

A theoretical study of Fe adsorption along Bi-nanelines on the H/Si(0 0 1) surface

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Abstract

We have investigated the energetic stability and equilibrium geometry of the adsorption of transition metal Fe atoms near the self-organized Bi lines on hydrogen passivated Si(0 0 1) surface. Our total energy results show that there is an attractive interaction between Fe adatoms along the Bi-nanelines. For the energetically most stable configuration, the Fe adatoms are seven-fold coordinated, occupying the subsurface interstitial sites aside the Bi-nanelines. With increased coverage, Fe atoms are predicted to form two parallel lines, symmetrically on both sides of the Bi line. Within our local spin-density functional calculations, we find that for the most stable geometries the Fe adatoms exhibit an antiferromagnetic coupling.

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1. Introduction

Thin solid films of metal silicide on semiconductor surfaces have been the subject of numerous studies due to their promising technological applications. In particular, iron silicide on silicon surfaces has attracted special attention. The initial stage of Fe adsorption on Si(0 0 1) was examined by Adams et al. [1], through scanning tunneling microscopy (STM) images. Further STM studies observed the formation of self-organized Fe nanowires on H₂O/Si(0 0 1), somewhat reflecting the silicon surface reconstruction [2]. In parallel, motivated by those experimental findings, the energetic stability and the electronic properties of FeSi compounds on silicon surfaces were studied based upon *ab initio* total energy calculations [3–5].

The formation of self-organized structures on semiconductor surfaces can be tailored by the presence of steps or a suitable surface reconstruction. On the other hand, through a self-organization process, Bi-nanelines on Si(0 0 1) provide an excellent example of an one-dimensional system. Although

details of the atomic geometry of the self-organized Bi-nanelines on Si(0 0 1) are rather controversial [6,7], it is generally agreed that these provide an excellent template for generating more interesting and useful nanostructures. For example, adsorption on the Bi-nanoline results in a line structure of In adatoms [8,9] and a nanocluster of Ag atoms [10,11]. Furthermore, very recently we have performed an *ab initio* investigation of Fe adsorption along Bi-nanelines on the hydrogenated Si(0 0 1) surface [12].

In this paper, we present an *ab initio* theoretical study of Fe adsorption along Bi-nanelines on the hydrogenated Si(0 0 1) surface. The energetically most stable configuration is obtained by comparing the Fe adatom binding energies, as a function of Fe coverage along the Bi-nanoline. Within the local spin density approximation (LSDA), we also examine magnetic coupling between the Fe adatoms.

2. Method of calculation

Our calculations were performed in the framework of the density functional theory [13], within the local spin density approximation (LSDA) [14]. The electron–ion interaction was treated by using norm-conserving, *ab initio*, fully separable

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pseudopotentials [15] for silicon, hydrogen and bismuth, and ultrasoft pseudopotential for iron [16]. The surfaces were simulated by using the slab method, with 10 monolayers of Si plus a vacuum region of about 10 Å, and surface periodicity 2×6 . The electronic charge density was calculated using a set of 4 special \mathbf{k} points, and the wave functions were expanded in a plane wave basis up to a kinetic energy of 25 Ry. The eight topmost layers were fully relaxed within a force convergence criterion of 25 meV/Å.

3. Results and discussion

We present results of preliminary investigations of Fe adsorption on the Bi-nanolines on H-terminated Si(0 0 1) surface. We first examined adsorption of Fe on the Si(0 0 1)–(1 × 1) surface for a coverage of half a monolayer in the first and second surface layers at interstitial sites. These sites are shown in Fig. 1(a and b), respectively. We find that the adsorption of Fe adatoms in the subsurface interstitial site, shown in Fig. 1(b), is more stable than the adsorption on the top layer by 0.38 eV/Fe-atom. This result is in agreement with previous *ab initio* calculations [5], where the relative stability is found to be 0.44 eV/Fe-atom.

For the equilibrium geometry, the subsurface interstitial Fe adatom is seven-fold coordinated, with Fe–Si bond lengths between 2.35 and 2.90 Å. It is interesting to note that such a configuration mimics the FeSi (B20) phase of iron-silicide. Within the LSDA, Moroni et al. [3] obtained a binding energy of 6.58 eV for the FeSi (B20) bulk. In this work, for the subsurface interstitial Fe adatom we obtained a similar binding energy of 6.05 eV/Fe-atom.

In Ref. [12] we investigated the electronic and magnetic properties of Fe adatoms patterned by Bi-nanolines on H/Si(0 0 1). We found that the energetically most stable configuration occurs with Fe adatoms lying aside the Bi-nanolines, with

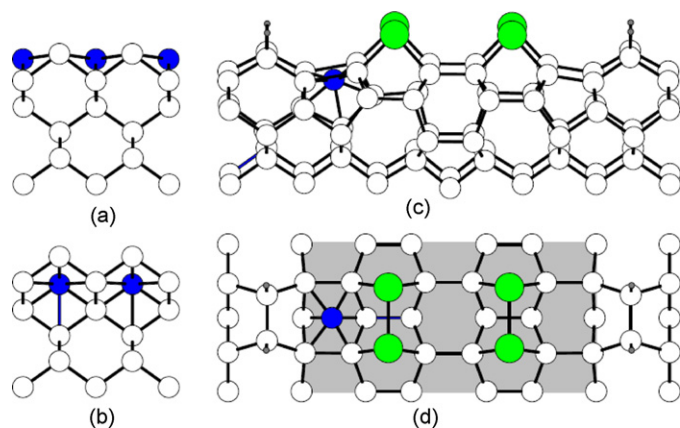


Fig. 1. Structural models for Fe adsorbed Si(0 0 1) surface. (a) On the topmost interstitial sites, (b) on the subsurface interstitial sites. (c) side view and (d) top view of Fe adsorbed Bi-nanolines. The shaded region in (d) represents a 2×8 surface area surrounding the Bi-nanoline. Within this 2×8 surface area we have a Fe coverage 1/8 ML. Silicon (bismuth) atoms are described by white (green) circles, and blue circles represent the Fe adatoms. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

Table 1

Binding energies (E_B), and net magnetization (m) of Fe adatoms along the Bi-nanolines

Structural model	E_B (eV/Fe-atom)	m (μ_B /Fe)
2a	5.79	0.00
2b	5.52	2.01
2c	5.22	1.94
2d	5.21	3.53
2e	5.14	3.42
2f	5.02	3.97
2g	5.73	0.00
2h	5.62	2.10

the top view and a side view depicted in Fig. 1(c and d), respectively. In this case there is one Fe atom within the 2×4 surface area, corresponding to 1/8 monolayer coverage, as indicated by the shaded region in Fig. 1(d). The Fe adatom resides in the subsurface region and is seven-fold coordinated. The calculated binding energy of this adsorption site is 5.31 eV/Fe-atom. We note that this binding energy is lower by 0.7 eV/Fe-atom than the binding energy of Fe on the clean Si(0 0 1)–(1 × 1) surface.

Fig. 2 shows a few plausible structural models for higher coverages of Fe adatoms along the Bi-nanolines: 1/4 monolayers in Fig. 2(a–f), and 1/2 monolayers in Fig. 2(g–h). In these models we assume that the Bi-nanoline structure has been preserved during the Fe adsorption process. Our calculated binding energies, summarized in Table 1, indicate that the Fe adatoms tend to adsorb close to each other. The structure with Fe adatoms lying in the subsurface interstitial sites aside the Bi-nanolines [model 2a in Fig. 2(a)], represents the energetically most stable configuration, with Fe coverage of 1/4 monolayers. The second most stable is the structural model 2g [Fig. 2(g)], corresponding to Fe coverages of 1/2 monolayers. For the 1/2 monolayer coverage in model 2g we have two symmetric lines of Fe adatoms aside the Bi-nanolines. It is interesting to note that the binding energies of the models 2a and 2g are very close, 5.79 and 5.73 eV/Fe-atom. This observation suggests a weak interaction between the two parallel lines of interstitial Fe adatoms in model 2g. For both structural models, 2a and 2g, the Fe adatoms exhibit an antiferromagnetic coupling. The energetic preference of the model 2a indicates an attractive interaction between Fe adatoms, giving rise to Fe lines. On the other hand, comparing the binding energies of the structural models 2g and 2h, we can infer a repulsive interaction between the parallel Fe lines.

For a higher Fe coverage of 3/4 ML (not shown in Fig. 2), we considered the formation of Fe stripes parallel to the Bi-nanolines. This requires filling up all the second layer interstitial sites along the Bi-nanolines. The binding energy of this structure is 5.30 eV/Fe-atom, indicating that this configuration is energetically less favourable than the models 2a and 2g. It should be mentioned that for higher coverages there are several plausible configurations for Fe adatoms along the Bi-nanolines. For instance, Fe nanocluster aligned with the Bi-nanolines as well as the interstitial segregation of Fe adatoms underneath the Bi-nanolines. Experimental observations indicate nanocluster

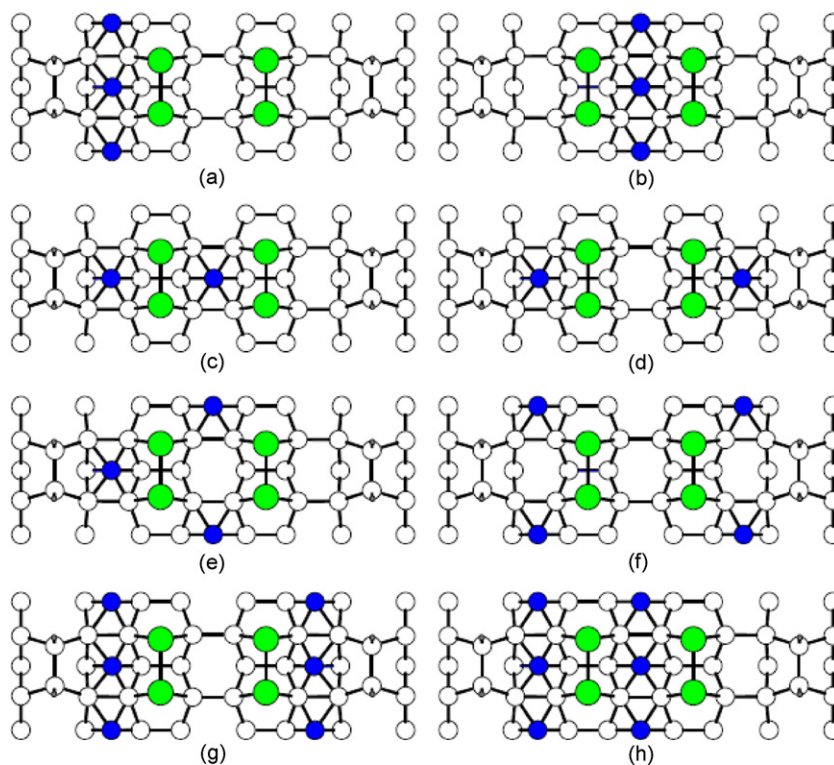


Fig. 2. Structural models for interstitial Fe adatoms along the Bi-nanolines. Fe coverages of 1/4 ML (a)–(f), and 1/2 ML (g) and (h).

formation of the noble-metal Ag atoms on the Bi-nanolines/Si(001) surface [10]. We believe that the latter proposition, *viz.* interstitial segregation, is quite reasonable for Fe adatoms, due to the following reasons. (i) The subsurface reconstruction below the Bi-nanolines gives rise to large empty spaces where the interstitial Fe adatoms can be easily accommodated [see Fig. 1(c)]. (ii) Previous *ab initio* total energy calculations indicate energetic preference of multi-layered subsurface FeSi films, compared with a single layer of FeSi, on the Si(001) surface. That is, the formation energy of FeSi films “decreases monotonously with increasing film thickness” [5]. Within such a scenario, the structural models 2a and 2g represent the initial stage for the formation of multi-layered FeSi quasi one-dimensional stripes underneath and parallel to the Bi-nanolines on H/Si(001). Further work on such considerations is in progress.

4. Conclusions

In summary, we examined the Fe adsorption on the interstitial sites nearby Bi-nanolines on the H/Si(001) surface. For sub-monolayer coverages, we find that the Fe adsorption aside the Bi-nanolines, forming a line of Fe adatoms aligned to the Bi-nanolines, represents the energetically most stable configuration. The Fe adatoms occupy the subsurface interstitial sites, being seven-fold coordinated with Si atoms. There is an energetic preference of Fe adsorption on the nearest neighbour sites (model 2a) and the Fe adatoms are coupled antiferromagnetically. For an increased Fe coverage closer to a monolayer, we find that the formation of two parallel and symmetric Fe lines aside the Bi-nanolines is the energetically most favorable configuration

(model 2g). Our calculated binding energy results indicate an attractive interaction between the Fe adatoms along a Fe line (2a) and a repulsive interaction between two parallel Fe lines (2g).

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