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Energetic stability and magnetic properties of Mn dimers in silicon

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We present an accurate first-principles study of magnetism and energetics of single Mn impurities and Mn dimers in Si. Our results, in general agreement with available experiments, show that (i) Mn atoms tend to aggregate, the formation energy of dimers being lower than the sum of the separate constituents, (ii) ferromagnetic coupling is favored between the Mn atoms constituting the dimers in *p*-type Si, switching to an antiferromagnetic coupling in *n*-type Si, (iii) Mn atoms show donors (acceptor) properties in *p*-type (*n*-type) Si, therefore they tend to compensate doping, while dimers being neutral or acceptors allow for Si to be doped *p*-type. © 2004 American Institute of Physics. [DOI: 10.1063/1.1688002]

The discovery of ferromagnetism in diluted magnetic semiconductors¹—a new class of materials having GaMnAs as a prototypical compound—has renewed the interest in the physics of transition metal (TM) atoms in semiconductors. While most of the early works were focused on the TM doping of III-V and II-VI² semiconductors, recently, ferromagnetic properties and magnetoresistance phenomena below room temperature have been reported for Mn_xGe_{1-x} (*x* up to 3%).³ This discovery opened the issue of ferromagnetism in Mn-doped group-IV semiconductors. It is well known that TM solubility in Si and Ge is very low and that Mn atoms tend to aggregate into clusters. Electron-paramagnetic resonance (EPR)⁴ investigations showed that isolated Mn impurities in Si can occur in different charge states, both at interstitial (Mn_I⁻, Mn_I⁰, Mn_I⁺, and Mn_I²⁺) and substitutional (Mn_{Si}²⁻ and Mn_{Si}⁺) sites.

From the theoretical point of view, pioneering first-principles Green's-function simulations were performed for isolated impurities in Si, taking into account spin multiplicities and charge states.^{5,6} However, a careful theoretical study focused on the interaction between Mn atoms in a Si matrix based on large supercell density functional calculations including structural relaxation, is still lacking. A thorough investigation of Mn clustering in Si and Ge is outside the scope of this work and, in general, of first principles investigations. Moreover, technical issues related to the well-known underestimation of the band gap width in the framework of density functional theory (DFT) (Ge is depicted as a nearly zero gap material) suggested limiting the present investigation to Mn in silicon. Therefore, in this work we focus our attention on the energetics and on the magnetic properties of Mn isolated impurities and dimers in the limit of low doping concentrations (~0.5%–1%).

We compute the formation energies for the defects studied using the standard formalism by Zhang and Northrup.⁷

Total energies and chemical potentials are computed within the DFT and the generalized gradient approximation of Perdew and Wang⁸ to the exchange-correlation functional, using the projector augmented wave method⁹ and the plane-waves code provided in the VASP package.¹⁰ Spin polarization of valence electrons is treated semirelativistically (i.e., without spin-orbit coupling). As for the chemical potential of bulk Mn, we use its calculated value in the antiferromagnetic (AFM) phase of its fcc metallic structure, while for silicon we refer to the equilibrium diamondlike structure. We simulate an isolated defect within the periodic boundary conditions via the repeated supercell approach, using a 3×3×3 cubic supercell. Test calculations show that this is the smaller supercell dimension necessary to get converged results for the magnetic moments of the dimer complexes considered in this work. A kinetic energy cutoff of 202 eV is used in all of the calculations. The supercell size and shape are kept fixed during the calculations. To minimize the effect of the interaction among the periodic images we use the **k** point set proposed by Makov, Shah, and Payne.¹¹

We investigated the most important defects involving up to two Mn atoms: (i) tetrahedral interstitial Mn_I, (ii) Mn substituting Si (Mn_{Si}), (iii) a Mn dimer (Mn_{Si}-Mn_{Si}) where two Mn_{Si} sit on neighboring sites, (iv) a complex (Mn_{Si}-Mn_I) formed by a Mn_I bound to a Mn_{Si}, (v) an interstitial dimer (Mn_I-Mn_I) where both Mn atoms occupy tetrahedral interstitial sites, (vi) a complex (Mn_{Si}-Si_I) where an interstitial silicon atom Si_I is bound to a Mn_{Si}. We performed a structural optimization allowing only lattice distortions compatible with C_{3v} symmetry. In Fig. 1 we show the formation energies for the defects involving a single Mn atom, i.e., Mn_{Si}, Mn_I, and the Mn_{Si}-Si_I complex. We find that, for isolated Mn atoms, interstitial atoms are energetically favored over substitutional ones for most of the allowed range of the electron chemical potential, in agreement with experimental evidence.¹² The formation energy difference between Mn_{Si} and Mn_I is larger in *p*-type conditions and decreases for increasing Fermi level positions. In *n*-type conditions Mn_{Si}

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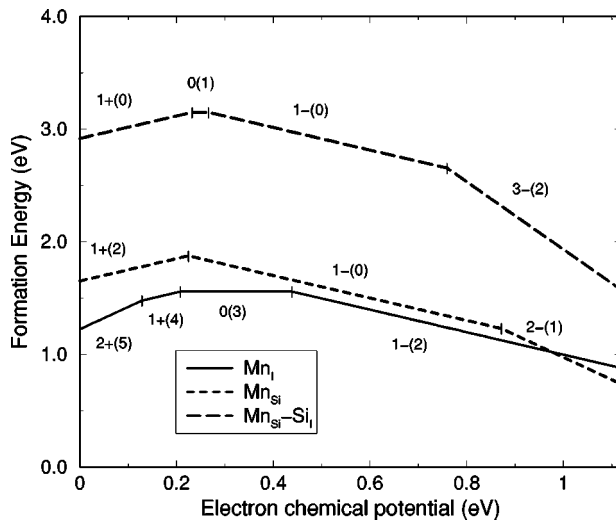


FIG. 1. Formation energy of single Mn impurities as a function of the Fermi level. Charge states are shown, along with the relative total magnetic moments, in Bohr magnetons (number in parentheses). To help readability, small vertical bars mark the ionization levels.

becomes a double acceptor and for E_F above 0.97 eV it becomes energetically favorable over Mn_I . Therefore, we predict, in n -type Si, the coexistence of Mn_I and Mn_{Si} . As for the charge states of the defects, experimental data available in literature⁴ show the existence of charge states from 1- to 2+ for the interstitial impurity, while for the substitutional one the only charge states detected are the 1+ and 2-. Besides a general agreement with experiments, our calculations reveal for the Mn_{Si} the possible existence of a 1- charge state that was not reported in literature. The latter corresponds to a nonmagnetic configuration for the impurity, whose existence cannot be detected by EPR spectroscopy.

The incorporation of Mn in silicon can be achieved during crystal growth or by ion implantation. The second approach induces in the host crystal a large number of defects, that have to be eliminated by thermal annealing. During the annealing, two processes can occur: (i) a recombination of Mn_I with silicon vacancies that favors the incorporation of Mn in the substitutional site and (ii) a “kick-out” process, where a substitutional Si is displaced by an interstitial Mn to a neighboring interstitial site. The final result of the latter is a Mn_{Si} - Si_I complex whose energy is plotted in Fig. 1. Our results clearly show that the Mn_{Si} - Si_I complex is strongly energetically unfavored. Therefore, we conclude that kick-out mechanisms are unlikely and most of the implanted Mn atoms will remain interstitial.

We now turn our attention to defects formed by two Mn atoms. In realistic conditions, high doping levels are achieved out of thermodynamical equilibrium. At these high concentrations, the pairing of Mn atoms is likely. In Fig. 2 the formation energy *per Mn atom* of the most important complexes involving Mn pairs is shown. The lowest energy configuration among those studied are Mn_{Si} - Mn_I for E_F up to 0.6 eV and the double substitutional Mn_{Si} - Mn_{Si} in n -type material, whereas the double interstitial Mn_I - Mn_I is always too high in energy to be an energetically stable configuration. A noticeable feature of Fig. 2 is that formation energies for Mn_{Si} - Mn_I and Mn_{Si} - Mn_{Si} complexes are lower in energy than the sum of the formation energies for their individual

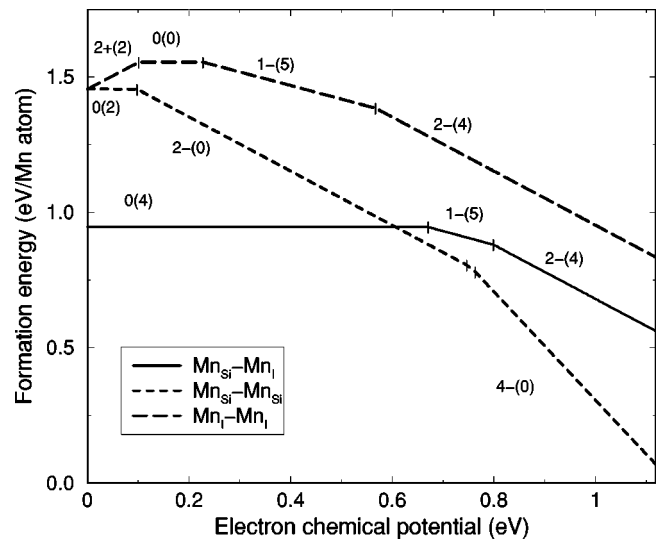


FIG. 2. Formation energy of Mn dimers as a function of the Fermi level, in unit of eV/Mn atom. Charge states are shown, along with the relative total magnetic moments, in Bohr magnetons (number in parentheses).

components (i.e., Mn_{Si} and Mn_I), meaning that an attractive interaction between Mn atoms exists. The binding energy between two Mn atoms of course depends on the Fermi level position, but it is always of the order of 1 eV; it is therefore large enough to ensure the formation of complexes, provided that Mn atoms can diffuse.

The formation of Mn dimers has important consequences on the magnetic properties of Mn-doped silicon. In Table I we show the preferred spin alignment [ferromagnetic (FM) or AFM] of the dimers complexes, along with the charge states, total magnetic moments, and atomic magnetic moments. It was found, in Ge or GaAs, that AFM pairing prevails when Mn impurities are brought together to form complexes. We find that dimers in silicon, at the considered concentrations, prefer FM spin alignment as ground state configuration, with the only exception of Mn_{Si} - $Mn_{Si}^{2-/4-}$ and Mn_I - Mn_I^0 . This finding has important consequences on the magnetic properties of Mn-doped silicon. Indeed, pairing seems not to quench the magnetic properties related to isolated Mn atoms. In particular, for E_F below 0.6 eV, Mn_{Si} - Mn_I dimers—as well as isolated interstitial—are defects with a large magnetic moment, ranging from 2 to 4 Bohr magnetons. For higher E_F , substitutional pairs are the lowest en-

TABLE I. Relevant information for the considered Mn dimers: charge state (Q , in electrons), favored spin configuration, total magnetic moment (M_{tot}), atomic magnetic moments (M_1 and M_2) in Bohr magnetons. In the case of the Mn_{Si} - Mn_I dimer magnetic moments M_1 and M_2 refers to the interstitial and substitutional atoms respectively.

	Q	Spin. conf.	M_{tot}	M_1	M_2
Mn_{Si} - Mn_I	2-	FM	4	2.33	1.75
	1-	FM	5	2.48	1.91
	0	FM	4	2.38	1.71
Mn_{Si} - Mn_{Si}	4-	AFM	0	-1.27	1.27
	2-	AFM	0	-1.61	1.61
	0	FM	2	0.83	0.83
Mn_I - Mn_I	2-	FM	4	2.28	2.28
	1-	FM	5	2.40	2.40
	0	AFM	0	-2.50	2.50
	2+	FM	2	1.40	1.40

ergy configuration, so that formation of dimers implies transition to an AFM spin alignment; we therefore expect that only p -type conditions are favorable for the existence of a magnetic activity in Mn-doped Si, while in n -type conditions large Mn concentrations do not necessarily lead to a net magnetization of the material.

So far we focused our attention on the energetics and magnetic properties of Mn impurities and dimers, considering the Fermi level as an independent variable. This is a reasonable assumption only at very low Mn doping concentrations. Indeed, as shown in Figs. 1 and 2, Mn is not an electrically neutral defect over most of the allowed range for the Fermi level. We find that isolated Mn tend to compensate both p and n doping. Indeed, in p -type (n -type) conditions Mn_I and Mn_{Si} are donors (acceptors). As for the dimers, they show a very different behavior. They are neutral defects in p -type conditions, and multiple acceptors in n -type material. Therefore Mn dimers do not interfere with p doping of Si. This is an important finding, since a ferromagnetic behavior in dilute magnetic alloys requires both the presence of magnetically active dopant and of free carriers. Therefore, we conclude that in p -doped Si the effect of clustering, at least in the form of dimers, seems to enhance the magnetic properties of the material.

In summary, our calculations show that in a crystalline silicon host an energy-driven force for Mn atoms to form complexes exists. We find that the most stable configurations involving up to two Mn atoms is the Mn_{Si} - Mn_I (Mn_{Si} - Mn_{Si}) complex in p -type (n -type) conditions. The Mn_{Si} - Mn_I dimer

is mostly a neutral defect and shows a FM spin alignment that allows a net magnetization of the material. On the contrary, Mn_{Si} - Mn_{Si} is an acceptor and shows a preference for AFM alignment in those doping conditions where it is energetically stable. Therefore, we expect that Mn-doped silicon will show magnetic activity only in p -type conditions.

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