Theoretical investigation of a possible Mn_xSi_{1-x} ferromagnetic semiconductor

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We investigate theoretically the possibility of growing, under appropriate conditions, a Mn_xSi_{1-x} sample with a high enough concentration of substitutional Mn impurities. Through the study of a variety of interstitial and substitutional sites, for a Mn impurity on the Si(100) bare and hydrogenated surface, as well as in adjacent inner layers, we have found that it might be indeed possible to grow such a compound, since the formation energies for the interstitial and substitutional sites at the Si(100) surface are identical. We also suggest means to identify and distinguish these structures experimentally.

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The recent development of diluted ferromagnetic semiconductors[1–4] (DMS's) in III-V (Ref. 5) and II-VI (Ref. 6) Mn-based compounds opened up the possibility of applications such as sensors, memories, as well as for computations based on the electronic spin degrees of freedom, which has brought a great deal of attention to this kind of material. Recently, a new class of ferromagnetic semiconductors, Mn_xGe_{1-x}, has been reported, which is based on the technologically important type-IV compounds.[7] Even though all these DMS materials are quite interesting from a technological point of view, it would be extremely important if a Si-based DMS material could be synthesized, given that Si is by far the most important semiconductor for electronic devices. In the present paper we address the issue of how feasible it would be to grow a high concentration Mn_xSi_{1-x}.

One question may be asked: Why can there be a DMS-Mn_xGe_{1-x} and not a DMS-Mn_xSi_{1-x}? Since the electronic structure of Si and Ge are so similar, one would expect that for large enough x, Mn_xSi_{1-x} would become ferromagnetic below some critical temperature, as it happens in Mn_xGe_{1-x}. Therefore, the important point is if these values of x can be achieved. The main difference between Si:Mn and Ge:Mn is that Mn is an interstitial impurity in Si, whereas in Ge it is a substitutional impurity. We suggest that this might be precisely the reason why Ge can be a ferromagnetic semiconductor: a substitutional impurity such as Mn in Ge cannot diffuse as easily as an interstitial one, such as Mn in Si.[8,9] Therefore, one can introduce a large enough impurity concentration without diffusing them until they can find other impurities and form clusters.

From the above, we decided to investigate theoretically if Mn can be grown under non-equilibrium conditions in substitutional sites in Si. Clearly, to achieve both this situation of Mn occupying a less stable site as well as a large x (the solubility of Mn in Si is known to be low[10]), the best possibility seems to be the deposition of Mn using low-temperature molecular-beam epitaxy (LT-MBE). This LT-MBE approach was fundamental in developing III-V based DMS's.[5] Therefore, we have studied in detail the stability of Mn atoms on the Si(100) surface, comparing these results with Mn in the bulk. We have found that the formation energy for a substitutional Mn impurity is the same as for an interstitial Mn impurity on the topmost surface layer. This indicates that it is, in principle, possible to grow a Mn_xSi_{1-x} material with Mn occupying substitutional sites.

We have performed *ab initio* calculations based on density-functional theory within the generalized gradient approximation (GGA).[11] We have used ultrasoft pseudopotentials[12] and a plane-wave expansion up to 230 eV, as implemented in the VASP code.[13] For the surface calculations we have used a supercell containing a slab with eight Si layers, with 16 Si atoms in each layer, saturated with H atoms at one side, and a vacuum region of 10.6 Å, as reported elsewhere.[14] The two bottom Si layers and the H atoms were held fixed. The Brillouin zone was sampled using the k point at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. For bulk calculations, we have used a 64-atom supercell and a Monkorst-Pack k-point sampling of $3\times3\times3$. All structures were considered relaxed when all force components were smaller than 0.02 eV/Å.

The formation energy of an interstitial neutral impurity, E_F^I, is calculated as

$$E_F^I = E_{tot}^{def} - E_{tot} - \mu_{Mn}, \tag{1}$$

where E_{tot}^{def} is the total energy of the supercell with the defect, E_{tot} is the total energy of the supercell without the defect, and μ_{Mn} is the Mn chemical potential.[15] For substitutional impurities the formation energy E_F^S is given by

$$E_F^S = (E_{tot}^{def} + \mu_{Si}) - E_{tot} - \mu_{Mn}, \tag{2}$$

where μ_{Si} is the chemical potential of Si.[15]

The formation energy of an interstitial tetrahedral impurity in Si is found to be 2.47 eV; as stated before, this is the most stable site for a Mn impurity in Si. The substitutional impurity has a formation energy of 2.90 eV, and the hexagonal interstitial has a formation energy of 3.00 eV. The magnetic moment for the substitutional impurity is higher than the interstitial one. In the substitutional site the magnetic moment is 3.14 μ_B, whereas in the tetrahedral interstitial it is 2.46 μ_B. The magnetic moment in the hexagonal site is 2.37 μ_B.

The usual way to study adatoms on surfaces is to place them in the desired sites and let the atoms relax to a local minimum in the potential-energy surface (PES). If constraints are applied, it is possible to study configurations that are not PES minima. We have studied many adsorption sites

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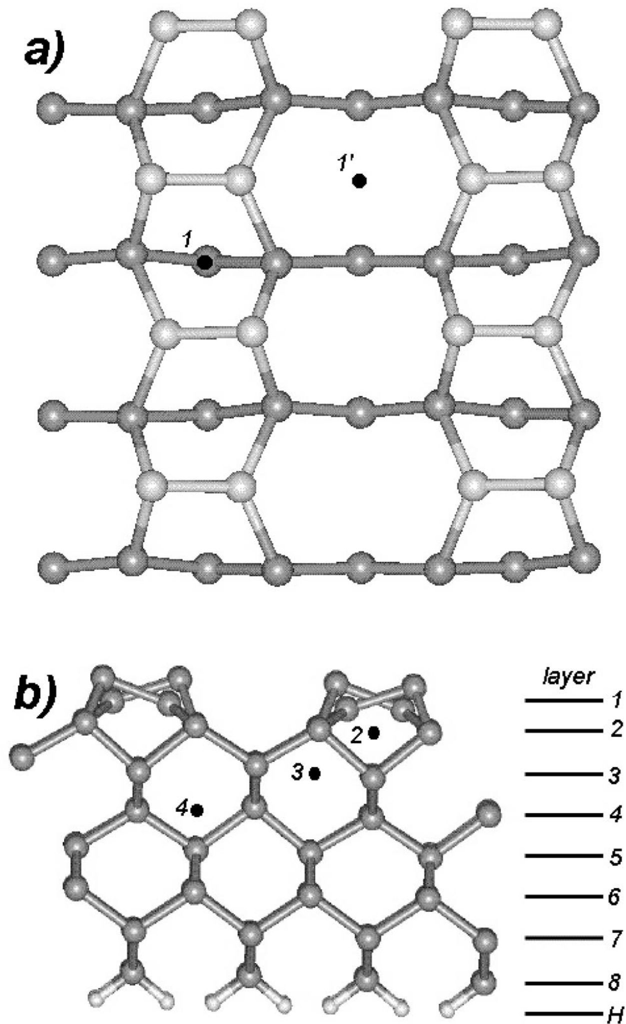

FIG. 1. (a) Top and (b) side view of the supercell used in the calculations. The Mn positions discussed in the text are marked as 1, 1′, 2, 3 and 4.

on the surface, and also on the inner layers, for many different spin configurations. In the following, we will discuss only the most stable sites (all of them being local minima in the PES) for the lowest-energy spin configuration in each case.

Figure 1 shows schematically five positions for the Mn impurity atom. For sites 1 and 1′, the Mn atom is adsorbed on the surface (topmost, or first, supercell layer), whereas for sites 2, 3, and 4 the Mn atom is located in the second, third, and fourth layers, respectively. The most stable site *on* the surface (first layer) is site 1, on top of a dimer row, between two dimers, the so-called pedestal site. It is followed by site 1′, which is 0.23 eV higher in energy. All the other investigated sites on the surface have energies that are higher than site 1 by at least 1.3 eV, which makes them less relevant to the present study. The overall lowest-energy configuration that we have found is for Mn in site 2, i.e., a site where the Mn atom occupies an interstitial position near the second layer, below a surface dimer. This dimer is displaced by $\simeq 1$ Å, away from the surface, and it becomes unbuckled. In

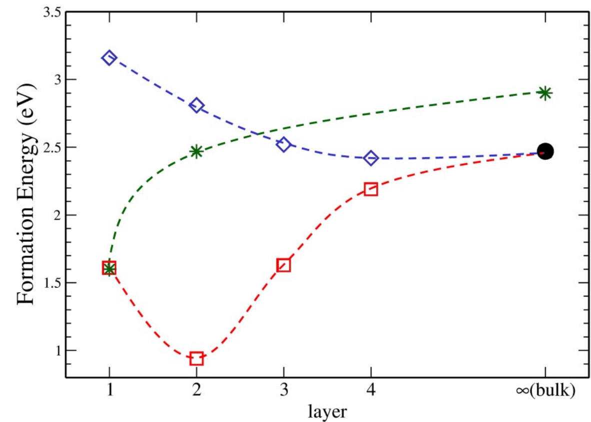

FIG. 2. (Color online) Variation of the formation energy with the depth of a Mn impurity in the slab. Squares are the results for interstitial sites (sites 1, 2, 3, and 4 in Fig. 1) and stars are the results for substitutional sites. The diamonds are also the results for interstitial sites, but for a hydrogenated Si surface. The large dot represents the limit of a Mn interstitial impurity in bulk Si. All lines are guides to the eyes.

this site, the Mn atom is highly coordinated, having nine Si atoms around it with distances between 2.22 Å and 2.62 Å. The energy difference between site 1, the most stable on the surface, and site 2, our global minimum, is 0.67 eV.

For all the studied sites, we have calculated their formation energies using Eqs. (1) and (2) above.[15] For site 1, we have found a formation energy of 1.61 eV, whereas for site 2, we have found a formation energy of 0.94 eV. As can be seen, these formation energies are much smaller than the lowest bulk E_F of 2.47 eV. In Fig. 2 we show the variation of the formation energy as the Mn atom is moved from the surface towards the bulk (i.e., as it is placed in deeper layers of our supercell). The results for the bare Si surface (nonhydrogenated) are represented by squares. We can observe that the formation energy initially decreases, as the atom goes from the first to the second layer, and then increases towards the bulk value as the Mn is moved further into deeper layers. In the fourth layer, the difference in the formation energy with respect to the impurity in the bulk crystal is already small, as can be seen in Fig. 2.

At sites 3 and 4, which have an approximate T_d local symmetry, the Mn atom already has a magnetic configuration very similar to the bulk one. The magnetic moment at site 3 is $3.00\mu_B$, and at site 4 it is $2.95\mu_B$. At both surface sites 1 and 1′, the Mn atoms has a magnetic moment of $3.78\mu_B$, which is higher than in the interstitial bulk case. This was expected, since on the surface the crystal field is supposed to be smaller than in the bulk. As a result, the exchange splitting will be larger than the crystal-field splitting, resulting in a high-spin system.[10,16,17]

Returning to the question if it would be possible to grow Mn_xSi_{1-x} with Mn at substitutional sites, we have, therefore, also studied Mn as a substitutional impurity on the Si(100) surface (first layer) and the subsurface (second layer) (see Fig. 2). The lowest-energy configuration in the first layer is with Mn in place of a Si dimer atom in the *up* position, with a formation energy of 1.60 eV. A similar configuration, with

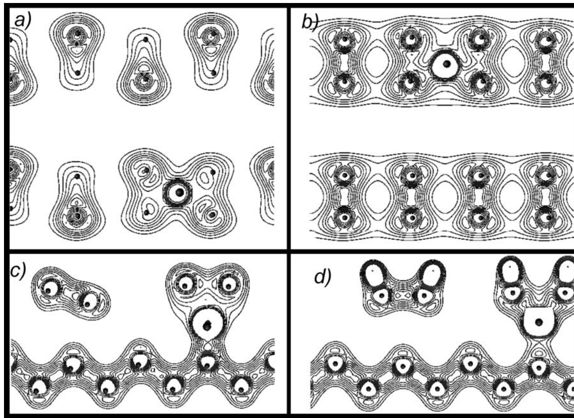

FIG. 3. Total charge densities for the Mn at different interstitial positions. Mn on the first layer (site 1) for (a) the bare and (b) the hydrogenated surface. The plane shown is in the growth direction, at the height of the Mn impurity. Mn in the second Si layer (site 2) for (c) the bare and (d) the hydrogenated surface. The plane shown is in the [100] direction, passing through the Mn impurity. It is possible to observe the surface dimers in all figures.

Mn replacing a Si dimer atom in the *down* position, has $E_F = 1.98$ eV. The formation energy of a substitutional site in the second layer is 2.47 eV, much higher than in the first layer, but still 0.33 eV lower than the formation energy of the substitutional impurity in bulk Si. The Mn magnetic moments are $3.87\mu_B$ and $2.65\mu_B$ for the substitutional sites in the first (lowest-energy configuration) and second layers, respectively. Using the same argument as before, it was expected to have a Mn impurity in the first layer with a higher magnetic moment because of a lower crystal field.

We have also investigated the Si(100) hydrogenated surface, which exhibits different characteristics from the bare surface. First of all, the dimers are not buckled anymore, with one H atom bonded to each Si surface atom. As there are no dangling bonds on this surface, it becomes less reactive. In this case, the most stable position for the adsorption of one Mn atom is on the trough, between two dimer rows, with a formation energy of 2.52 eV. In the bare surface, the adatom is bonded to Si dimer atoms. On the hydrogenated surface, on the other hand, this cannot happen since the Si atoms are fully saturated. Site 1, now, is 0.5 eV higher in energy than the trough site. As the Mn atom is moved into deeper layers, the formation energy decreases monotonically towards the bulk value. Contrary to the bare surface, the second-layer site is not the most stable one anymore. In the fourth layer, the formation energy is already very close to the bulk crystal value (see Fig. 1). The Mn substitutional impurities for the hydrogenated surface configuration are also highly unfavorable. For example, the formation energy for a Mn impurity in a second-layer substitutional site is 3.30 eV, much higher than in the bare surface case. In order to better understand this difference between the hydrogenated and bare surfaces, we have analyzed the total charge-density distribution for both cases (Fig. 3). In Figs. 3(a) and 3(b) we present contour plots for the total charge density in planes that are parallel to the surface and that contain the Mn atom, for Mn adsorption on the Si surface. For the clean surface

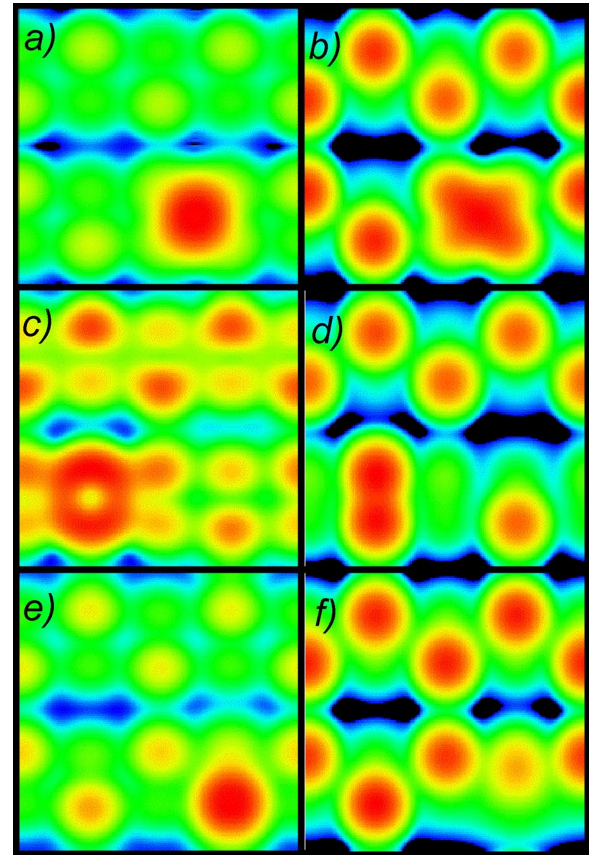

FIG. 4. (Color online) Theoretical STM images. Left side: empty state images. Right side: filled state images. Panels (a) and (b): interstitial Mn at site 1, located at the brightest spot in both images. Panels (c) and (d): interstitial Mn at site 2, located under the unbuckled dimer, which is observed as a bright, symmetrical spot in both images. Panels (e) and (f): substitutional Mn on the Si(100) surface. In panel (e) Mn is observed as the brightest spot, whereas in image (f), it is basically invisible. All images were generated integrating in an energy window of 2 eV from the Fermi energy.

[Fig. 3(a)], it is possible to observe the tendency of the Mn to bind to four Si surface atoms, whereas in the hydrogenated case [Fig. 3(b)], where the Si dangling bonds are fully saturated, there is only a small interaction between two Si surface atoms and the Mn. This explains the higher formation energy in these latter case. For a Mn interstitial in the second layer (site 2 of Fig. 1), we observe that for both the bare [Fig. 3(c)] and the hydrogenated [Fig. 3(d)] surfaces, the Mn atom interacts strongly with the Si atom right under it (at the fourth layer). In the case of the bare surface, we can observe that the surface dimer becomes symmetric and there is no strong, direct bond between these atoms and the Mn impurity. It is also possible to see how these Si dimer atoms are pushed out from the surface due to the presence of the Mn impurity just below them. For the hydrogenated surface, on the other hand, the impurity seems to bind more strongly to both these atoms from the first surface layer, causing a "rupture" of the dimer bond, with the overall result of an increase in the formation energy.

From our calculations, we observe that (i) the formation

energy of a Mn impurity on the bare surface is very much reduced when compared to the bulk value and (ii) for this situation, the substitutional site has the same formation energy as the interstitial site. As a result, it seems that it could be feasible to grow, under appropriate conditions, a Mn_xSi_{1-x} with a desirable concentration of substitutional Mn impurities. However, we also obtained that the preferential site, close to the surface, is an interstitial position at the second layer. To achieve the goal of growing Mn_xSi_{1-x} with substitutional Mn, it would be interesting if Mn could be, somehow, prevented from reaching this site. We have estimated the diffusion barrier[18] for the Mn atom to go from site 1 to site 2 (see Fig. 1), and we have found a value of 0.96 eV. This value is smaller than the diffusion barrier for a Mn impurity to diffuse in bulk Si (1.17 eV).[9] Therefore, it seems that the growth temperature would have to be relatively small in order to reduce the occupation of this adsorption site. It should be mentioned that, assuming that it will be possible to place a high enough number of Mn_{Si}, many other relevant effects will have to be understood in detail, such as what will be the interaction between the substitutional and interstitial Mn atoms, and if this interaction will lead also to clustering and, potentially, to difficulties in attaining a ferromagnetic semiconductor. However, albeit these points might be important the really crucial question that will determine if one should pursue this detailed understanding any further is can a Mn_xSi_{1-x} alloy, with Mn_{Si}, be grown experimentally?

Finally, it is fundamental to have a practical way to identify Mn at interstitial sites 1 and 2 and also a Mn substitutional on the surface, in order to monitor, for example, if the growth conditions are leading to an increase of the desired configuration. With this in mind, we calculate theoretical scanning tunneling microscopy (STM) images[14] for these configurations, i.e., Mn interstitials at sites 1 [Figs. 4(a) and 4(b)] and 2 [Figs. 4(c) and 4(d)] and a substitutional Mn at the surface [Figs. 4(e) and 4(f)]. As can be seen, the STM images will be sufficiently different to allow for a clear identification of Mn impurities at these different sites, even when they are buried at site 2, since in this case the Si dimers on top of Mn will provide the clue to distinguish this configuration.

In conclusion, our results suggest that it might be possible to grow, probably using low-temperature MBE, Mn_xSi_{1-x} samples with a high enough concentration of substitutional Mn to show magnetic properties similar to Mn_xGe_{1-x} DMS.[7] We suggest that temperature controlled MBE experiments, for small Mn coverage on Si(100), using STM measurements to monitor where the Mn atoms are going, similar to what has been done for Si and Ge growth on Si(100),[19] should be performed to test the feasibility of the ideas presented here. Finally, the use of small amounts of Ge might help to stabilize the substitutional Mn, since in a Si-rich SiGe alloy, a Mn substitutional atom prefers to be in a Ge rich environment rather than in a Si rich environment.[20]

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