Structural and magnetic properties of Mn-doped GaAs(110) surface

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Abstract

We have investigated STM images of the (110) cross-sectional surface of Mn-doped GaAs using first principles total-energy pseudopotential calculations. We focus on configurations with Mn interstitial in the uppermost surface layers. In particular, we have found that Mn impurities, surrounded by Ga or As atoms, introduce in both cases strong local distortions in the GaAs(110) surface, with bond length variations up to 8% on surface and non-negligible relaxations effects propagating up to the third sub-surface layer. In both cases interstitial Mn induces a spin-polarization on its nearest neighbors, giving rise to a ferromagnetic Mn–As and to antiferromagnetic Mn–Ga configuration.

*Keywords:* Gallium arsenide, Manganese, Magnetic semiconductors, Doping effects
1. **INTRODUCTION**

Diluted magnetic semiconductors (DMS’s) have been considered of tremendous scientific and technological importance.[1–3] This is essentially due to the combination of ferromagnetism with semiconducting properties in the same host material which enable the use of the spin degree of freedom to process, to transfer as well as to store information, giving rise to the emerging field of *Spintronics.*[4]

Among DMS’s materials, ferromagnetic (Ga,Mn)As has attracted considerable attention. Substitution of Mn for Ga in GaAs introduces a local spin $\frac{5}{2}$ magnetic moment, and acts as an acceptor, providing itinerant holes which mediate the ferromagnetic order.[5] An important step toward near future device applications was achieved some years ago, when it was recognized that annealing at temperatures close to the growth temperature can result in an important improvement of the Curie temperature (the highest $T_C$ for the past few years was 110 K). The observed changes have been attributed to out diffusion of Mn interstitials towards the surface.[6] Therefore, it is of great importance for practical applications to clearly understand the role of Mn-dopant in determining the magnetic and electronic properties.

It is clear that the properties of such systems strongly depend on the type and concentration of defects.[6] In this perspective, experimental and theoretical studies of the atomic-scale structure of (Ga,Mn)As are highly motivated.

From the experimental point of view, Mn $\delta$-doped GaAs samples have been recently grown in (001) direction at TASC Laboratory in Trieste.[7] The cleavage of these sam-
ples along the natural (110) cleavage plane yields large automatically flat surfaces with Mn dopants on or close to the exposed surface, thus allowing to study Mn defects environment with surface sensitive techniques.

In this context, *Cross-sectional Scanning Tunnelling Microscopy* (XSTM) is a powerful tool. With the purpose of characterizing the local environments of defects, we have simulated XSTM images for different Mn configurations and compared with available experimental images. We focus our attention here on the impurity interstitial surface configurations.

This paper is organized as follows: in the next section we describe the computational method; in Sect. 3 we present our results for the structural and magnetic properties; in Sect. 4 we discuss the XSTM images; finally, in Sect. 5 we draw our conclusions.

2. COMPUTATIONAL DETAILS

Our calculations have been performed within Density Functional Theory (DFT) framework in the Local Density Approximation for the exchange-correlation functional[8, 9], using state-of-the-art first-principles pseudopotential self-consistent calculations, as implemented in the ESPRESSO/PWscf code[10]. Ultrasoft (US) pseudopotential (PP)[11] has been used for Mn atom, while norm-conserving PPs have been used for Ga, As and H atoms. Test calculations have shown that a kinetic energy cutoff for the wave functions equal to 22 Ry and a 200 Ry cutoff for the charge density are sufficient to get well converged results. We estimate the numerical uncertainty to be $\sim 0.001$
nm for relative atomic displacements and $\sim 0.01 \mu_B$ for the magnetic moments. The relaxed internal atomic positions have been obtained by total-energy and atomic-force minimization using the Hellmann-Feynman theorem.[12]

We model the surface using the supercell approach, with periodically repeated cell containing one Mn atom; a (110) slab geometry with a $4\times4$ in-plane periodicity has been used. The simulation cells are made up of 5 atomic layers and a vacuum region equivalent to 8 atomic layers. The bottom layer has been passivated with Hydrogen atoms. Only the three uppermost layer are allowed to relax, while the others are kept fixed. Two different configurations have been considered for Mn on the surface, namely Int$_{Ga(As)}$ (see next Section). In each case, the distances between the Mn atom and its periodic image on the (110) plane are 1.57 nm along the [1\bar{1}0] and 2.22 nm along [001]: test calculations demonstrate that the supercell is large enough to neglect the Mn-Mn interactions.

XSTM images are simulated using the model of Tersoff-Hamann[13, 14], where a point-like tip is assumed and the tunneling current is derived from the local density of states at the Fermi energy, $E_f$. Within this approximated model, the constant current STM images are simulated from electronic structure calculations by considering surfaces of constant local density of states integrated over an energy window from $E_f$ to $E_f+V$, where $V$ is the voltage applied between the sample and the tip. In this model the tip near the surface does not influence the electronic states.
3. **STRUCTURAL AND MAGNETIC PROPERTIES**

1. **Structural properties**

The GaAs(110) relaxed structure is well known from experimental as well as theoretical point of view. In the relaxed surface, the electronic charge is transferred from Ga to As atoms with the occupied state density being localized around surface As atoms and the unoccupied density around the Ga atoms.[15] This charge transfer is accompanied by an approximately bond-length-conserving rotation with As atoms moving upward and Ga atoms moving downward, still preserving the $1 \times 1$ bulk periodicity. Due to overbinding in the LDA approximation, our theoretical GaAs lattice constant (0.555 nm) is smaller than the experimental one (0.565 nm) but the relevant calculated structural parameters for the clean surface such as $\Delta_{1,\perp}$ (relative displacement of the anion and cation positions in the uppermost layer, normal to the surface) and $\alpha$ (the buckling angle) are 0.068 nm and 30.36° respectively, which well compare with the experimental values 0.065 nm and 27.4°.[16] The clean surface remains semiconducting with a calculated energy gap $\sim$ 0.72 eV.

Throughout this work, we have considered only *tetrahedral* interstitial position, as the total energy corresponding to the *hexagonal* interstitial one is higher by more than 0.5 eV.[6, 17, 18] In the bulk zinc-blende crystal structure, there are two inequivalent tetrahedral interstitial position which differ in the local environment. We call them Int$_{Ga(As)}$, to denote that Mn is surrounded by four Ga(As) atoms. The tetrahedral interstitial positions
in the ideal geometry is equidistant from its four nearest-neighbor (NN) atoms with a distance equal to the ideal host bond length $d_1$. There are six next-nearest-neighbor (NNN) atoms at the distance $d_2 = \frac{2}{\sqrt{3}}d_1$, which are As(Ga) atoms for Int$_{Ga(As)}$, respectively.

At surface, the tetrahedral interstitial position has three NNs and four NNNs instead of four and six respectively as in the bulk case. To start with, we consider the clean and relaxed GaAs(110) surface with the Mn position such that the NN bond lengths are all equal. This configuration will be referred to as initial in the following. Due to symmetry breaking because of the surface and the consequent buckling of the outermost surface layers, the NNN bond lengths are no longer equal.

After relaxations, the two configurations, Int$_{Ga}$ and Int$_{As}$, are almost degenerate, differing by $\sim 130$ meV/Mn atom (Int$_{Ga}$ is favoured).

In Fig.1 we show a ball and stick side (a) and top (b) view of the relaxed Int$_{Ga}$ and Int$_{As}$ configurations. Only the three topmost layers and the atoms closest to Mn are shown. Grey spheres are cations (Ga atoms), white spheres are anions (As atoms); Mn is explicitly indicated. It is easy to see that the presence of Mn strongly reduces the surface buckling. In Fig.1b, atomic moments are also indicated for atoms close to Mn and the numbers in parenthesis specify the atomic layer from the surface. To characterize the relaxed configurations, in Table I we report the NN and NNN bond lengths in the relaxed and initial (in square brackets) configurations. The atomic types are in round brackets and 1$^{st}$ and 2$^{nd}$ denote the two uppermost layers.

For Int$_{Ga}$, the two surface Mn-Ga bonds increase by $\sim 4.6 \%$, from 0.237 to 0.248 nm, whereas the backbond to the Ga atom in the layer beneath increase by $\sim 8.0 \%$ (from
0.237 to 0.256 nm). The NNN bond-lengths relaxations are less pronounced with elongations of about ~2-5 %. In the other configuration, the two surface bonds between Mn and As elongate by 2.2 % from 0.247 nm to 0.252 nm whereas the bond with subsurface As shrinks by 1.2 % (from 0.247 nm to 0.244 nm). The relaxations leave almost unchanged the NNN bond lengths when Ga atom belongs to 2nd layer whereas the surface interatomic Mn–Ga distance is strongly reduced with respect to the initial one. From Fig. 1a, we see that small relaxations effects are still present in the third layer, in both configurations.

In conclusion, the largest local distortions with respect to the clean surface occur in the Int\text{Ga} configuration resulting in a remarkable repulsion of the NNs and NNNs whereas, in Int\text{As}, the lattice relaxations around the Mn impurity involve mainly the NNN Ga atom on surface.

2. Magnetic properties

In the following, we analyze the magnetic properties for the two configurations. In Fig.1b (top views), we report the spin-polarizations for Mn and for the NN and NNN atoms. The highest value of Mn spin-polarization is found in Int\text{As}, with μ\text{Mn}=3.96 μ\text{B}. In the other configuration, the Mn magnetic moment is 3.67 μ\text{B}. From the angular-momentum, spin- decomposed charge, one recognizes that the Mn magnetic moment mostly derives from d polarization while the s-Mn states are only slightly polarized with 0.07(0.05) μ\text{B} for Int\text{Ga(As)}. The total and absolute magnetization in the supercell are different in both cases. This corresponds to the presence of antiferromagnetic regions coupled to Mn. The
total and absolute magnetization are 3.41(4.23) and 4.71(4.84) µB for \text{Int}_{Ga(As)} respectively thus suggesting that the region of negative magnetization should be larger in \text{Int}_{Ga} respect to \text{Int}_{As}.

Let us focus on \text{Int}_{Ga} configuration. The two surface Ga NN of Mn have an induced polarization opposite to Mn magnetic moment, equal to -0.17 µB, mostly due \(p\) polarization (induced through hybridization with \(d\) states); the other Ga atoms have a negligible polarization. The induced polarization on surface As atoms are negligible, while it is equal to 0.05 µB for the atom on the 2\text{nd} layer.

For \text{Int}_{As}, the NN As atoms show a ferromagnetic coupling with Mn (see Fig.1b), with a magnetic moment equal to 0.05 µB. The induced polarization in more distant As atoms is strongly reduced although non negligible up to the fourth-layer As atom. When considering the Ga atoms around the Mn, we see an antiferromagnetic coupling between Mn and surface Ga atom, with an enhanced polarization compared to As (the Ga moment is 0.14 µB). The polarization on the other closest Ga atoms is negligible.

Our results for the magnetic properties can be summarized as follows: in both cases, the surface Ga atom(s) close to Mn are coupled antiferromagnetically, whereas those subsurface have negligible spin-polarization; the As atoms are in all cases coupled ferromagnetically to Mn, with spin-polarization on the surface as well as on subsurface atoms.
4. **STM IMAGES**

We show the schematic front and side views of the relaxed underlying structure lattice and the XSTM images, with the actual size ($\approx 2.2 \text{ nm} \times 1.6 \text{ nm}$) of the supercell used in the simulations, at negative and positive bias voltages (from $V = -2.0 \text{ V}$ to $+2.0 \text{ V}$).

In the simulated images, the $E_f$ is near the Valence Band Maximum (VBM), in order to simulate the experimental conditions of $p$-doped samples.[7]

1. **Isolated Mn Interstitial ($\text{Int}_{\text{Ga}}$)**

In Fig. 2, we show the simulated STM images for the isolated Mn in the $\text{Int}_{\text{Ga}}$ relaxed configuration. A dark region appears around Mn atom at filled states. At positive bias voltages, the two NN surface Ga atoms of Mn appear very bright with features extending towards the Mn and the atoms in the neighbourhood also looking brighter than normal. These features change a little bit according to the specific positive bias applied, but do not disappear.
2. Isolated Mn Interstitial (Int$_{As}$)

In Fig.3, we show the simulated XSTM images for Mn in Int$_{As}$ configuration. At negative bias Mn appears as an additional bright spot close to its neighbouring surface As atoms. If we change V from -1 to -2 V this feature remains but it is attenuated. A very bright elongated spot in the center of the surface unit cell delimited by As is visible at positive bias voltage which is contributed mainly by Mn atoms, specifically by Mn 3d spin-up electron and surface Ga empty states. When we increase the bias voltage to 2 V, the interstitial Mn atom still appears brighter. For this case, the simulated XSTM images show common features with the experimental images.[7]

5. CONCLUSION

In summary, we have used first-principles simulations to characterize Mn interstitial impurity on the GaAs(110) surface. From total energy calculation, Int$_{Ga}$ and Int$_{As}$ are almost degenerate in energy. Strong local distortions on the (110) GaAs surface are introduced by Mn, especially when it is surrounded by Ga atoms. Small relaxations effects are found up to the third sub-surface layer. In both case, Mn polarizes the NN and NNN atoms, giving rise to a ferromagnetic Mn–As and to an antiferromagnetic Mn–Ga configuration. Comparison of simulated XSTM images with experimental ones preliminary available seem to indicate an Int$_{As}$ configuration in the experimental samples.
6. ACKNOWLEDGMENTS

The authors would like to thank S. Modesti and D. Furlanetto for fruitful discussions. Computational resources have been obtained partly within the “Iniziativa Trasversale di Calcolo Parallelo” of the Italian *Istituto Nazionale per la Fisica della Materia* (INFM) and partly within the agreement between the University of Trieste and the Consorzio Interuniversitario CINECA (Italy).

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FIG. 1: Schematic side (a) and top (b) views of the relaxed Int$_{Ga}$ (left) and Int$_{As}$ (right) configurations. Only the three topmost layers are shown. Grey spheres are cations (Ga atoms), white spheres are anion (As atoms), Mn is explicitly shown. Atomic moments for atoms close to Mn are shown in the top views (b) and the numbers in brackets specify also the atomic layer, when not evident. Units are in $\mu_B$. 
FIG. 2: Simulated STM images of isolated Mn interstitial in GaAs(110) surface, with Ga NNs (Int\textsubscript{Ga}). Top panel: ball and stick model of the relaxed surface, top and side view (Ga: empty circle, As: filled circle, Mn: square). Bottom panels: simulated STM images at occupied states and empty states respectively, for different bias voltages.
FIG. 3: Simulated STM images of isolated Mn interstitial in GaAs(110) surface, with As NNs: (Int$_{As}$ in the text). See caption of Fig. 2 other details.
TABLE I: Nearest-neighbor (NN) and next-nearest neighbor (NNN) bond-lengths for relaxed Int$_{Ga}$ (upper part) and Int$_{As}$ (lower part); 1$^{st}$ and 2$^{nd}$ refer to the atomic layer from the surface and the kind of atoms bonded to Mn (See Fig. 1) are in round brackets; the numbers in square brackets refer to initial bond lengths (see text). Units are in nm.
|                | NN(nm) | NNN(nm) |
|----------------|--------|---------|
| **Int\textsubscript{Ga}** |        |         |
| 1\textsuperscript{st}(Ga) | 0.248[0.237] | 0.255[0.237] |
| 2\textsuperscript{nd}(Ga) | 0.263[0.254] | 0.268[0.257] |
| 1\textsuperscript{st}(As) | 0.252[0.247] | 0.244[0.247] |
| 2\textsuperscript{nd}(As) | 0.249[0.298] | 0.290[0.291] |

| **Int\textsubscript{As}** |        |         |
| 1\textsuperscript{st}(As) | 0.248[0.237] | 0.255[0.237] |
| 2\textsuperscript{nd}(As) | 0.263[0.254] | 0.268[0.257] |
| 1\textsuperscript{st}(Ga) | 0.252[0.247] | 0.244[0.247] |
| 2\textsuperscript{nd}(Ga) | 0.249[0.298] | 0.290[0.291] |
Fig. 1
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