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Theoretical investigation of Mn adsorbates aside self-organised Bi nanolines on hydrogenated Si(001) surface

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ABSTRACT

We have theoretically investigated the atomic structure, magnetic behaviour, and electronic properties of Mn adsorbates on hydrogen passivated self-organised Bi nanolines on the Si(001)surface. It is found that the most stable geometry for $\frac{1}{6}$ monolayer (ML) coverage of Mn is just underneath the first Si(001) surface layer. The Mn atoms in the optimised configuration are seven-fold coordinated with their neighbouring Si atoms. Total energy calculations suggest that the Mn adsorbates form a degenerate state of ferromagnetic and anti-ferromagnetic lines parallel and adjacent to the self-assembled Bi lines. The density functional band structure calculation within the local-spin density approximation shows that the ferromagnetic system behaves like a metal in both spin channels. On the other side, the anti-ferromagnetic phase exhibits a half-metallic phenomenon with semiconducting character for the majority spin channel and semi-metallic character for the minority spin channel.

1. Introduction

Dilute magnetic semiconductor (DMS) materials have been known for a long time as the gate for great industrial applications and semiconductor technologies. Recently, the magnetoelectronics or spin electronics (spintronics) has opened the possibility for fabricating up-to-date unique type of multi-functional devices [1–3]. Use of both the charge and spin of the electron is expected to provide an opportunity of creating a remarkable new generation of microelectronic devices which might be used for processing and information storage. Technologically, it is most desirable to use transition metals and silicon surfaces in building up heterostructures [4]. Experimentally, this can be done by either using a ferromagnetic thin film as a coating layer or depositing ferromagnetic metals on the silicon surface. It is found that the latter is more energetically favoured due to the strong coupling between the silicon atoms and the transition metals.

Several works have examined the possibility of developing magnetoelectronics using silicide films involving transition metals such as Fe, Co, and Ni [5]. However, such silicides are known to be either weakly magnetic or non-magnetic, and thus not expected to be useful for spintronics applications. On the other hand, it is found that Mn silicide displays a considerably better magnetic behaviour [2,3]. In fact, it has also been reported that the ferromagnetic phase with a Curie temperature above room temperature can be created by Mn ion implantation into Si [6]. Various experimental and theoretical studies have been devoted to investigate progressive changes in the atomic geometry and electronic structure of the Si(001) surface upon Mn adsorption. Detailed calculations of the electronic properties and magnetic moments of Mn adatoms have indicated the possibility of achieving ferromagnetic semiconductor Si(001) surfaces [7–9]. Experimental studies have demonstrated that the deposition of Mn atoms on clean Si(001) surfaces leads to the possibility of growing super doped Si:Mn thin films [10]. Very recently, Liu and Reinke [11] have studied the formation of Mn nanostructures on the Si(001)-(2 × 1) surface using scanning tunnelling microscope (STM) as a function of Mn coverage. They have concluded that Mn wire formation dominates at low coverages. It has been also reported that some Heusler alloys, such as Co_2MnX (X = Si, Ge or Sn) are ferromagnets [12] and would have the capability of providing spin polarised carriers for spintronics usage [13]. In Heusler half metals, the density of states near Fermi level is finite only for one spin channel. This is in marked contrast to usual ferromagnetic metals for which both spin channels contribute at the Fermi level. The polarisation-dependent behaviour of carriers in Heusler alloys has led to studies of the adsorption of Mn atoms on the Si(100) surface [8].

Self-assembled atomic arrangements on semiconductor surfaces have been the subject of intense experimental and theoretical investigations. Bi nanolines on the Si(001) surface, in particular, have received a great deal of attention. Long, straight, kink- and defect-free Bi nanolines can be formed by annealing the Bi-covered Si(001) surface at around the Bi desorption temperature (at about

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580 °C). Up to date, there have been three different proposals for the geometry of the Bi nanolines on the Si(001) surfaces. From careful investigations of STM images, Miki et al. [14] reported that two parallel Bi dimers form the a line with a missing dimer row between them (known as the Miki model). Naitoh et al. [15] (Naitoh model), on the other hand, suggested that the Bi lines are formed by two parallel and adjacent Bi dimers substituting for four Si dimers, with a missing dimer row next to each Bi dimer. From a detailed theoretical study, Owen et al. [16,17] proposed the Haiku model, demonstrating that the Bi dimers are separated by a missing Si dimer line and the Si substrate below the Bi lines is heavily reconstructed, forming fivefold and sevenfold Si rings. In this model the Bi nanolines are 1.5 nm wide. Total energy calculations indicate that the Haiku model represents the energetically most favourable configuration for Bi nanolines on the Si(001) clean surface [16,17] as well as on the hydrogen passivated Si(001) surface [18,19].

Although Bi nanolines on Si(001) do not exhibit any useful electronic or optical properties, these provide an excellent template for generating more interesting and useful nanostructures. Several experimental and theoretical studies have been reported on the formation of self-organised species on the Bi nanoline template. The adsorption of group-III elements (such as In, Al, etc.) and nobel metals (like Au, Ag, etc.) provide examples of such a system. In particular, it has recently been found that the formation of In-line structure or In-cluster structure can be fabricated by adsorption of In adatoms on the Bi nanoline template [20,21]. In these investigations the formation of In cluster in the vacancy site between the Bi dimers is energetically more preferable configuration. Moreover, Owen and Miki [22] and Koga et al. [23] have reported on the fabrication of a line structure of Ag atoms on the Bi nanolines. The adsorption and growth of group-IV elements (such as Ge) along the Bi nanolines template has also been theoretically investigated [24]. In that study, it was concluded that Ge atoms form mixed dimers with the Si atoms aside the Bi nanolines. In a more recent work, Orellana et al. [25,26] have presented a theoretical study of the adsorption of various sub-monolayer coverages of Fe atoms along the self-organised Bi nanolines on a hydrogenated Si(001) surface. They addressed the equilibrium adsorption sites and bonding of Fe adatoms with the Si substrate and the Bi nanolines. They reported that for 1/4 and 1/2 monolayer (ML) coverages neighbouring Fe adatoms are coupled together anti-ferromagnetically or non-magnetically with equal binding energy. For these low coverages, Fe was concluded to form line structures. Further work is desirable for examining structural formation, electronic structure, and development of magnetic properties with adsorption of other transition metal atoms on the Bi nanoline template.

In the present work, we attempt to report an ab initio theoretical investigation on the electronic and magnetic properties of the Bi nanoline template upon the adsorption of 1/6 ML of Mn atoms. Information about the energetic stability and equilibrium geometry are detailed within the local-spin density approximation of the density functional theory. The magnetic properties of the system is determined in terms of the magnetic moment. Furthermore, the electronic properties have been investigated by examining the electronic band structure and charge density. We discuss similarity and dissimilarity of the results for Mn adsorption with Fe adsorption.

2. Theoretical method

We have modelled the system by using a repeated supercell structure [27]. Each unit cell is based on a (2×6) reconstructed Si(001) surface mesh and contains ten silicon layers, bismuth layer, and a vacuum region equivalent to about four substrate layers in thickness. This corresponds to the Mn surface coverage of 1/6 monolayers (ML). The back surface of the slab was saturated with two pseudo-hydrogen atoms per Si atom. The dangling bonds of the upper Si atoms were also saturated by hydrogen atoms. In this work we consider the Haiku model [16–18] for the Bi nanolines on the hydrogenated Si(001) surface. This requires considering a large reconstructed surface mesh.

Experimental investigations (see e.g., [11]) suggest that the deposition of Mn on Si(001) can result in the formation of different types of structures, such as line, islands, and clusters. These observations, as well as observations made on the adsorption of atoms of non-transition metals [20–22], indicate that adsorption of transition metal adsorbates on the Bi nanoline template may lead to alloying between the metal adsorbate and the Bi atoms. However, this is less likely to happen for the sub-monolayer coverage (1/6 ML) of Mn considered in this work.

Previous theoretical investigations, based on ab initio calculations, [3] have concluded that, for a given coverage, transition metals such as Mn, Fe, Co, and Ni all occupy similar adsorption sites on the Si(001) surface. This work also concludes that for a sub-monolayer coverage of 0.5 ML, transition metal adsorbates occupy the interstitial site below the top Si atomic layer with a lower formation energy than above the top surface layer. Guided by that work, as well as more recent works [25,26], we have examined several trial adsorption sites for the 1/6 ML coverage of Mn adatoms, and the results are discussed for the most stable geometry.

The results of all calculations presented in this paper are obtained by using the density functional theory [28] in its local-spin density approximation (DFT–LSDA). The Ceperley-Alder exchange-correlation scheme [29] is considered in the form parametrised by Perdew and Zunger [30]. The electron-ion interactions were treated by using the norm-conserving [32] and fully separable pseudopotentials [31]. The single-particle Kohn-Sham [33] wave functions were expanded in the framework of a plane wave basis set with a kinetic energy cutoff of 25 Ryd. Throughout the calculations we use the calculated Si equilibrium lattice constant of 5.39 Å, which is slightly smaller than the measured value of 5.43 Å. Self-consistent solutions of the Kohn-Sham equations were obtained by employing a $4 \times 2 \times 1$ **k**-points (viz four special **k**-points) Monkhorst-Pack set [34] within the surface Brillouin zone. The Hellmann-Feynmann forces on ions were calculated and minimised to obtain the relaxed atomic geometry. The equilibrium atomic positions were determined by relaxing all atoms in the unit cell except the bottom Si-layer which was frozen into its bulk position.

Energy convergence with respect to cell size, energy cut-off, and **k**-points was tested for bulk Mn (fcc structure) as well as for one of the Mn adsorption sites on the surface. Calculations for bulk Mn produce reasonably well converged results for the equilibrium lattice constant and magnetic moment for 25 Ryd energy cut-off. The (2×6) reconstructed Si(001) surface mesh was found to be the minimum acceptable size from energetics point of view. Increasing the cell size to (2×7) and (2×8) decreases the total energy, respectively, by 0.01 and 0.02 eV/(2×1) unit cell. Similarly, the choice of four special **k**-points for self-consistent calculation of charge density is also found to be quite acceptable, as consideration of eight special **k**-points only decreases the total energy by 0.08 eV/(2×6) cell. Increasing the energy cut-off from 25 Ryd to 30 Ryd decreases the total energy by only 0.01 eV/(2×6) cell. It is well documented in several previous publications that energy differences between two competing structures converge much faster than do the total energies for individual structures. The FM and AFM states were theoretically prepared by assigning suitable initial magnetic moment values at the Mn sites. For the FM case, we assigned magnetic moments of +0.7 μ_B at each of the two Mn sites within the unit cell. For the AFM case, we assigned magnetic