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Mn doping in model amorphous Si and Ge: a theoretical investigation

Alessandra Continenza and Gianni Profeta
CNISM at Dipartimento di Fisica, Università degli Studi dell’Aquila, I-67100 L’Aquila, Italy
E-mail: alessandra.continenza@aquila.infn.it

Abstract. We present a theoretical study on the structural, electronic and magnetic properties of Mn-doping in amorphous group IV-semiconductors. In order to understand the effect of local disorder on the properties of the system, we consider the ST12 structure, a 12-atom unit cell which is known to locally reproduce the coordination of amorphous semiconductors. Based on ab-initio calculations we predict enhanced magnetic properties and higher solubility of Mn ions in model amorphous systems suggesting that amorphous semiconductors can represent an alternative route for spintronic applications.

1. Introduction
Mn-doping in technologically relevant semiconductors is still catching the scientific community interest due to possible spintronic applications. The attention has so far been devoted mainly to III-V compounds achieving ferromagnetic temperatures up to 170K in GaAs[1]. Mn-doping in group IV semiconductors has also been experimentally achieved with more puzzling results. Low temperature MBE-growth of Mn-diluted Ge showed two different ferromagnetic transitions at 12K and 112K[2] compatible with an inhomogeneous distribution of dopants and the formation of bound magnetic polarons[3]. Solid solution methods[4] lead to Curie temperatures as high as 285K in partial agreement with co-deposition of Mn and Co in Ge which gave a transition temperature of 270K[5]. In all these reports the samples, doped with Mn-concentrations of the order of a few percent, are insulators with rather low carrier densities (mainly holes) while GaMnAs shows metallic behavior. Although most of the experiments are performed on crystalline samples, several experimental techniques used to achieve Mn-dilution within the semiconductor matrix cause a loss of short-range order making the structure locally more similar to an amorphous rather than to a perfect crystalline material. This is established by several structural studies performed, for example, on ion-implanted samples[6] showing their disordered short-range nature depending on the implantation temperature, the ion dose and subsequent annealing treatments. In addition, Mn- and Cr-cosputtering has been realized for both Ge[7] and Si[8] revealing interesting magnetic properties of samples at quite large impurity concentrations (up to 22 %) still preserving the dilution limit and avoiding precipitation of impurity-rich compounds. In fact, large impurity concentrations are expected to enhance the magnetic properties of such materials: however, rather poor ferromagnetism was revealed and indeed paramagnetic behavior has been reported for Mn-doped amorphous Si. This behavior was ascribed to a large number of dangling bonds that trap carriers locally generated by dopants.
We here investigate the case of doping in a model cell reproducing the coordination of amorphous materials at 8% concentration, very close to the optimal doping dose reported (≈ 12 %)[8] and, due to space limitations, we focus only on the structural properties of these systems deferring detailed analysis of the electronic and magnetic properties to a forthcoming publication. The main result of our investigation is that Mn-doping is energetically less costly in ST-12 structures and that local disorder per se is not depressing the magnetic properties of Mn impurity in group-IV semiconductors but, in the case of Si, is rather bringing the material towards half-metallicity.

2. Computational details
In order to represent the disordered structure we consider a model structure, namely, the so called ST12 structure that has been taken as representative of disordered structures since it still keeps the characteristic tetrahedral coordination of group IV elements. In particular, the ST12 structure is found as metastable phase[9] of Ge upon pressure release from the high pressure β-tin phase. It has not been found in Si, probably due to the large bond-angle deviations from the ideal tetrahedral angle in the diamond phase[10, 11].

The ST12 structure has a tetragonal cell containing 12 atoms occupying two different Wyckoff positions with different symmetries as shown in Fig.1 (blue and red balls label the different atomic types): the first atomic type (red, hereafter referred as mix-ch sites) bonds exclusively with the other atom type (blue, hereafter referred as chain sites) while the second one bonds with two atoms of its same type (blue) and two of the former (red). Along the z-axis, atoms are linked into two different chains: one connects symmetry equivalent atoms while the other one binds alternating red and blue atoms. Given the two different symmetry sites allowed in the structure, substitutional Mn-atoms may occupy either one of them with possibly different energy cost and electronic/magnetic properties. In the following, we will focus on the structural properties
compared to those of the diamond-structure counterpart for Si and Ge at 8.3% Mn-concentration. Our ab-initio calculations are performed within the generalized gradient corrections (GGA) [12] to density functional theory and using the VASP code[13]. PAW pseudopotentials[14] were used for both Ge and Mn-atoms, with semicore 3p and 3s states kept in the core shell. The kinetic energy cutoff used for the wave functions was fixed at 250 eV for both Mn-doped Si and Ge. Shells of (444) and (888) k-points were used to obtain converged results within few meV. All the structural parameters of the ST12 structure (volume and c/a ratio) were optimized via total energy calculations, while internal positions were relaxed following the ab-initio calculated forces. The heat of formation was calculated[15] as the difference of the total energy of the defective cell ($E_{\text{def}}$) and of the constituent atoms ($\mu$) in the reference structure (i.e. diamond for Si and Ge and antiferromagnetic fcc for Mn):

$$\Delta H = E_{\text{def}} - n_{\text{IV}}\mu_{\text{IV}} - n_{\text{Mn}}\mu_{\text{Mn}}$$

where $n_{\text{Mn}}$ ($n_{\text{IV}}$) indicates the number of Mn (group-IV) atoms in the defective cell.

3. Results

Before looking at the effects of doping in the ST12 structure we studied the equilibrium structure of both Si and Ge in this phase determining the equilibrium volume, the c/a ratio and all the 8 internal free parameters from first-principles. Crystallization in the ST12 structure results in a smaller volume per atom (18.44 and 21.75 Å$^3$ for Si and Ge, respectively) with respect to the diamond phase (about 10%) with bond-lengths ranging between 2.38-2.40 and 2.53-2.56 Å for Si and Ge, respectively, to be compared with 2.37 and 2.45 Å of the corresponding diamond equilibrium phases. The smaller volume per atom results in a more compact structure where bond angles, more than bond-lengths, sensibly deviate from the ideal tetrahedral coordination. This is probably the reason why, as a difference with Ge, this phase is not easily stabilized in silicon where bond bending is energetically quite costly[16, 11].

Table 1. Heat of formation of the defective cells considered. For reference, the corresponding values for Mn-doping in the diamond structure at 12.5 % concentration are shown in parenthesis.

|            | $\Delta H$ (eV) | $\mu$ ($\mu_B$) | $d_{\text{Mn-X}}$ (Å) |
|------------|----------------|----------------|----------------------|
| Si         |                |                |                      |
| Mn chain   | 1.82 (2.32)    | 3.00 (2.89)    | 2.43 (2.38)          |
| Mn mix-ch  | 1.75 (2.32)    | 3.00 (2.89)    | 2.43 (2.38)          |
| Mn int     | 0.81 (2.15)    | 1.30 (2.78)    | 2.30 (2.49)          |
| Ge         |                |                |                      |
| Mn chain   | 1.49 (1.58)    | 3.00 (3.00)    | 2.50 (2.40)          |
| Mn mix-ch  | 1.44 (1.58)    | 3.00 (3.00)    | 2.50 (2.40)          |
| Mn int     | 0.93 (2.75)    | 2.55 (3.35)    | 1.41 (2.52)          |

We now move to the study of Mn impurities in ST12 structure. Our structural and energetic results are reported on Table 1 for both ST12 Si and Ge and should be compared with analogous theoretical results for Mn impurities in Si and Ge in the diamond structure (values in parenthesis on Tab 1) at the closer concentration possible (12.5 % corresponding to 1 Mn every 8 group IV atoms). We note that the formation heats in diamond Ge do not show a large Mn-concentration dependence: moving from 12.5 % to 3.125 % these value change less than 0.10eV[17].
The first interesting feature to observe is that in silicon the heat of formation for Mn-doping is much lower (more than 0.5 eV) in the ST12 structure than in the diamond. This same difference is much less pronounced in Ge (of the order of 0.10 eV). This is in line with experiments that report a larger solubility of dopants in non-crystalline silicon[8] with respect to the diamond phase. As in diamond silicon, the interstitial site appears to be more stable than the substitutional one[18]. Unexpectedly, the same is true for Ge: in both cases disorder favors the non-bonding coordination of interstitial Mn, allowing for larger local relaxations with consequent energy gain. Interestingly, the two different substitutional sites (chain and out of chain) show slightly different formation energies in Si while are much closer in Ge, due to different bond-angle deviations. Mn-group IV bond-lengths are larger in ST-12 with respect to diamond structure keeping the same trend observed for pure Si and Ge in ST-12 phase.

Finally, the integer magnetic moment found in substitutional Mn in ST12 Si at variance with diamond Si indicates that the defective structure is completely half-metallic, as a possible consequence of the larger bond-length and of the resulting lower p-d hybridization.

To summarize, we studied the structural and magnetic properties of Mn-doping in a model disordered structure for group IV semiconductors. We find that Mn-doping in model amorphous Si and Ge brings to magnetic structures with rather large magnetic moments; in addition, the formation heat is in all cases lower in the ST12 structure with respect to the ordered diamond structure indicating that indeed disorder could help Mn solubility not disrupting half-metallicity nor the magnetic moment of the defective alloy. As shown so far, our calculations predict ferromagnetism - enhanced in the case of Si - for Mn-doping in the model-amorphous structures considered. The weak magnetism experimentally found in Mn-doped amorphous Si could then be ascribed to defects that may destroy local tetrahedral coordination, as some experiments seem to suggest[8].

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