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Formation of ferromagnetic/ferrimagnetic epitaxial interfaces: Stability and magnetic properties

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ABSTRACT

We have studied the formation of epitaxial ferromagnetic/ferrimagnetic MnGa(0 0 1)/Mn_4N(0 0 1) heterostructures by using spin polarized first principles calculations. In particular, we have analyzed the stability of the surface and interface as function of the N content. Since the Mn_4N(0 0 1) has two stable surface terminations with a (1×1) periodicity, we have used them as substrates to grow MnGa. The interface formation energy formalism has been applied to describe the stability of all proposed models. Our calculations show that Mn at the interface is energetically favorable. Moreover, stability of the MnGa surface has a direct nitrogen dependence. Specifically, without extra N, the Ga-terminated surface is stable in the whole range of chemical potential for both substrates. Once N is added to the surface, the MnN-terminated surface becomes stable in both substrates for different ranges of chemical potential. Although MnGa and Mn_4N are not antiferromagnetic materials, they form a local antiferromagnetic-like arrangement at the interface. This thermodynamically stable system could have potential applications in the construction of new generation spintronic devices.

1. Introduction

Magnetic heterojunctions have caught the interest of the scientific community in recent years. This is in part due to the amazing physical effects that may appear at the interface between a magnetic and a semiconductor material or between two magnetic materials [1,2] as well as their potential applications in the spintronic industry. Different kinds of heterojunctions can be formed combining semiconductors and magnetic materials which may serve, for example, as spin injectors [3], and photocatalytic devices [4]. Also, different magnetic materials can be joined together resulting in new interesting properties. As example: Fe_3O_4/Ni heterojunctions show a spin-valve magnetoresistance effect [5], tera-hertz spin current pulses are controlled by using Fe/Ru magnetic heterostructures [6]. Furthermore, junctions formed by ferrimagnetic iron oxide with bi-magnetic cobalt display exchange bias and thermal stability, those physical effects may be applied to construct random-access magnetic recording devices [7]. Also, an exchange bias effect appears in ferromagnetic/antiferromagnetic/ferromagnetic arrangements [8,9]. In order to construct and understand the magnetic properties of such interesting heterostructures, it is indispensable to have a good knowledge of the substrate, deposited film, and their interface as well as the thermodynamic stability of the full junction considering real growth conditions.

A very interesting system that has not received the deserved attention is the Mn_4N(0 0 1) surface. This surface presents perpendicular magnetic anisotropy [10]. Such effect has been proposed as a key factor in the construction of magnetic random-access memories [11]. Experimental reports show that Mn_4N grows in the (0 0 1) direction, showing a Mn-N terminated 1×1 surface [12]. Moreover, we have demonstrated, by means of spin-polarized first principles calculations, that the $Mn_4N(0\,0\,1) - 1 \times 1$ surface may be MnN (Mn-rich conditions) and MnN + N (N-rich conditions) terminated [13].

On the other hand, the MnGa alloy is a well-known ferromagnetic material with intriguing properties and a rich variety of surface reconstructions for different growth directions. It is possible to create ferromagnetic surfaces with 1×1 and 2×2 periodicities, and with magnetic moments that are highly dependent on the flux ratio [14]. Also, Mandru et al. [15] have demonstrated the heteroepitaxial growth of 1×2 and 2×2 surfaces on GaN substrates, making emphasis in the control of their magnetic properties through surface structure [15]. Moreover, it has been found that the magnetic properties of MnGa strongly depend on the substrate on which it is deposited: being ferromagnetic, hard

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ferrimagnetic, soft ferrimagnetic, and even non-magnetic [16,17]. Recently, it has been reported a highly unexpected perpendicular giant magnetic anisotropy induced by reduction of the films size [16]. This magnetic anisotropy can be tailored by the right choice of substrate [18].

Taking into account that both Mn_4N and MnGa present magnetic anisotropy, it is interesting to study their interface. In particular, to describe the energetically favorable atomic arrangements and to explain their possible intriguing physical properties. Since, as discussed before, MnGa has the ability to adjust its magnetic behavior as function of the substrate on which it is deposited, it is interesting to study its growth behavior on ferrimagnetic Mn_4N substrates. The lattice mismatch of the two structures is about 1% in the (0 0 1) growth direction, meaning that epitaxial growth is viable. Also, these interfaces may be used as part of magnetic tunnel junctions, which are key in the construction of magnetic random access memories and magnetic storage devices. Corbett [19] has experimentally obtained and characterized similar $MnGa/Mn_3N_2$ interfaces by a combination of reflection high-energy electron diffraction and scanning tunneling microscopy measurements. Therefore, we report on first principles total energy calculations to describe the thermodynamic stability of the $MnGa/Mn_4N$ interfaces and their magnetic arrangements. Our paper is organized as follows: in Section 2 we describe the computational procedure, in Section 3 we describe our findings and finally in Section 4 we make conclusions.

2. Computational methods

Spin-polarized first principles total energy calculations have been applied to describe the stability and the structural and magnetic properties of the non-strained MnGa(0 0 1)/Mn_4N(0 0 1) heterostructures. All the calculations were carried out using the density functional theory, as implemented in the PWscf code of the Quantum ESPRESSO package [20]. To approximate the exchange and correlation energy, we have used the generalized gradient with the Perdew-Burke-Ernzerhof parametrization [21]. The electron-ion interactions have been approached by using Vanderbilt ultra-soft pseudopotentials [22]. Plane waves were used in order to expand the Kohn-Sham electronic states. The cutoff radii for the kinetic energy and charge density were set to 30 Ry and 240 Ry, respectively. An equally spaced k-points grid of $6 \times 6 \times 1$ has been employed to sample the Brillouin zone [23]. Additionally, for the structure and magnetic alignments optimization, energetic convergence was achieved when total energy differences were less than 0.0001 Ry.

To construct the interface models, we have used the surface terminations reported in Ref. [24] for MnGa(0 0 1) and in Ref. [13] for Mn_4N(0 0 1). There are two stable Mn_4N(0 0 1) – (1×1) surfaces: a MnN ideally terminated (for Mn rich conditions) and a MnN + N, completing a full N monolayer at the surface (for N rich conditions) [13]. In the absence of nitrogen, the MnGa(0 0 1) – (1×1) is terminated in a Ga layer [24] as found also experimentally in Ref. [25]. In the presence of N, a MnN terminated structure is more stable than the Ga terminated surface [24]. Since the lattice parameters of MnGa and Mn_4N differ by less than 1%, the interfaces are not under strain. The lattice parameter of the substrate is 3.84 Å, which corresponds to a (1×1) periodicity of Mn_4N. For the calculations we have used slabs with (1×1) in-plane periodicity, and having inversion symmetry. Then, we have two equivalent surfaces (one at each side of the slab) which are separated by an empty space of ~15 Å. The vacuum space is large enough to avoid undesirable interactions between the slab and its equivalent image generated by the virtual periodicity induced along the perpendicular direction.

3. Results

3.1. Interface formation energy formalism

To describe the interface surface formation energy (ISFE), we have combined the formalisms of Refs. [26–29]. In our case we have taken advantage of the slab inversion symmetry, and two equivalent interfaces are formed. From Fig. 1(a) we can see a schematic picture of the individual surfaces which form the interface. There are four equivalent MnGa surfaces with formation energy Ω^f_{MnGa}, and two Mn_4N surfaces with formation energy equal to $\Omega^f_{Mn_4N}$. To set the interfaces, we put together the three sections, as seen in Fig. 1(b). After that, two equivalent interfaces appear, having an interface formation energy Λ^f_{MnGa/Mn_4N}. Also, the effect of the MnGa surface in each side (with surface formation energy Ω^f_{MnGa}) must be considered to correctly describe the stability of the system. The total energy of the system is defined as:

$$E^{slab}_{MnGa/Mn_4N} = 3n_{Mn}\mu_{Mn} + 2n_{Ga}\mu_{Ga} + n_N\mu_N + 2A\Omega^f_{MnGa} + 2A\Lambda^f_{MnGa/Mn_4N} \quad (1)$$

where n_i and μ_i are the number of atoms of the ith species and the chemical potentials of each ith species per surface, respectively, and A is the surface and interface area in Å^2. Moreover, the total energies of the surfaces are:

$$E^{slab}_{Mn_4N} = n_{Mn}\mu_{Mn} + n_N\mu_N + 2A\Omega^f_{Mn_4N}, \quad (2)$$

and

$$E^{slab}_{MnGa} = n_{Mn}\mu_{Mn} + n_{Ga}\mu_{Ga} + 2A\Omega^f_{MnGa}, \quad (3)$$

from them, we can write:

$$\Delta E^{slab} = E^{slab}_{MnGa/Mn_4N} - 2E^{slab}_{MnGa} - E^{slab}_{Mn_4N}. \quad (4)$$

Then, the interface formation energy can be defined as:

$$\Lambda^f_{MnGa/Mn_4N} = \frac{\Delta E^{slab}}{2A} + \Omega^f_{MnGa} + \Omega^f_{Mn_4N} \quad (5)$$

By writing $\Omega^f_{Mn_4N}$ and Ω^f_{MnGa} as function of $\Delta\mu_1 = 4\mu_{Mn} - \mu_N$ and $\Delta\mu_2 = \mu_{Mn} - \mu_{Ga}$ [13,24], respectively, the ISFE takes the following form:

$$\Lambda^f_{MnGa/Mn_4N} = \frac{\Delta E^{slab}}{2A} + \frac{1}{2A}\left\{E^{slab}_{Mn_4N} - \frac{1}{2}\left(\frac{1}{4}n_{Mn} + n_N\right)\mu^{bulk}_{Mn_4N} - \frac{1}{2}\left(\frac{1}{4}n_{Mn} - n_N\right)\Delta\mu_1\right\} + \frac{1}{2A}\left\{E^{slab}_{MnGa} - \frac{1}{2}(n_{Mn} + n_{Ga})\mu^{bulk}_{MnGa} - \frac{1}{2}(n_{Mn} - n_{Ga})\Delta\mu_2\right\} \quad (6)$$

The allowed range of chemical potential for the ISFE (6) is defined by the formation enthalpies of the most stable bulk structures ($\Delta H^f_{Mn_4N} = 1.25$ eV and $\Delta H^f_{MnGa} = 0.41$ eV), then, $-\Delta H^f_{Mn_4N} \leqslant \Delta\mu_1 \leqslant +\Delta H^f_{Mn_4N}$ and $-\Delta H^f_{MnGa} \leqslant \Delta\mu_2 \leqslant +\Delta H^f_{MnGa}$. The lower limits define N-rich and Ga-rich conditions, respectively, and the upper limits correspond to Mn-rich conditions in each case. The ISFEs are plotted as bi-linear (three dimensional planes) functions of the Mn-Ga and Mn-N chemical potential differences.

3.2. Thermodynamic stability analysis

We have chosen the following proposed interface models: I_n which describes the heterojunction of MnGa with the MnN-terminated Mn_4N surface and I_{nN} which defines the interfaces