our results show that a ferrimagnetic Mn cluster is more stable than the ferromagnetic Mn configuration along the [110] direction, indicating that Mn impurities tend to gather and create undesired magnetic clusters in Ge and Si hosts. We conclude that the vicinal Ge(111) and Si(111) surfaces play an important role in the growth process of Mn doped Ge and Si in obtaining a ferromagnetically stable Mn configuration.

Diluted magnetic semiconductors (DMS) [1] have attracted much attention in recent years because of their potential in relation to spin-dependent phenomena, such as spin injection into semiconductors [2]. In particular, the realization of group-IV based DMS having high Curie temperature (T_c) is very much required, because the processes and device-related techniques of the present silicon technology can be applied in the fabrication of group-IV based DMS. Recently, Park *et al* [3] have succeeded in fabricating Ge based DMS ($\text{Ge}_{1-x}\text{Mn}_x$) by using molecular beam epitaxy and confirmed their carrier induced ferromagnetism, p-type semiconducting character and T_c increasing linearly with the Mn concentration up to 120 K. They have also performed theoretical investigations and shown that the long range ferromagnetic interaction between Mn impurities dominates over the short range antiferromagnetic interaction. Since this work, several experimental and theoretical studies have been carried out for the Ge based DMS [4–7]. There also exist theoretical works on Si, C and SiGe based DMS [6, 8, 9]. In spite of the existence of these works, reports on T_c for group-IV based DMS are still fewer than those for III–V based DMS [1]. In particular, a

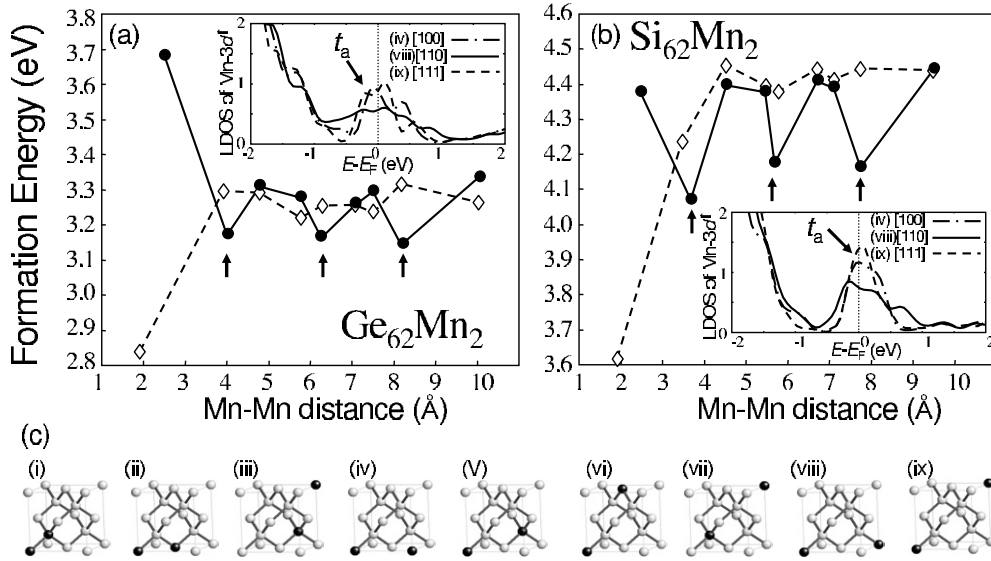


Figure 1. The formation energy of (a) Ge₆₂Mn₂ and (b) Si₆₂Mn₂ as a function of the Mn–Mn distance d . Solid circle and open diamond points correspond to the parallel (ferromagnetic) and antiparallel (antiferromagnetic) spin alignments, respectively. (c) Schematic positions of two Mn impurities for each d , where black and grey spheres correspond to Mn and Ge (or Si) atoms, respectively. The labels (i)–(ix) are in order of increasing d . Insets show the local density of majority-spin states of Mn 3d near the Fermi level, when two Mn are located along [100], [110] and [111] directions (corresponding to positions (iv), (viii) and (ix), respectively).

report of T_c for Si based DMS is lacking. It is considered that a high level of magnetic impurity concentration could cause a clustering of magnetic atoms and/or the formation of undesired compounds with host atoms as well as interstitial magnetic impurities. In order to obtain higher T_c for group-IV based DMS, it will be important to find the impurity configuration leading to ferromagnetically stable group-IV based DMS and explore how to realize that.

The purpose of this work is to gain theoretical insight into the ferromagnetically stable configuration of Mn doped group-IV (Ge and Si) based DMS. To this end, we perform first-principles density functional calculations for Mn doped group-IV (Ge and Si) based DMS. In the calculations, we adopt bulk $2 \times 2 \times 2 a^3$ supercells including 64 Ge or Si atoms in the diamond structure, where a is the initial lattice constant of the Ge or Si hosts optimized for the bulk Ge ($a_{\text{Ge}} = 5.78 \text{ \AA}$) and Si ($a_{\text{Si}} = 5.46 \text{ \AA}$). We replace the host atoms by two or four Mn atoms, corresponding to the Mn concentrations 3.125% (Ge₆₂Mn₂ and Si₆₂Mn₂) and 6.25% (Ge₆₀Mn₄ and Si₆₀Mn₄). The atomic positions, cell volume and cell shape are fully relaxed using total energy calculations within the generalized gradient approximation [10], as implemented by the Vienna *ab initio* simulation package [11, 12]. The projector augmented wave method [13, 14] was used with a cut-off energy of 337.33 eV. We use $3 \times 3 \times 3$ Monkhorst–Pack sampling in the Brillouin zone.

We show in figures 1(a) and (b) the formation energies of Ge₆₂Mn₂ and Si₆₂Mn₂ with parallel (ferromagnetic) and antiparallel (antiferromagnetic) spin alignment of two Mn impurities as a function of the Mn–Mn distance d and in figure 1(c) schematic positions of the two Mn atoms for each d . Note that the formation energies take the bulk Ge and Si in the diamond structure and antiferromagnetic α -Mn as reference. It is found that energetically most favourable configuration is the first-nearest neighbour Mn configuration (position (i))

with antiparallel spin alignment (which we call the ‘Mn dimer’) in both Ge and Si hosts. If the lattice relaxation were not included for Mn doped Ge [5], the most stable Mn configuration would be position (viii) with parallel spin alignment. This means that the lattice relaxation is crucial for considering the stable configuration of Mn impurities in Ge and Si hosts. The bond length of the Mn dimer ($d_{\text{Mn-Mn}} \approx 1.9 \text{ \AA}$) is shortened as compared with those of Ge ($d_{\text{Ge-Ge}} \approx 2.5 \text{ \AA}$) and Si ($d_{\text{Si-Si}} \approx 2.3 \text{ \AA}$) hosts. Due to the short range interaction between Mn impurities with the antiparallel spin alignment, the Mn dimer would not influence other ferromagnetic interactions; i.e., it only creates magnetically inactive Mn dimers, reducing the total magnetic moment [5].

Furthermore, it is found that the formation energies of $\text{Ge}_{62}\text{Mn}_2$ and $\text{Si}_{62}\text{Mn}_2$ with the parallel spin alignment strongly depend on the Mn positions, resulting in oscillation of the energy difference between parallel and antiparallel spin alignments, i.e., the exchange coupling constant, as a function of the Mn–Mn distance d . Zhao *et al* [5] attributed the oscillation to the Ruderman–Kittel–Kasuya–Yosida interaction between two localized moments through the induced spin density. However, we show that the oscillation can be explained by the crystallographic effects. As can be seen in figure 1, there are apparently three Mn positions which exhibit lower formation energy than the parallel spin alignment (see the upper arrows both for $\text{Ge}_{62}\text{Mn}_2$ and for $\text{Si}_{62}\text{Mn}_2$). They are the positions (ii), (v) and (viii), where one Mn atom is located at (0, 0, 0) and the other is located at (1/2, 1/2, 0), (3/4, 3/4, 1/4) and (1, 1, 0) respectively. This indicates that the parallel (ferromagnetic) spin alignment is stabilized when two Mn atoms are located along the [110] direction in Ge and Si hosts. Since the ferromagnetism of the Mn doped group-IV based DMS is stabilized by itinerant carrier spins [3], similar to the III–V based DMS case [15, 16], the stability is characterized by the band width of the itinerant carriers. In the Mn doped Ge and Si, the majority-spin band near the Fermi level mainly has antibonding t_2^g character caused by the hybridization between the Mn 3d ϵ (d_{xy} , d_{yz} and d_{zx}) and Ge 4p or Si 3p. Since the Mn 3d ϵ has a spatial distribution toward the [110] direction, the exchange path leading to strong ferromagnetic interaction between Mn impurities appears when two Mn atoms are located along the [110] direction in Ge and Si hosts. This can be confirmed by the atom orbital projected local density of states of Mn 3d (see the insets of figures 1(a) and (b)). It is observed that the width of the majority-spin t_2^g band near the Fermi level is sensitive to the position of the two Mn atoms, both in Ge and Si hosts. Apparently, the band width for the system of two Mn atoms along the [110] direction (position (viii)) broadens as compared with those for [100] (position (vi)) and [111] (position (ix)) directions. The broad t_2^g band indicates the presence of the exchange path along the [110] direction which stabilizes the ferromagnetic interaction between Mn impurities. The exchange path along the [110] direction is also found in $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ and $\text{Zn}_{1-x}\text{Cr}_x\text{Te}$ [17].

Our results suggest that we might obtain group-IV based DMS having higher T_c due to the strong ferromagnetic exchange interaction if we could dope the Mn impurities along the [110] direction in Ge and Si hosts. This leads us to ask an obvious question: how can we position the Mn impurities along the [110] direction? Our results for the formation energies of $\text{Ge}_{60}\text{Mn}_4$ and $\text{Si}_{60}\text{Mn}_4$ show that the ferrimagnetic cluster is more stable than the ferromagnetic Mn configuration along the [110] direction and this trend is more noticeable for Si than for Ge. Note that we assume the ferrimagnetic Mn cluster¹ to be composed of four nearest neighbour Mn atoms in the diamond structure, where one Mn atom centred in the cluster couples antiferromagnetically with the other three Mn atoms. Therefore, the Mn impurities would not spontaneously locate along the [110] direction, but would gather and create ferrimagnetic

¹ Non-collinear magnetism like that of α -Mn will not be observed, because no spin frustration occurs in the Mn cluster.

clusters, especially in the Si host. We propose that by utilizing the vicinal Ge(111) and Si(111) surfaces, we can position the Mn impurities along the [110] direction in Ge and Si hosts. On the vicinal Ge(111) and Si(111) surfaces, the Mn atoms would be predominantly trapped at the [110] step edge and create linear Mn chains along the [110] direction. After additional deposition of host atoms, the Mn chains would form a ferromagnetic Mn configuration along the [110] direction. We have also confirmed that the inter chain coupling between two parallel Mn chains along the [110] direction is ferromagnetic when one Mn chain is located at a distance of a_{Ge} or a_{Si} from the other Mn chain. This means that the ferromagnetism in the Mn doped Ge and Si would be retained in the case where the system includes some isolated Mn chains. In future work, it will be very interesting to investigate experimentally and theoretically whether the growth processes of Mn doped Ge and Si utilizing vicinal Ge(111) and Si(111) surfaces give a ferromagnetically stable Mn configuration along the [110] direction.

In summary, we have investigated magnetically stable configurations of the Mn doped group-IV (Ge and Si) based DMS by using first-principles calculations. We have concluded that the ferromagnetism of Mn doped Ge and Si based DMS is stabilized when two Mn atoms are located along the [110] direction. In order to obtain group-IV based DMS having higher T_c , it will be very important to utilize the vicinal Ge(111) and Si(111) surfaces during the growth process.

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