Stabilization of substitutional Mn in silicon-based semiconductors

Antônio J. R. da Silva and A. Fazzio
Instituto de Física, Universidade de São Paulo, CP 66318, 05315-970, São Paulo SP, Brazil

Alex Antonelli
Instituto de Física, Unicamp, C.P. 6165, 13083-970 Campinas SP, Brazil
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We systematically investigate, using *ab initio* density-functional theory calculations, the properties of interstitial and substitutional Mn in both Si and Ge, as well as in the $Si_{1-x}Ge_x$ alloy. We show that volume effects are not the main reason Mn prefers to be a subsitutional impurity in pure Ge, and chemical effects, therefore, play an important role. Using realistic models of $Si_{1-x}Ge_x$, we show that for $x \gtrsim 0.16$ substitutional Mn in Ge-rich neighborhoods become more stable than interstitial Mn, which may allow the growth of Si-based diluted magnetic semiconductors.

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Diluted magnetic semiconductor (DMS) materials[1–4] have been know for a long time,[5] however, it was the relatively recent growth of III-V[3,6] Mn-based ferromagnetic DMS that have brought these materials to the spotlight, motivated by the possibility of fabricating useful spintronic devices. Although these accomplishments are rather significant, if one considers the possible technological impact there is no doubt that the synthesis of a Si-based DMS material would be of great relevance. Ferromagnetism in the Mn_xGe_{1-x} compound has been reported by more than one group,[7] which makes one ask the obvious question: would it be possible to grow a similar Mn_xSi_{1-x} ferromagnetic material?

Considering this question in a recent article,[8] we have argued that: (i) as Si and Ge have similar electronic structures, it is reasonable to expect that for large enough x, Mn_xSi_{1-x} would become ferromagnetic below some critical temperature, in the same way Mn_xGe_{1-x} does it. This hypothesis is supported by a recent calculation[9] where both Mn_xGe_{1-x} and Mn_xSi_{1-x} were studied. The question then is if the required values of x can be achieved; (ii) in Si, a Mn impurity favors an interstitial site, whereas in Ge it prefers a substitutional site (see below); (iii) as a consequence, a Mn substitutional impurity in Ge cannot diffuse as easily as an interstitial Mn in Si,[10–12] allowing the introduction of a large enough number of impurities without their diffusion and subsequent clustering. Therefore, *it seems that a crucial issue to obtain a* Mn_xSi_{1-x} *material is to find a way to have the* Mn *occupying substitutional sites*. As in Ge Mn prefers to be a substitutional impurity, whereas in Si it is at interstitial sites, the SiGe alloy seems to be a good candidate where a change in this behavior might happen, i.e., if one starts with a Si crystal and increases the Ge content, we expect to see an increase in the stability of sustitutional Mn impurities. If this seemingly obvious trend is correct, one then has a possible way to dope a Si-based material with large and stable enough contents of Mn atoms to obtain a DMS material, like the Mn_xGe_{1-x} compound.[7]

In this paper we address the following questions: (i) Is it simply a volume effect that would make Mn prefer a tetrahedral interstitial site in Si whereas it prefers a substitutional site in Ge? (ii) Will a Ge rich environment in the SiGe alloy also favor a substitutional Mn site? Regarding question (i), we find that the cause Mn is substitutional in Ge is not simply a volume effect, and therefore finding ways to increase the Si lattice parameter would not suffice to stabilize the substitutional Mn impurity. However, since specific chemical interactions are the possible explanation for the differences between Mn in Si and Ge, this implies that the answer to question (ii) above is yes. We actually find that the substitutional Mn site should be the predominant one for Ge concentrations in the $Si_{1-x}Ge_x$ alloy for $x \lesssim 0.16$. Therefore, as it is easier to grow unstrained alloys of SiGe rather than strained Si, the behavior described above will have the important technological consequence that it will be easier to grow Mn in SiGe alloys with a suitable Ge concentration than if one had to strain Si to mimic Ge. All these findings have the important consequence that a Mn doped SiGe alloy may present similar ferromagnetic properties as the Mn_xGe_{1-x} material, opening up the possibility of Si-based spintronics.

All our results are based on *ab initio* calculations, based on spin-polarized density functional theory within the generalized gradient approximation (GGA).[13] We have used ultrasoft pseudopotentials[14] and a plane wave expansion up to 230 eV, as implemented in the VASP code.[15] We have used a fcc-based supercell containing 128 sites, and the L points for the Brillouin zone sampling. In all calculations the positions of all atoms in the supercell were relaxed until all the forces components were smaller than 0.02 eV/Å. We estimate that the errors in energy differences due to all our approximations are of the order of 0.1 eV, which is similar to the variations in the results due to the statistical fluctuations related to different neighborhoods in the alloy (see below).

We initially considered pure Si and Ge crystals. We placed a Mn atom both at an interstitial as well as at a substitutional site. The formation energy of a neutral interstitial impurity,[16] E_f^I, is calculated as $E_f^I = E_{\rm def} - E_{\rm bulk} - \mu_{\rm Mn}$, where $E_{\rm def}$ is the total energy of the supercell with the defect, $E_{\rm bulk}$ is the total energy of the supercell without the defect (either pure Si or pure Ge), and $\mu_{\rm Mn}$ is the Mn chemical potential.[17] For neutral substitutional impurities[16] the formation energy (E_f^S) is given by $E_f^S = (E_{\rm def} + \mu_X) - E_{\rm bulk} - \mu_{\rm Mn}$, where μ_X is the chemical potential of either Si or Ge.[17]

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TABLE I. Formation energies (in eV) for interstitial and substitutional Mn in bulk Si and Ge. For both materials, the results are reported for the Si (a_{Si}) as well as the Ge (a_{Ge}) lattice constants.

Lattice constant	Mn_I^{Si}	Mn_{Si}	Mn_I^{Ge}	Mn_{Ge}
a_{Si}	2.5	2.8	3.4	1.7
a_{Ge}	2.5	2.7	2.1	1.5

In Table I we present the results for Mn atoms in Si and Ge at their equilibrium lattice constants (we find $a_{Si}=5.445$ Å for Si and $a_{Ge}=5.750$ Å for Ge). As expected,[11,12] for silicon the Mn atoms prefer to be at interstitial sites, with an energy difference ΔE^{S-I} between the substitutional and interstitial sites of $\Delta E^{S-I}=0.3$ eV. For Mn in Ge, on the other hand, we show that the Mn substitutional impurity has a lower formation energy by $\Delta E^{S-I}=-0.6$ eV. In order to investigate how much of this difference between Si and Ge is a result of their lattice parameter difference, i.e., how much is due to a volume effect, we repeated the same calculations for Si (Ge) in the lattice parameter of Ge (Si).[17] The results are also presented in Table I. In silicon, no significant changes were observed, with a small reduction in the substitutional Mn formation energy, which led to $\Delta E^{S-I}=0.2$ eV instead of 0.3 eV. For Mn in Ge, the interstitial site becomes highly unfavorable, with the formation energy changing by more than 1 eV. The formation energy for the substitutional site, on the other hand, changed very little. This leads to a large increase in the energy difference between the substitutional and interstitial sites: $\Delta E^{S-I}=-1.7$ eV. Therefore, even though increasing the Si lattice parameter has a small tendency towards favoring a Mn atom in a substitutional site, *the difference in lattice parameter between* Si *and* Ge *cannot account, by itself, for the distinct behavior of* Mn *in these materials*. Thus, specific chemical interactions between the Mn atom and the host atoms, most likely related to the presence of *d* electrons in Ge, are crucial in determining the distinct behavior in Si and Ge. This suggests that in the $Si_{1-x}Ge_x$ alloy the Mn atoms may prefer to be at a substitutional site with a Ge rich environment, instead of at an interstitial site. In order to confirm this possibility, we performed calculations for both interstitial as well as substitutional Mn in $Si_{1-x}Ge_x$, for $x=0.25$, 0.5, and 0.75. Since the $Si_{1-x}Ge_x$ is a substitutionally disordered alloy, the vicinity of a Mn impurity is not uniquely determined, and for either the substitutional or the interstitial Mn, there are five different types of sites, if only the nearest-neighborhood is considered, i.e., a Mn surrounded by a configuration of Si and Ge atoms that can be labeled as $Si^{\nu}Ge^{4-\nu}$, for ν varying from 0 to 4.

To simulate the $Si_{1-x}Ge_x$ disordered alloys, we used supercells with 128 atoms where the atoms were distributed as special quasirandom structures (SQS).[18] Details of the preparation of the supercells were given elsewhere,[19] and a similar procedure has already been used to study vacancies in this alloy.[20,21] It should be mentioned that due to the SQS approach, the disorder of the alloy is taken into account in an explicit way. As we have shown,[19] the alloy lattice parameter follows very closely the Vegard's law, and we therefore use $a_{Si_{1-x}Ge_x}=(1-x)a_{Si}+xa_{Ge}$.

TABLE II. Formation energies (in eV) for the interstitial and substitutional Mn in $Si_{(1-x)}Ge_x$, for $x=0.25$, 0.5, and 0.75, and for the distinct neighborhoods $Si^{\nu}Ge^{4-\nu}$. For the substitutional cases, Mn was always replacing a Si atom, except for $x=0.5$ where Mn replacing Ge atoms were also considered (results in parentheses).

	$x=0.25$		$x=0.5$		$x=0.75$	
ν	E_f^I	E_f^S	E_f^I	E_f^S	E_f^I	E_f^S
4	2.5	2.6	2.4	2.3 (2.2)	2.2	2.0
3	2.4	2.5	2.5	2.2 (2.2)	2.2	1.9
2	2.6	2.4	2.6	2.2 (2.1)	2.5	1.8
1	2.8	2.3	2.7	2.0 (2.1)	2.5	1.8
0	2.9	2.3	2.8	2.0 (2.0)	2.6	1.7

To study the interstitial Mn defects, we randomly selected five sites with distinct first neighborhoods. As these sites will also have different second, third, etc., neighborhoods, an averaging procedure should be performed. From previous studies of vacancies in the alloy,[20,21] we estimate an overall variation in the formation energies of the order of ±0.1 eV due to the different vicinities, and hence this averaging will not alter our conclusions in any significative way. The formation energy $E_f^I(\nu,x)$ of a neutral interstitial[16] Mn in the $Si_{1-x}Ge_x$ alloy, in a given neighborhood $Si^{\nu}Ge^{4-\nu}$, labeled by ν, is given by $E_f^I(\nu,x)=E_I(\nu,x)-E_{bulk}(x)-\mu_{Mn}(x)$. Here $E_I(\nu,x)$ is the total energy of the SQS structure with the Mn interstitital, $E_{bulk}(x)$ is the total energy of the SQS alloy without any defects, and $\mu_{Mn}(x)$ is the Mn chemical potential in the $Si_{1-x}Ge_x$ alloy, which we determine[22] as $\mu_{Mn}(x)=(1-x)\mu_{MnSi}+x\mu_{MnGe}-\mu_{Si_{(1-x)}Ge_x}$.

To study substitutional Mn defects a similar procedure as described above was employed. Since an atom from the original SQS structure must now be removed, there is the extra possibility of having the Mn replacing either a Si or a Ge atom. The formation energy $E_f^S(X,\nu,x)$ of a neutral[16] Mn substituting an atom X (X=Si and Ge), in the $Si_{1-x}Ge_x$ alloy, with a neighborhood $Si^{\nu}Ge^{4-\nu}$, labeled by ν, is given by $E_f^S(X,\nu,x)=E_S(X,\nu,x)-E_{bulk}(x)+\mu_X(x)-\mu_{Mn}(x)$. Here $E_S(X,\nu,x)$ is the total energy of the SQS structure with the Mn in place of an atom X (X=Si and Ge), which has a chemical potential $\mu_X(x)$ in the $Si_{1-x}Ge_x$ alloy.[23]

All our results are presented in Table II and Fig. 1. For the substitutional Mn calculations, we always removed a Si atom to place the Mn impurity, except for $x=0.5$ where a Ge atom was also removed. These latter results are shown in parentheses in Table II. As can be seen, the formation energies are always very similar, indicating that our conclusions do not depend on Mn replacing either a Si or Ge atom. For interstitial Mn, the differences between the formation energies for the local configurations Si^0Ge^4 and Si^4Ge^0 are always 0.4 eV, for all x, with the lowest values occurring in Si-rich vicinities (Si^4Ge^0). For substitutional Mn this formation-energy spread is also independent of x, and has a value of 0.3 eV. Ge-rich neighborhoods, however, have lower formation energies. An important result is the fact that the lowest formation energy for a substitutional Mn *is always smaller* than the lowest formation energy for an interstitial Mn. The

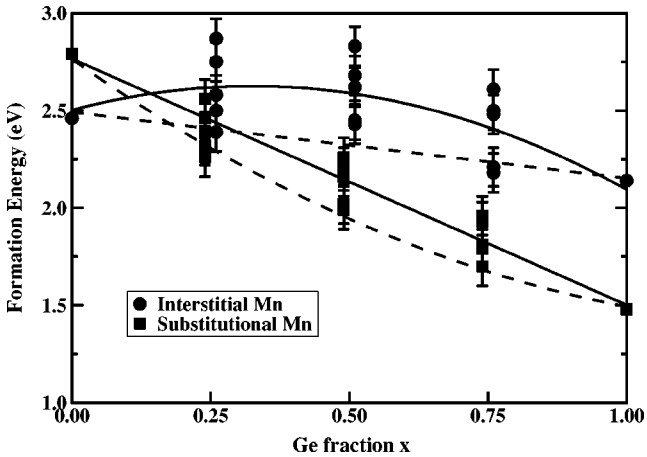

FIG. 1. Formation energies for interstitial and substitutional Mn in $Si_{(1-x)}Ge_x$, for $x=0.25$, 0.5, and 0.75, and for the distinct neighborhoods $Si^{\nu}Ge^{4-\nu}$. The results are slightly displaced in x ($x=x\pm0.01$) for clarity. Error bars (±0.1 eV) are estimates of the influence of vicinities beyond the nearest-neighborhood. Data for pure Si and Ge are also shown. The continuous lines are fits to average formations energies, whereas the long-dashed curves are fits to lowest formation energies.

difference between these two lowest formation energies is 0.1 eV for $x=0.25$, 0.4 eV for $x=0.5$, and 0.5 eV for $x=0.75$. This indicates that for the $Si_{0.75}Ge_{0.25}$ alloy, there are local configurations that make substitutional Mn the lowest energy structure. Another significant result is the fact that for $x\geqslant0.5$, *all* substitutional configurations have formation energies that are smaller than the smallest formation energy for interstitial Mn. The overall image of our results can be appreciated in Fig. 1. Curve fittings to both the average values (continuous curves) of the formation energies as well as to the lowest values (long-dashed curves) of the formation energies are also presented in Fig. 1. The average values curves cross at $x\simeq0.14$, whereas the lowest values curves cross at $x\simeq0.18$. These results indicate that for $x\gtrsim0.16\pm0.02$ there should be Ge-rich neighborhoods in $Si_{(1-x)}Ge_x$ where substitutional Mn atoms becomes more stable than interstitial Mn.

At thermodynamic equilibrium, and assuming that the defects are independent of each other, the population of Mn interstitial defects in $Si_{1-x}Ge_x$ is given by[20]

$$N^I(\nu) = N_S P^{\nu}(x)\exp[-G_f^I(\nu)/k_BT], \tag{1}$$

where N_S is the total number of sites in the lattice, $P^{\nu}(x)$ is the probability[24] for the ν configuration to exist in the x-concentration alloy, $G_f^I(\nu)$ is the Gibbs free formation energy of interstitial Mn at configuration ν, and T is the temperature. Note that $N_S P^{\nu}(x)$ is the effective number of interstitial sites of type ν. Under the same assumptions, the population of Mn substitutional defects in $Si_{1-x}Ge_x$ are given by

$$N^S(\nu) = N_S P^{\nu}(x) f(X,x)\exp[-G_f^S(X,\nu)/k_BT], \tag{2}$$

where $f(X,x)=(1-x)$ if $X=$Si and $f(X,x)=x$ if $X=$Ge, and $G_f^S(X,\nu)$ is the Gibbs free formation energy of substitutional Mn at configuration ν, with Mn replacing an atom X ($X=$Si and Ge). Assuming that, for a given temperature and composition, the vibrational entropies of all defects are similar and independent on their vicinities, we can calculate the relative population of the Mn defects as

$$n^D(\nu,x,T) = \frac{P^{\nu}(x)\exp[-E_f^D(\nu)/k_BT]}{\sum_{\nu,D} P^{\nu}(x)\exp[-E_f^D(\nu)/k_BT]}, \tag{3}$$

where $D=I$ and S represents both the interstitial and substitutional defects. For substitutional defects, since the formation energies for Mn replacing either a Ge or a Si atom are quite similar, and given that $\Sigma_X f(X,x)=1$, the above expression for $n^S(\nu,x,T)$ is obtained after a summation over X is performed.

In Table III we present the relative populations for the interstitial and substitutional Mn impurities in the $Si_{(1-x)}Ge_x$ alloy, for $x=0.25$, 0.5, and 0.75, for two temperatures, $T=300$ K and $T=600$ K. In all cases the overall population of substitutional Mn is larger than the interstitial one. At 300 K, even for $x=0.25$ we already have ~78% of Mn at substitutional sites. As the temperature is increased to 600 K, this percentage decreases to 56%. The significance of this result can be appreciated by noting that in bulk Si, at $T=300$ K, basically 100% of Mn are at interstitial sites, whereas at $T=600$ K there are approximately 99.7% of interstitial Mn. This means that by alloying with Ge one can revert the overall population of defects from interstitial to substitutional Mn.

TABLE III. Relative populations for the interstitial and substitutional Mn in $Si_{(1-x)}Ge_x$, for $x=0.25$, 0.5, and 0.75, and for the distinct neighborhoods $Si^{\nu}Ge^{4-\nu}$. The results were obtained according to Eq. (3), using the data from Table II.

	$T=300$ K						$T=600$ K					
	$x=0.25$		$x=0.5$		$x=0.75$		$x=0.25$		$x=0.5$		$x=0.75$	
ν	n^I	n^S	n^I	n^S	n^I	n^S	n^I	n^S	n^I	n^S	n^I	n^S
4	0.	0.	0.	0.	0.	0.	0.04	0.01	0.	0.00	0.	0.
3	0.22	0.01	0.	0.	0.	0.	0.40	0.11	0.	0.02	0.	0.
2	0.	0.11	0.	0.00	0.	0.01	0.	0.21	0.	0.06	0.	0.06
1	0.	0.36	0.	0.56	0.	0.04	0.	0.18	0.	0.64	0.	0.18
0	0.	0.30	0.	0.44	0.	0.95	0.	0.05	0.	0.28	0.	0.76

In conclusion, we have shown that volume effects cannot be the main reason Mn prefers to be a subsitutional impurity in pure Ge. Chemical effects, therefore, must clearly play an important role. Through a systematic study of interstitial and substitutional Mn atoms in realistic models of the $Si_{(1-x)}Ge_x$ alloy, we have shown that for $x \gtrsim 0.16$ the substitutional Mn in Ge-rich neighborhoods becomes more stable than the interstitial Mn. By playing with the temperature and the concentration x, and maybe also using nonequilibrium growth conditions,[8] it should be possible to obtain $Si_{(1-x)}Ge_x$ alloys with a large enough concentration of substitutional Mn atoms. Considering that in all calculations in the alloy we obtained a Mn local moment with the same value as in the pure crystals, and given that recent studies[9] have shown that both Mn_xSi_{1-x} and Mn_xGe_{1-x} should have similar magnetic properties, all these facts indicate that $Mn:Si_{(1-x)}Ge_x$ is potentially a magnetic material like Mn_xGe_{1-x},[7] opening up in this way the road towards Si-based DMS.

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[16] Even though Mn in Si, Ge, and the alloy has many charge states (e.g., Ref. 11 and references therein), the results for the neutral impurities should suffice to illustrate the main point of our work, which is to propose that in $Si_{1-x}Ge_x$ substitutional Mn will be stabilized against interstitial Mn in Ge-rich neighborhoods. Based on some calculations for representative configurations for the $Si_{0.5}Ge_{0.5}$ alloy, we estimate that for the electronic chemical potential close to the middle of the gap not only our main conclusion will not change, but there would be also negligible modifications in our numerical results. Moreover, even for values of the electronic chemical potential closer to the band edges, there will be substitutional sites with energies that are lower than that of the interstitial ones. This may cause a shift of the Ge concentration for which the substitutional configurations become the dominant ones, however, again that would not change the main conclusion.

[17] For Mn in Si, we have used the MnSi compound [see B. Roessli, P. Böni, W. E. Fischer, and Y. Endoh, Phys. Rev. Lett. **88**, 237204 (2002)], as the source of Mn atoms. A similar MnGe structure was used when studying Mn in Ge. For Si (Ge) we have considered the bulk silicon (germanium). When calculating the formation energies of Mn defects in Si (Ge) at the lattice constant of Ge (Si), the Si (Ge) chemical potential was obtained from a bulk silicon (germanium) calculation in the Ge (Si) lattice constant.

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[22] One can write $\mu_{Mn}(x)=(1-x)\mu_{Mn}(Si)+x\mu_{Mn}(Ge)$, which gives the proper limits for $x=0$ and $x=1$, together with $\mu_{Mn}(Si)=\mu_{MnSi}-\mu_{Si}$ and $\mu_{Mn}(Ge)=\mu_{MnGe}-\mu_{Ge}$, where μ_{MnX} and μ_X, for $X=\{Si,Ge\}$, are obained as in Ref. 17. These give $\mu_{Mn}(x)=(1-x)\mu_{MnSi}+x\mu_{MnGe}-[(1-x)\mu_{Si}+x\mu_{Ge}]$. It is a good approximation, however, to use $\mu_{Si_{(1-x)}Ge_x} \simeq (1-x)\mu_{Si}+x\mu_{Ge}$ (see Ref. 23), which results in $\mu_{Mn}(x)=(1-x)\mu_{MnSi}+x\mu_{MnGe}-\mu_{Si_{(1-x)}Ge_x}$. The chemical potential $\mu_{Si_{(1-x)}Ge_x}$ is obtained as the total energy of the SQS structure, $E_{bulk}(x)$, divided by the number of atoms.

[23] The chemical potentials, $\mu_X(x)$, depend on growth conditions. For (element-X)-rich growth conditions, $\mu_X(x)$ equals μ_X, the chemical potential of element X in the bulk, independently of x. In Si-rich conditions, the Ge chemical potential must satisfy $[\mu_{Si_{(1-x)}Ge_x}-(1-x)\mu_{Si}]/x \leqslant \mu_{Ge}(x) \leqslant \mu_{Ge}$, whereas in Ge-rich conditions the Si chemical potential must satisfy $(\mu_{Si_{(1-x)}Ge_x}-x\mu_{Ge}/(1-x) \leqslant \mu_{Si}(x) \leqslant \mu_{Si})$. In $Si_{(1-x)}Ge_x$, independently if we have a Si- or Ge-rich condition, the $\mu_X(x)$ are always very close to μ_X in the bulk, for all values of x and for X equals Si or Ge. Therefore, we always use $\mu_X(x)=\mu_X$ (X=Si,Ge), with μ_X as determined in Ref. 17.

[24] For a $Si^{\nu}Ge^{4-\nu}$ vicinity in $Si_{(1-x)}Ge_x$, $P^{\nu}(x)=\frac{4!}{\nu!(4-\nu)!}(1-x)^{\nu}(x)^{4-\nu}$.