Fe adatoms along Bi nanolines on H/Si(001)

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The stability and electronic and magnetic properties of Fe atoms adsorbed on the self-assembled Bi-line nanostructure on the H/Si(001) surface are addressed by spin-density functional calculations. Our results show that Fe adatoms are much more stable on sites closer to the Bi nanolines suggesting that they form one-dimensional atomic arrays. The most stable structure occurs on a missing dimer line beside the Bi dimers, which corresponds to an array with distances between Fe adatoms of about 8 Å. In this array the irons are coupled antiferromagnetically with spin magnetic moment of about $1.5\mu_B$ per Fe atom, whereas the coupling exchange interactions is found to be of about 14.4 meV. We also estimate a large magnetic anisotropy energy of 3 meV/at. originated on the structural anisotropy of the Fe-adatom site. In addition, the electronic band structure of the Fe array at the most stable structure shows a magnetic half-metal behavior.

Self-organized nanostructures on surfaces have attracted much attention during the last few years owing to their promising applications in the patterning of low-dimensional magnetic systems. Suitable epitaxial techniques make it possible to build one-dimensional (1D) arrays of $3d$ magnetic atoms by step decoration of metallic substrates, which is currently a very active topic of research in magnetism from both experimental[1–3] and theoretical[4,5] viewpoints. New fundamental physical phenomena, such as magnetic ordering and giant magnetic anisotropy, have been observed in self-assembly 1D arrays of magnetic atoms.[6] Despite the recent interest in magnetic semiconductors, little is known about the spin interactions of magnetic atoms in contact with semiconducting surfaces.

Following up early studies on magnetism in 1D atomic arrays supported on metallic substrates, we explore the possibility that similar magnetic arrays can be constructed by decoration of the Bi-dimer line structure which grows by self-assembly on the Si(001) surface. These lines, obtained by the Bi deposition onto Si(001) above the desorption temperature of 500 °C, consist of two parallel rows of symmetric Bi dimers which are about 0.6 nm apart and can be over 500 nm in length. Additionally, their structures are free of defects such as kinks or breaks, as they have a remarkable straightness.[7–9] Possible template applications require the hydrogen exposure of the Si(001) substrate, since it is more reactive than the Bi line. After hydrogenation only Si atoms are passivated, leaving the Bi lines clean and preserving their 1D structures.[7] Recently, the arrangement of nonmagnetic atoms on the Bi-line structure as well as their use as a template have been experimentally investigated.[10,11] In this letter we study from a theoretical viewpoint the stability and electronic and magnetic properties of Fe atoms adsorbed on the neighborhood of self-assembled Bi lines on H/Si(001) surfaces.

The calculations were performed in the framework of the density functional theory within the local-spin-density approximation (LSDA),[12] considering noncollinear magnetic ordering as implemented in the SIESTA code.[13] The basis set consists of numerical pseudoatomic orbitals, namely, double-ζ plus polarization functions. Standard norm-conserving pseudopotentials in their separable form were used to describe the electron-ion interaction, including nonlinear core correction for Fe and Bi atoms.[14] Currently, two structural models are used to explain the observed self-assembled Bi-dimer lines on clean and hydrogenated Si(001) substrates. These are the Miki[8] and the Haiku[9] structures. We adopt the latter one because it exhibits the highest stability as recently shown by *ab initio* calculations.[15] To simulate the Bi lines in the Haiku model structure we used the repeated slab method within a 2×6 surface unit cell, containing 10 ML of Si atoms plus a vacuum region of about 11 Å. The bottommost Si dangling bonds were saturated by hydrogens. Four special $k_\parallel$ points were used to sample the surface Brillouin zone. The topmost 8 ML were fully relaxed until the force components became smaller than 0.05 eV/Å.

We investigate six adsorption sites for the Fe atom on the Bi-dimer structure formed on the hydrogenated Si(001) substrate (hereafter the clean Bi line), as shown in Fig. 1(a). In the clean Bi line, two parallel Bi dimers align along the [110] direction which are separated by a missing dimer line (MDL). In addition, two adjacent MDLs form beside the Bi dimers. The Bi-dimer bond lengths and the lateral distance between them are found to be 3.15 and 6.36 Å, respectively. Our results for the equilibrium geometry of the clean Bi line is in good agreement with previous plane-wave *ab initio* results.[15]

Figure 1(b) shows the equilibrium geometry for the most stable structure of the Fe adatom at the MDL beside the Bi dimers (C site). We find that the Fe atom tends to increase the number of Fe–Si bonds occupying an interstitial subsurface position, about 0.5 Å below the topmost Si atoms, be-
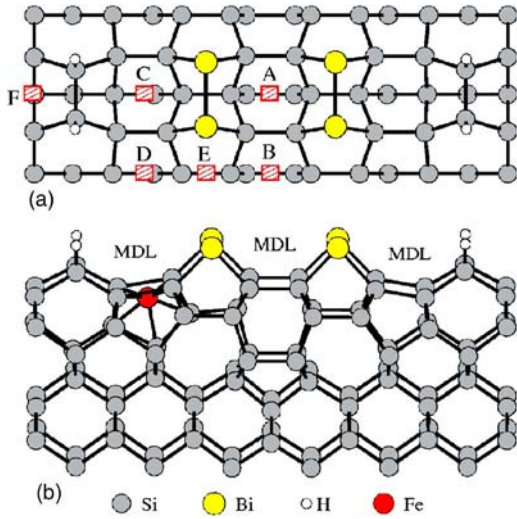
FIG. 1. (Color online) (a) Top view equilibrium geometry for the clean Bi line on H/Si(001). Dashed squares indicate the Fe adsorption sites under consideration. (b) The most stable equilibrium geometry resulting from the Fe adsorption on the site C.
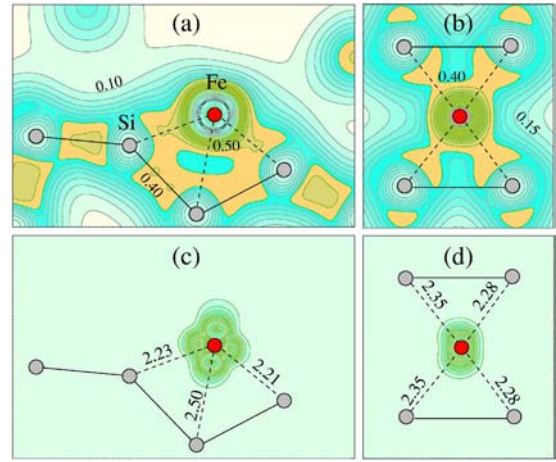

FIG. 2. (Color online) (a) and (b) show total charge density on a plane perpendicular to the Bi dimers passing by the Fe atom, and through a plane passing by the topmost four Si atoms nearest neighbors to the Fe atom, respectively. (c) and (d) show the magnetization through the same planes as (a) and (b). Numbers in the upper panel correspond to the contour charge density in $e/Å^3$, and those of the lower panel correspond to bond lengths in Å.

coming sevenfold coordinated with bond lengths ranging from 2.2 to 2.5 Å. Similar coordination numbers are found for the Fe adsorption on the other sites. The binding energy of the Fe adatom on the C site is found to be about 6 eV. These results somewhat mimic the B20 phase of iron silicide FeSi. The Fe atoms in FeSi (B20) have seven nearest-neighbor Si atoms, and binding energy of 6.58 eV, obtained by LSDA calculations.[16] Table I shows relative total energies for the Fe adatom at each site. We note that the Fe adatom on sites A, B, and D are close in energy than that of the most stable one. This suggests that the MDLs are the energetically favorable positions for the Fe adsorption. On the other hand, Fe adatom between Bi dimers of the same line and on the hydrogenated Si(001) far from the Bi dimers, sites E and F, respectively, are 0.82 and 1.07 eV higher in energy. At the E site, the Fe adatom breaks the Bi dimers, forming two Fe–Bi bonds with lengths of 2.58 Å and four Fe–Si bonds with lengths of 2.2 and 2.7 Å. This is the only case where the Bi dimers break. We also find that all Fe adatom structures are magnetic with magnetic moment ranging from 1.5 to $2.0\mu_B$ per Fe atom. The above results suggest that the Bi lines would be effective to adsorb Fe atoms, supporting the proposed formation of 1D magnetic arrays. It is important to note that the energetic preference for the adsorption sites A to D indicates that the Bi-line structure would not be destroyed by the Fe adsorption.

TABLE I. Total energy (ΔE) with respect to the most stable structure (C site), binding energy (E_b) of the Fe adatom, and spin magnetic moment (m) of ferromagnetically coupled Fe arrays. CN is the Fe adatom coordination number.

Sites	ΔE (eV)	E_b (eV/Fe)	m (μ_B/Fe)	CN
A	0.134	5.834	1.83	6
B	0.350	5.618	1.63	6
C	0.000	5.968	1.53	7
D	0.120	5.848	1.27	7
E	0.816	5.152	1.99	8
F	1.072	4.896	1.95	7

Figures 2(a) and 2(b) show total charge densities for the Fe adatom site C on planes perpendicular to the Bi dimers passing by the Fe atom, and parallel to the surface passing by the topmost four Si atoms nearest neighbors to Fe, respectively. Here we see that the iron binds with their seven silicon nearest neighbors, forming metallic bonds. Typically, pairs of Fe–Si bonds have the same lengths whereas an extra one is longer, showing a highly anisotropic environment. Similar results are found for the other Fe adsorption sites. High-coordinated Fe adatoms at subsurface have also been verified in several studies addressing the formation of iron silicide thin films on Si(001).[17,18]

The electronic structure of the clean Bi line on H/Si(001) shows that this system is semiconducting with energy gap of about 1 eV. The occupied Bi states lie resonantly close to the top of the valence band, whereas the electronic states attributed to the Si-dimer dangling bonds are suppressed by the hydrogen saturation, opening the gap. Figures 3(a) and 3(b) show the band structure of the Fe adatoms on the Bi lines at the most stable structure for both majority and minority spin channels, respectively. Here, the $\bar{\Gamma}\bar{J}'$ ($\bar{\Gamma}\bar{J}$) direction corresponds to wave vectors parallel (per-
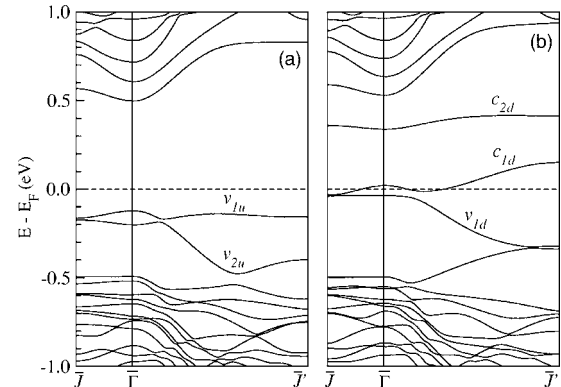

FIG. 3. Electronic band structure for the Fe adatom on the Bi lines at most stable structure. (a) and (b) indicate the majority and minority spin bands, respectively.
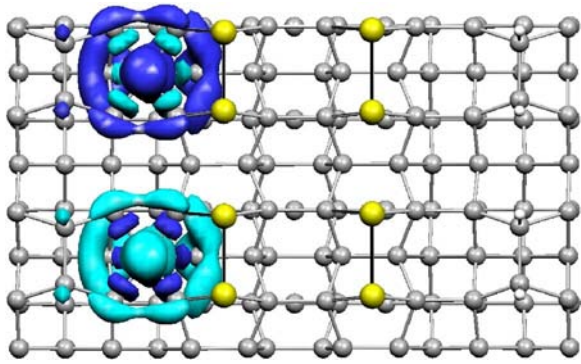
FIG. 4. (Color online) Isosurfaces of the antiferromagnetic magnetization induced by the Fe adatoms along the Bi lines in the most stable structure. The clear (dark) isosurfaces correspond to the majority spin (minority spin) density of +0.004 (−0.004) $e/Å^3$.

pendicular) to the Bi lines. We find that the electronic states v_{1u}, v_{2u}, v_{1d}, and c_{2d} come from the $3d$ orbitals of Fe adatom, with negligible contribution from Si and Bi atoms. We observe that the c_{1d} state gives a semimetallic character in the minority spin channel along the Bi line; however, the majority spin channel behaves as a semiconductor with a band gap of about 0.6 eV. This behavior, known as magnetic half-metals, was initially predicted by band structure calculations in Heusler alloys.[19] Similar magnetic half-metal behavior is found for the Fe adatom at the A site. However, for the Fe adatom at the B and D sites, both spin channels have a metallic character.

Figures 2(c) and 2(d) show contour plots for the net magnetization, defined as $m(\mathbf{r})=\rho_\uparrow(\mathbf{r})-\rho_\downarrow(\mathbf{r})$, where $\rho_\uparrow$ and $\rho_\downarrow$ represents the total charge density for the majority and minority spin channels, respectively. In order to stablish the strength of the magnetic coupling between Fe adatoms (J), we calculate the difference in energy of the ferromagnetic (FM) and antiferromagnetic (AFM) ordering by doubling the supercell size. Our results show that the Fe adatoms at the C site are coupled antiferromagnetically with a weak exchange interaction of $J=14.4$ meV. The presence of nonmagnetic Si substrate intermediating the Fe adatoms suggests a superexchange origin for the AFM coupling. Figure 4 shows isosurfaces of the AFM magnetization calculated within the double supercell scheme. We observe that the Fe adatom polarizes with an opposite spin density the electronic charge between the Si–Fe bonds. Magnetic moments of the ferromagnetically coupled Fe atoms in the different adsorption sites are shown in Table I. We note that the highest magnetizations occur for the configuration E. Here, the Fe adatom binds with the Bi atoms, breaking the dimer. This suggests that the increased magnetizations are due to the polarization of the Bi atoms which contribute with additional electrons when forming the Fe–Bi bonds. For the Fe adsorption on the H-saturated Si dimers, site F, we find a magnetic moment of $1.95\mu_B$ per Fe atom, in close agreement with a previous calculation.[20]

We find that the structural anisotropy of the Fe adatom site induces a magnetic anisotropy which would be originated in the magnetic dipolar interactions. We estimate a lower limit for the magnetic anisotropy energy (MAE) by taking the difference in energy for the magnetization pointing in a direction of low energy (easy axis) toward one of high energy (hard axis). By noncollinear spin calculations we

find that the easy axis occurs at $\theta\approx0°$ and $\theta\approx117°$, whereas the hard axis occurs at $\theta\approx50°$, where θ is the azimuth angle. In both cases, the magnetization vector is parallel to the Bi dimers. We find a very large MAE of about 3 meV/at. without considering spin-orbit contributions, which are not included in the present calculations. Although the orbital moment would be important for the magnetic anisotropy of adatoms on metallic surfaces, for instance, Co adatom on Pt(111),[6] it would be small or even quenched for Fe adatom on the Bi-line structure due to its enhanced coordination, which resembles a bulklike environment.

In summary, we found that the Fe adatoms tend to occupy highly coordinated subsurface positions beside the Bi-dimer lines, forming a magnetic 1D array. At the most stable configuration the Fe array couples antiferromagnetically with a weak exchange coupling of 14.4 meV. We estimate a large magnetic anisotropy energy of about 3 meV/at., originating on the structural anisotropy of the Fe-adatom site. In addition, the electronic band structure of the most stable Fe array shows a magnetic half-metal behavior for the spin channels. Our results suggest possible applications in nanomagnetic devices as well as in spintronics, requiring experimental confirmation.

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