Dopant-Assisted Concentration Enhancement of Substitutional Mn in Si and Ge

Wenguang Zhu,[1,2,3,4] Zhenyu Zhang,[4,3] and Efthimios Kaxiras[1]

[1]*Department of Physics and Division of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts 02138, USA*

[2]*Center for Computational Materials, Institute for Computational Engineering and Sciences, Departments of Physics and Chemical Engineering, University of Texas, Austin, Texas 78712, USA*

[3]*Department of Physics and Astronomy, University of Tennessee, Knoxville, Tennessee 37996, USA*

[4]*Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA*

(Received 7 January 2007; published 17 January 2008)

The influence of *p*- and *n*-type electronic dopants on Mn incorporation in bulk Si and Ge is studied using first-principles calculations within density functional theory. In Si, it is found that the site preference of a single Mn atom is reversed from interstitial to substitutional in the presence of a neighboring *n*-type dopant. In Ge, a Mn atom is more readily incorporated into the lattice when an *n*-type dopant is present in its immediate neighborhood, forming a stable Mn-dopant pair with both impurities at substitutional sites. A detailed analysis of the magnetic exchange interactions between such pairs reveals a new type of magnetic anisotropy in both systems.

DOI: 10.1103/PhysRevLett.100.027205 PACS numbers: 75.50.Pp, 66.30.J−, 75.30.Hx

Diluted magnetic semiconductors (DMS) provide a fascinating platform for fundamental studies of ferromagnetic ordering mechanisms [1–3]. The discovery of ferromagnetism in Mn-doped III-V semiconductors [4] has revived interest in DMS as promising materials for developing spintronic devices that employ the spin of electrons, in addition to charge, as the signal carrier [5,6]. Recent observations of ferromagnetic ordering in Mn-doped bulk Ge open the possibility of integrating magnetism with existing silicon technology [7–9]. However, the low critical (Curie) temperature of ferromagnetic ordering (much lower than room temperature) remains one of the main obstacles for potential device applications of DMS. Extensive theoretical and experimental studies of Mn-doped III-V and group IV semiconductors indicate that the Curie temperature depends sensitively on the ability of magnetic dopants to occupy substitutional versus interstitial sites [10–13]. To precisely control the magnetic dopant distribution inside the host semiconductors, it is necessary to understand both the kinetics and thermodynamics involved in the growth process [11]. A detailed understanding of the growth kinetics is particularly important, because the DMS are typically in metastable states, grown by codoping the magnetic dopants and host semiconductor atoms using molecular beam epitaxy technique under nonequilibrium conditions [4,7,8].

Separately, doping a pure semiconductor with electronic impurities is a common approach in semiconductor technology to alter its electrical properties. It is natural to expect that, for some electronic dopants, their binding with the neighboring host atoms will be weaker than that between host atoms. This aspect can be exploited to enhance the population of substitutional Mn in heavily doped semiconductors.

In this Letter, we investigate the influence of conventional *n*-type (P, As, Sb), and *p*-type (Al, Ga) electronic dopants on the thermodynamic, kinetic, and magnetic properties of Mn atoms in bulk Si and Ge. Our first-principles calculations show that in Ge, an interstitial Mn atom can easily replace a host atom adjacent to an *n*-type dopant but cannot directly exchange with the dopant, leading to the formation of a Mn-dopant pair with both impurities residing at substitutional sites. In Si, the site preference of Mn is reversed from interstitial to substitutional in the presence of an adjacent *n*-type dopant. The strong thermodynamic stability of the substitutional Mn–*n*-type-dopant pair structure is attributed to the opposite charge states of the two elements in the host semiconductors: A substitutional Mn, acting as a *p*-type double acceptor [14] in bulk Si or Ge, is attracted to a substitutional *n*-type dopant. Moreover, a detailed analysis of the relative stability of antiferromagnetic (AFM) and ferromagnetic (FM) orderings of such Mn–*e*-dopant pairs reveals that ferromagnetic coupling is favored in Ge, whereas it is slightly weakened in Si. In addition, a new type of strong magnetic anisotropy in the coupling of the magnetic dopants is observed in both systems, and the underlying physical reason is revealed.

Our spin-polarized first-principles calculations were carried out using VASP [15], a density functional theory approach using the projector augmented wave (PAW) method [16], the generalized gradient approximation (PBE-GGA) [17] for exchange-correlation, and computational parameters that ensure high accuracy and convergence [18]. The ''climbing image nudged elastic band'' (NEB) method [19] is used to locate transition state geometries for the calculation of activation energy barriers. One extra Mn atom is introduced per 64-atom cell (a $2 \times 2 \times 2$ cubic supercell), corresponding to 1.56% Mn concentration, comparable to what was achieved experimentally [7–9].

We begin by examining the equilibrium structure of a single Mn atom in bulk Si and Ge. To this end, we calculate

the energy difference $\Delta E_1 = (E_{\text{subst}} + \mu_{\text{host}}) - E_{\text{inter}}$ between the interstitial and substitutional sites, using the bulk as the natural reservoir for the displaced host atom, with energy μ_{host} given by the bulk formation energy per atom. Our calculations show that Mn has different site preference in Si and Ge: In Si, $\Delta E_1 = +0.58$ eV, that is, the interstitial site has lower energy and is preferred, whereas in Ge, $\Delta E_1 = -0.63$ eV, that is, the substitutional site is preferred, consistent with previous work [20]. However, if we consider an actual exchange process, which consists of an interstitial Mn atom kicking out an adjacent host atom to an interstitial site, with the Mn atom ending up in the substitutional site left by the host atom and the host atom remaining at the interstitial site near the Mn atom, we find that the initial state (E_i) is more stable than the final state (E_f) for both Si (by $\Delta E = E_f - E_i = 2.03$ eV) and Ge (by $\Delta E = 0.82$ eV). The calculated energy barrier for this process is well over 2 eV in Si. In Ge, this barrier is $\varepsilon_a = 1.12$ eV, whereas the reverse process has an energy barrier of only $\varepsilon_a{}' = \varepsilon_a - \Delta E = 0.30$ eV. Therefore, at moderate growth temperatures, it is not feasible for interstitial Mn atoms to incorporate into the substitutional sites in pure Si or Ge. As an alternative, we investigate the influence of n- or p-type electronic dopants in the immediate neighborhood of an interstitial Mn atom.

As a first candidate, we consider the process in which an interstitial Mn atom exchanges directly with a substitutional electronic dopant (referred to as process I in Fig. 1). In the initial state, the Mn atom resides at a nearest interstitial site to the substitutional electronic dopant. We find that the lowest energy configuration for the interstitial Mn atom is the tetrahedral interstitial (I_T), shown in Fig. 1(a)

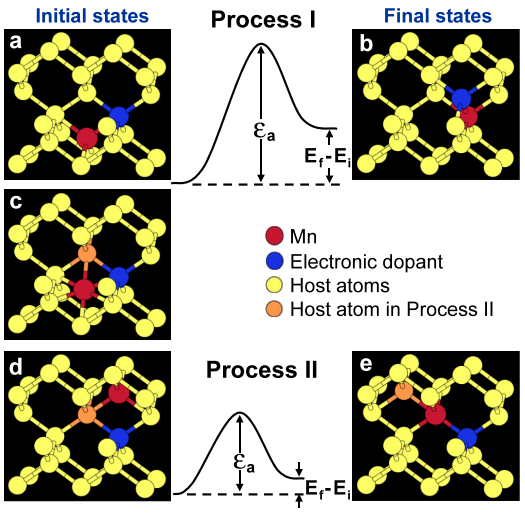

FIG. 1 (color online). Atomic structures and schematic energy profiles of process I and process II. (a) Initial state of process I with Mn in the I_T position (except for n-type doped Ge); (b) Final state of process I; (c) Initial state of process I and process II for n-type doped Ge with Mn at the I_H position; (d) Initial state of process II (except for n-type doped Ge), with Mn at the I_T position; (e) Final state of process II.

for either n- or p-type dopant in Si or p-type dopant in Ge. For n-type doped Ge, our first-principles calculations indicate that the hexagonal interstitial site I_H shown in Fig. 1(c) is energetically preferred than the I_T site. In $I_T(I_H)$, the Mn atom has four (six) nearest neighbors with the electronic dopant as one of the neighbors. In the final state, the electronic dopant is pushed to an adjacent interstitial site and the Mn atom moves into the substitutional site, as shown in Fig. 1(b). Table I summarizes the calculated energy differences ΔE between the final and initial states for n- and p-type dopants in Si and Ge. As noted earlier, there is an energy cost associated with the transition from initial to final state, which in undoped Si and Ge is prohibitively high. This energy cost, defining the lower bound of the activation energy barrier for the exchange process, must be reduced to a value lower than ~0.8 eV, a necessary condition to produce a realistic time scale for efficient incorporation (assuming a standard attempt frequency of 10^{12} sec^{-1}). As the results in Table I clearly indicate, this is possible only for the P and As dopants in bulk Ge (with $\Delta E = 0.33$ eV and 0.42 eV, respectively). For $\Delta E < 0.8$ eV, it becomes important to calculate the relevant activation energy barriers for incorporation, which should also be below the ~0.8 eV threshold. The activation energy barriers for P and As in Ge are 0.88 and 0.98 eV, respectively, making those processes unlikely to occur under usual conditions. Furthermore, the reverse processes (0.55 and 0.56 eV for P and As in Ge, respectively) are more likely to occur, pushing the Mn atom back into the interstitial site. The only possibility to keep the Mn atom at the substitutional site is if the dopant atom can diffuse away rapidly after being kicked out to the interstitial site, so that the reverse exchange process cannot take place. However, our calculations exclude this possibility. Therefore, the Mn atom cannot easily incorporate into the substitutional sites in bulk Si or Ge via such a direct exchange process.

We consider next another possible exchange process, in which an interstitial Mn atom adopts the position of a host semiconductor atom next to a substitutional electronic dopant (process II in Fig. 1). Similar to the cases for process I, the low-energy initial structure for process II is for the Mn atom to occupy the interstitial I_T site but not as a nearest neighbor of the electronic dopant atom, as shown in Fig. 1(d). The exception is the case of n-type doped Ge, where the preferred initial state is for the Mn to occupy the interstitial I_H site [Fig. 1(c)]. The common final state is shown in Fig. 1(e), where the interstitial host atom, the substitutional Mn atom, and the electronic dopant are nearly collinear. Table I summarizes the calculated ΔE values for n- and p-type dopants in Si and Ge for process II. For n-type doped Ge, these values are substantially lower than the corresponding values for process I, and considerably below the threshold value of ~0.8 eV. Especially for the n-type dopants P and As, the initial and final states have almost equal energies (ΔE close to zero). The corresponding activation barriers for all the three

TABLE I. Calculated energy differences $\Delta E = E_f - E_i$ (in eV) between the final and initial states of process I and process II, illustrated in Fig. 1. ε_a (in eV) is the activation energy for a transition from the initial to final state. Results highlighted in bold correspond to processes for which ΔE or ε_a or both are <0.8 eV.

	Bulk Si			Bulk Ge			
X	ΔE		X	ΔE		ε_a	
	Process I	Process II		Process I	Process II	Process I	Process II
Si	2.03		Ge	0.82			
P	1.46	0.89	P	**0.33**	**0.03**	0.88	**0.34**
As	1.55	1.09	As	**0.42**	**0.05**	0.98	**0.25**
Sb	2.48	1.27	Sb	1.42	**0.22**		**0.38**
Al	1.24	2.05	Al	0.94	1.54		
Ga	1.79	2.43	Ga	1.05	1.52		

n-type dopants are also much lowered, less than 0.4 eV. These, then, appear to be much more likely kinetic processes, leading to substitutional Mn atoms in close proximity to n-type electronic dopants. Qualitatively, the energetic and kinetic modifications obtained here can be attributed to the electrostatic attraction between the p-type Mn and n-type electronic dopants.

We note that the energy differences between the initial and final states depend on the Mn concentration, but the qualitative picture that the n-type dopants facilitate substitutional incorporation of Mn is valid for all the experimentally accessible Mn concentrations considered here [21].

An obvious concern arising from the above discussions is the thermodynamic stability of the Mn-dopant pair structure. To address this, we have calculated the energy difference $\Delta E_2 = (E_{\text{pair}} + \mu_{\text{host}}) - E_{\text{inter}}$, where E_{pair} is the total energy of the Mn-dopant pair complex without the kicked-out host interstitial Si or Ge atom nearby, and E_{inter} is the total energy of the Mn interstitial in the initial configuration of process II. In doing so, we take the preferred structure of the Mn-dopant pair to be the final state of the easy exchange process (process II) but with the interstitial host atom having diffused away and become a bulk atom. As before, the bulk chemical potential μ_{host} of Ge or Si represents the reservoir energy for the displaced host atom. Table II lists the calculated values of ΔE_2. The sign and magnitude of this quantity determines the thermodynamic stability of the Mn-dopant pair complex. Table II shows that the substitutional Mn in Ge becomes much more stable in the presence of a neighboring substitutional n-type dopant, as compared to undoped Ge. More interestingly, for Si, the site preference of Mn is reversed from interstitial to substitutional by introducing a neighboring n-type dopant. Therefore, the substitutional Mn-dopant pair structure will be stable once it is formed in either Si or Ge.

We finally focus our attention on the magnetic property of the hybrid Mn-dopant systems. Because the hole concentration associated with the Mn dopants might be partially compensated by the n-type electronic dopants, their presence could be undesirable at first sight, as the magnetic coupling between the Mn ions relies on the mediation of the delocalized holes [1–3]. This concern can be addressed by investigating the influence of the n-type dopants on the magnetic coupling between Mn atoms incorporated in Ge or Si. To this end, we calculate the total energy difference between the AFM and FM states of two Mn-dopant pairs as a function of the distance of the two Mn atoms at 3.13% concentration, analogous to previous calculations for Mn-Mn interaction in pure semiconductor hosts [22–24]. The results are shown in Fig. 2. Since a substitutional Mn atom has four nearest neighbors, each of which can be the site of the n-type dopant atom, there are a total of 16 possible combinations for the positions of the two electronic dopants for a given Mn-Mn distance. We have considered all the possible nonequivalent configurations, for each of seven Mn-Mn distances in the range 2.4–9.5 Å in Si and 2.5–10.0 Å in Ge. The number of nonequivalent configurations is 2, 6, 3, 7, 7, 3, and 2 at the different Mn-Mn distances of increasing order. The corresponding energy differences are represented by the open circles in Fig. 2 for the case of As as the electronic dopant, and the energy difference averaged over all the different configurations at a given Mn-Mn distance is by the solid circle. As references, we also show the AFM-FM energy differences for two Mn ions in pure Ge, represented by the diamonds in Fig. 2. The behavior of the AFM-FM energy difference is oscillatory between positive and negative values as a function of the distance (but decreasing along different directions [22–24]). In contrast, here we find that the average interaction energy between the two Mn/As pairs in Ge always favors FM coupling except at the nearest Mn-Mn

TABLE II. Relative energy of substitutional and interstitial Mn with the existence of a neighboring substitutional n-type dopant, defined as: $\Delta E_2 = (E_{\text{pair}} + \mu_{\text{host}}) - E_{\text{inter}}$ (in eV). Negative values indicate higher stability of the substitutional configuration over the interstitial. The relative energy of substitutional and interstitial Mn in pure Si or Ge are included for comparison.

	P	As	Sb	Undoped
Si	−0.84	−0.87	−0.81	+0.58
Ge	−1.35	−1.42	−1.42	−0.63

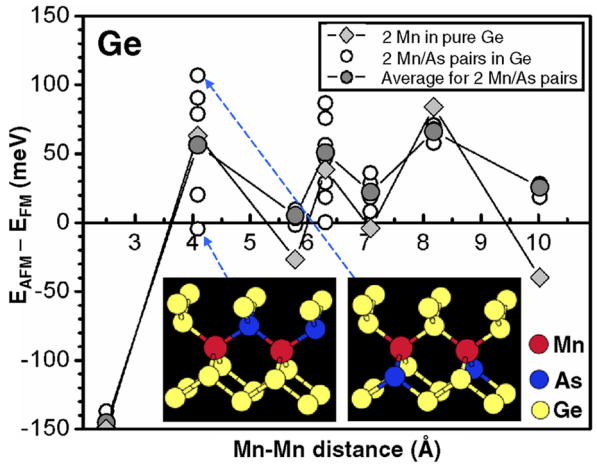

FIG. 2 (color online). Total energy difference between AFM and FM states versus Mn-Mn separation at 3.13% Mn concentration in bulk Ge with only two Mn impurities (diamonds), or with two Mn/As pairs (open circles). The solid circles are averaged over the open circles for a given Mn-Mn distance. Insets: the atomic structures of two representative *n*-dopant configurations with the strongest and weakest magnetic coupling between a Mn-Mn pair, whose locations are fixed at the next nearest neighboring distance.

distance. Furthermore, by examining the magnitudes, we conclude that the presence of the *n*-type dopants at least preserves the strength of the FM coupling between the two magnetic ions rather than substantially weakens it. More importantly, at a given Mn-Mn distance, the relative stability of the AFM and FM states exhibits strong anisotropy, which is more pronounced at the Mn-Mn distances of 4.1 Å and 6.3 Å. Detailed analysis [21] reveals that As as *n*-dopant can enhance the local magnetic moments of neighboring Mn atoms, but itself can only be weakly spin polarized (much weaker than Ge). Therefore, when As substitutes a bridging atom between two Mn atoms, the global magnetic coupling will be weakened; when As is located only to enhance the magnetic moments of Mn, with Ge still bridging the Mn-Mn coupling, the global magnetic coupling will be enhanced. Similar results are also observed in As doped Si.

In summary, we have studied the influence of different types of conventional electronic dopants on the thermodynamic, kinetic, and magnetic properties of Mn atoms in bulk Si and Ge using first-principles calculations. For both systems, it is energetically favorable and kinetically accessible for an interstitial Mn to occupy a substitutional site neighboring an *n*-type dopant, thereby increasing the concentration of substitutional Mn ions. Furthermore, the magnetic coupling between two Mn-dopant pairs exhibits strong anisotropy at certain Mn-Mn distances, and in Ge ferromagnetic coupling is always favored for all Mn-Mn distances larger than the nearest neighboring distance. Both enhancements, in the substitutional Mn concentration and magnetic anisotropy, may offer new opportunities for increasing the Curie temperature of group-IV-based diluted magnetic semiconductors.

This work was supported in part by NSF Grants No. DMR-0325218 and No. DMR-0606485, by DOE Grant No. DE-FG02-05ER46209, and in part by the Division of Materials Sciences and Engineering, Office of Basic Energy Sciences, DOE. The calculations were performed at NERSC of DOE and NCCS of ORNL.

Note added.—After the submission of this paper, a related study appeared, reporting experimental evidence on the drastically different influences on the magnetic properties when a low concentration of *n*-type (I) or *p*-type (N) electronic dopants are co-doped with the magnetic dopants (Cr) in a host semiconductor (ZnTe) [25].

[1] T. Jungwirth *et al.*, Rev. Mod. Phys. **78**, 809 (2006).
[2] H. Ohno, Science **281**, 951 (1998).
[3] T. Dietl *et al.*, Science **287**, 1019 (2000).
[4] H. Ohno *et al.*, Appl. Phys. Lett. **69**, 363 (1996).
[5] I. Žutić, J. Fabian, and S. Das Sarma, Rev. Mod. Phys. **76**, 323 (2004).
[6] S. A. Wolf *et al.*, Science **294**, 1488 (2001).
[7] Y. D. Park *et al.*, Science **295**, 651 (2002).
[8] A. P. Li *et al.*, Appl. Phys. Lett. **86**, 152507 (2005).
[9] S. B. Ma *et al.*, Solid State Commun. **140**, 192 (2006).
[10] R. Wu, Phys. Rev. Lett. **94**, 207201 (2005).
[11] S. C. Erwin and A. G. Petukhov, Phys. Rev. Lett. **89**, 227201 (2002).
[12] K. M. Yu *et al.*, Phys. Rev. B **65**, 201303(R) (2002).
[13] C. Timm, J. Phys. Condens. Matter **15**, R1865 (2003).
[14] S. Picozzi, M. Ležaić, and S. Blügel, Phys. Status Solidi (a) **203**, 2738 (2006).
[15] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11 169 (1996).
[16] P. E. Blöchl, Phys. Rev. B **50**, 17 953 (1994); G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).
[17] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[18] The default plane-wave energy cutoff for Mn, 269.9 eV, is consistently used in all calculations. These choices produce a bulk lattice constant for Ge of 5.78 Å (experimental value 5.66 Å) and for Si 5.47 Å (experimental value 5.43 Å). A uniform $4 \times 4 \times 4$ mesh including the Γ point (0,0,0) is chosen for Brillouin zone sampling in the $2 \times 2 \times 2$ supercell. Optimized atomic geometries are obtained when the forces on all the unconstrained atoms are smaller in magnitude than 0.01 eV/Å.
[19] G. Henkelman, B. P. Uberuaga, and H. Jónsson, J. Chem. Phys. **113**, 9901 (2000).
[20] A. J. R. da Silva, A. Fazzio, and A. Antonelli, Phys. Rev. B **70**, 193205 (2004).
[21] W. Zhu, Z. Y. Zhang, and E. Kaxiras (to be published).
[22] Y.-J. Zhao, T. Shishidou, and A. J. Freeman, Phys. Rev. Lett. **90**, 047204 (2003).
[23] H. Weng and J. Dong, Phys. Rev. B **71**, 035201 (2005).
[24] P. Mahadevan, A. Zunger, and D. D. Sarma, Phys. Rev. Lett. **93**, 177201 (2004).
[25] S. Kuroda *et al.*, Nat. Mater. **6**, 440 (2007).