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Mg adsorption on Si(001) surface from first principles

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First-principles calculations using density functional theory based on norm-conserving pseudopotentials have been performed to investigate the Mg adsorption on the Si(001) surface for 1/4, 1/2, and 1 monolayer (ML) coverages. For both 1/4 and 1/2 ML coverages it has been found that the most favorable site for the Mg adsorption is the cave site between two dimer rows consistent with the recent experiments. For the 1 ML coverage we have found that the most preferable configuration is when both Mg atoms on 2×1 reconstruction occupy the two shallow sites. We have found that the minimum energy configurations for 1/4 ML coverage is a 2×2 reconstruction while for the 1/2 and 1 ML coverages they are 2×1.

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I. INTRODUCTION

Adsorption of overlayers of Mg atoms on silicon surfaces has been a subject of growing interest during the last decade because of its importance in technological applications such as the efficient photocathodes and thermionic energy converters. Even though several experimental and theoretical studies have been carried out for studying the Mg/Si(111) systems[1] only few have been reported for the adsorption of Mg on Si(001) surfaces.[2–8] The understanding of Mg adsorption on Si(001) has been especially an interesting problem to investigate because of the possible use of Si substrates for the growth of Mg_2Si films. More recently, after the report of superconductivity in MgB_2, its growth on Si(001) surfaces[9,10] has become the current aim.

One of the earliest experiments of Mg adsorption on Si(001) were carried out by Kawashima *et al.*,[3] who have obtained low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES) results starting from full coverage to lower coverages by allowing for thermal desorption. They observed that as the coverage decreased the various structural phases appeared in the order 1×1, 2×3, 2×2, another 2×3, and finally the clean 2×1 which correspond to the coverages of 1, 1/3, 1/4, 1/6, and 0 monolayer (ML), respectively. They concluded that Mg atoms were adsorbed on hollow site (valley-bridge site, in their notation) for each coverage mentioned above.

Hutchison *et al.*,[4] in their scanning tunnel microscope (STM) results for the low coverage-Mg/Si(001) case, have reported three types of adsorption geometries at room temperature. Type I is the most favorable phase and it refers to a single Mg atom adsorbed on a cave site. The least frequently observed type II, being a localized phase, corresponds to two Mg atoms adsorbed on cave sites to relieve the stress on the chain of type I phases. Type III phase, which may occur everywhere but next to a type II phase, contains multiple Mg adatoms (three at most) adsorbed on a combination of adjacent sites.

Similar observations also with the use of STM have been reported by Kubo *et al.*[5] for Mg adsorption at room temperature. However, they speculated another interpretation differing from that of Hutchison *et al.*, such that according to Kubo *et al.*, type I may correspond to two Mg atoms adsorbed on adjacent hollow sites and type III may correspond to a single Mg atom adsorbed on a pedestal site. In addition, for the annealed case at high temperature, they have tentatively suggested two models possessing the 2×2 symmetry by incorporating an extra Si on the shallow site (see Fig. 1) bonding to Mg adatom. The first model consists of a single Mg atom adsorbed on the neighboring shallow site bonding across the hallow site, and second one consists of two Mg atoms adsorbed on cave sites on each side of the extra Si atom.

Kim *et al.*[6] have reported in their LEED data that the 2×2 reconstruction corresponding to 1/2 ML coverage occurs at 280 °C, whereas for 1/3 ML coverage with 2×3 symmetry, it occurs at 390 °C, showing the dependence of surface reconstruction on coverage. Kubo *et al.*[5] did not reject the possibility of 1/2 ML as saturation coverage for 2×2 surface, either. Cho *et al.*[7] have performed high resolution core-level photoelectron spectroscopy for 2×2 and 2×3 structures. They did not find any difference in the behavior of Mg adsorption on Si(001) surface for these two configurations. They have found that the most preferable adsorption site for both of these low coverages is the cave site between two dimers (bridge site, in their notation).

On the theory side, Khoo and Ong[8] using a semiempirical self-consistent molecular orbital method have performed complete neglect of differential overlap calculations to investigate the adsorption of Mg atom on Si(001) at 1/2 ML coverage. According to their results the Mg atom resides on the

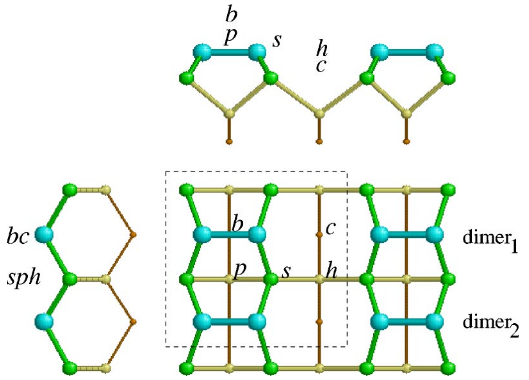

FIG. 1. Schematics of the adsorption sites for Mg atom on Si(001) surface from three different views. The symbols stand for b = bridge, p = pedestal, h = hallow, s = shallow, and c = cave. (The dimers are shown symmetric here for visual convenience.)

bridge site above the midpoint of Si dimer.

Wang *et al.*,[11] have done first-principle calculations for the adsorption of another group II element Ba on Si(001) at a rather low coverage of 1/16 ML, and they have shown that the minimum energy site is the hollow site (cave-bridge site, in their notation) where the Ba atom is surrounded by four buckled dimers leading to a solitonlike defect in the original $c(4\times2)$ configuration.

The aim of this paper is to perform first-principle calculations for different coverages, i.e., 1/4, 1/2, and 1 ML, of Mg on Si(001) to get a clear understanding of the adsorption mechanisms and to investigate the atomic structure of the surface covered with magnesium. To the best of our knowledge this is the first detailed work to investigate theoretically the Mg/Si(001) system for different coverages from first principles.

II. METHOD

We used pseudopotential method based on density functional theory in the local density approximation. The self-consistent norm conserving pseudopotentials are generated by using the Hammann scheme[12] which is included in the fhi98PP package.[13] Plane waves are used as a basis set for the electronic wave functions. In order to solve the Kohn-Sham equations, conjugate gradients minimization method[14] is employed as implemented by the ABINIT code.[15,16] The exchange-correlation effects are taken into account within the Perdew-Wang scheme[17] as parametrized by Ceperley and Alder.[18]

The unit cell included an atomic slab with eight layers of Si plus a vacuum region equal to about 9 Å in thickness. Each Si atom at the back surface is saturated with two hydrogen atoms in order to prevent the charge transfer between the surfaces. Single-particle wave functions were expanded using a plane-wave basis up to a kinetic energy cutoff equal to 16 Ry. The integration in the Brillouin zone was performed using eight special $\vec{k}$ points sampled using Monkhorst-Pack[19] scheme. Although a couple of cases were repeated with 18 special $\vec{k}$ points, no significant improvement has been observed.

We have used our theoretical equilibrium lattice constant for the bulk Si (5.405 Å) in the surface calculations. The bulk modulus for Si is found to be 96 GPa in rather good agreement with the experimental result of 98 GPa.[20] Our results for Mg bulk lattice parameter being 3.12 Å, and the c/a ratio being 0.607, obtained using 76 special $\vec{k}$ points, are very close to the experimental results of 3.20 Å and c/a of 0.614, respectively. As another check for our pseudopotentials, the lattice parameter for Mg_2Si was calculated to be 6.28 Å which is also in close agreement with the experimental value of 6.39 Å.[21] The energy bands of this compound gives a semiconducting gap of E_g equal to 0.14 eV. These tests suggest that the inclusion of the nonlinear core corrections to Mg pseudopotential is not needed.

We have used the 2×2 surface unit cell in our calculations to study the adsorption of Mg at a low coverage such as 1/4 ML and to include various combinations of adsorption sites for the half- and full-monolayer coverages. The first step was to optimize the clean Si(001)-2×2 surface while keeping the two lowest substrate layers (out of eight) frozen into their bulk positions and all the remaining substrate atoms and the hydrogen atoms were allowed to relax into their minimum energy positions. The $p(2\times2)$ was found to have the lowest total energy with a dimer length of 2.32 Å and a tilt angle of 19° which is in good agreement with the experimental dimer-length values of 2.40 ± 0.10 Å (Ref. 22) and 2.20 ± 0.05 Å.[23]

III. RESULTS AND DISCUSSION

We have studied the adsorption of Mg atom on the Si(001) surface for 1/4, 1/2, and 1 ML starting with the reconstructed $p(2\times2)$ surface unit cell. We have chosen five different sites for adsorption, namely, cave, hallow, pedestal, bridge, and shallow. The cave site (c) is located above the fourth layer Si, hallow (h) and pedestal (p) sites are above the third layer Si, shallow site (s) above the second layer Si between two Si dimers, and the bridge site (b) is located above the dimer as indicated in Fig. 1. Note that in the Figs. 1–4 we have not shown the whole slab but depicted only a few layers from the surface for the sake of clearness. The adatom and the upper three monolayers of the substrate were then relaxed to their minimum energy configurations by performing structural optimization using the Broyden-Fletcher-Goldfarb-Shanno method[24] until the force on each atom reduces to a value less than 25 meV/Å. All of the calculations were done without any symmetry restrictions. Relaxation of more number of layers improved neither the energy values nor the atomic positions significantly.

In Table I we introduce the structural parameters and bond lengths for different adsorption sites as well as the adsorption energy per adatom E_{ad} (negative of the binding energy of the adatom) given by

$$nE_{\mathrm{ad}}=(E_{\mathrm{Si(001)}}+nE_{\mathrm{Mg}})-E_{\mathrm{Mg/Si(001)}}, \tag{1}$$

where $E_{\mathrm{Mg/Si(001)}}$ is the total energy of the covered surface, $E_{\mathrm{Si(001)}}$ the total energy of clean surface, n is the number of Mg adatoms in the surface unit cell, and E_{Mg} is the total energy of a single Mg atom with spin polarization obtained in a separate *ab initio* calculation using the same pseudopotential and the same energy cutoff in a larger unit cell with a size of about 15 Å.

A. 1/4 ML Coverage

The adsorption of Mg atom on cave site was found to be the most favorable one among the five different adsorption sites, shown in Fig. 1. The other cases, namely, the *s* site and the *b* site occupations by an adatom are also stable. However, in the case of adsorption of Mg on *p* or *h* sites, they migrate to different sites with lower energies. In fact, the adatom on *p* site migrates to the *s* site, while the adatom on *h* site migrates to the neighboring *c* site. The adsorption of Mg on *c* site corresponds to an adsorption energy of 2.26 eV and *s* and *b* sites were found to be 0.25 eV and 0.68 eV lower than

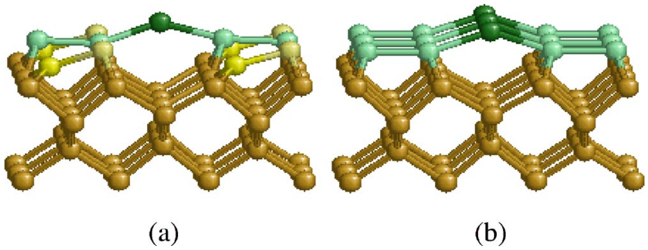

FIG. 2. Mg overlayer adsorbed on Si(001) surface (a) for 1/4 ML coverage on *c* site and (b) for 1/2 ML coverage on *c*-*c* site.

that of *c* case, respectively. A natural pathway for surface diffusion might be $b \rightarrow s \rightarrow c$ in addition to $h \rightarrow c$ and $p \rightarrow s$.

For all stable cases in 1/4 ML coverage we have found that the surface dimers get partially symmetrized. Only one dimer (“dimer$_1$” to which Mg adatom bonds) becomes symmetric (with a tilt angle less than $\sim 6°$), while the other one (“dimer$_2$” with no charge transfer from Mg adatom) is still tilted [e.g., Fig. 2(a)]. The tilting angles for dimer$_2$ in *c*, *b*, and *s* cases being 16.0°, 17.1°, and 13.0°, respectively, are still close to the clean surface value of 19° while dimer$_1$ for all of them are almost flat as seen from Table I.

The height of Mg atom on cave site is found to be 0.75 Å which is in good agreement with the STM results of Hutchison *et al.*[4] Fig. 2(a) shows for the 1/4 ML coverage that the two Si atoms bonded to the same Mg adatom are still in an asymmetric environment. The one whose neighbors are tilted down is 2.68 Å away from Mg atom whereas the other has a bond length of 2.65 Å. In a different calculation for Mg_2Si we have found Mg-Si bond length to be 2.70 Å which is close to the back-bond lengths of Mg in this environment.

B. 1/2 ML Coverage

For the case of 1/2 ML coverage, (i.e., 2 Mg atoms per 2×2 unit cell), we have considered the adsorption at combinations of pairs of the five different sites resulting in 15 different cases among which the most favorable case was found to be the *c*-*c* sites in our calculations. The structure then possesses 2×1 reconstruction with symmetric dimers stretched to 2.54 Å, shown in Fig. 2(b).

Even though *s* was stable for the low 1/4 ML coverage, we found that *s*-*s* is not always stable for 1/2 ML coverage. Out of four *s* sites in a 2×2 surface unit cell there are three inequivalent *s*-*s* geometries as shown in Fig. 3. For instance, it is unstable if the other adatom occupies the next *s* site along the [110], i.e., dimer row direction, as shown in Fig. 3(c). However, if the second adatom were added on the other *s* site along $[\bar{1}10]$, i.e., the direction of dimers, as seen in Fig. 3(a), this 2×2 configuration will be stable and it will have an adsorption energy almost equal to that of the *c*-*c* case, differing by only 0.01 eV per adatom. This small difference in their energies might be due to the saturation of dangling bonds in the *s*-*s* case. The last case *s*-*s*′ with the second *s* site along the [010] direction as shown in Fig. 3(b), is also stable with an adsorption energy of 2.14 eV per adatom. The larger difference in adsorption energies between the latter two cases, on the other hand, is believed to be due to different Mg-Mg interactions.

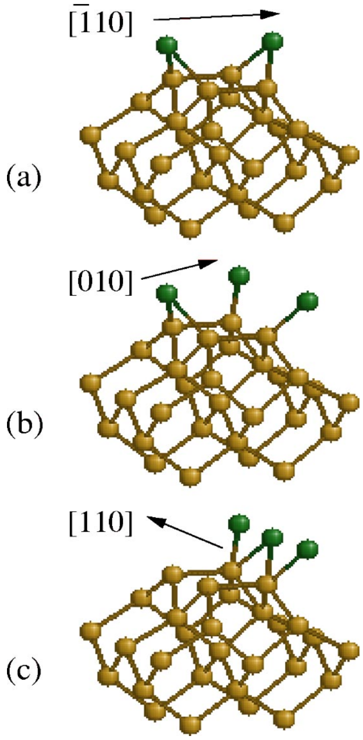

FIG. 3. Adsorption of two Mg atoms on *s* sites for half coverage: (a) *s*-*s* stable, (b) *s*-*s*′ stable, and (c) *s*-*s*″ unstable configurations.

Although neither of *p* and *h* sites are stable at 1/4 ML coverage, combination of them at 1/2 ML coverage, i.e., the *p*-*h* case with one atom occupying a pedestal site while the other occupying the neighboring *h* site was found to be stable and it is more favorable than the occupation of *p*-*p* sites that is also stable. In the case of *p*-*p* adsorption the adsorbed atoms are fourfold coordinated with the neighboring Si dimer atoms with a bond length of 2.68 Å and with symmetrical dimers stretched to a length of 2.52 Å. The case of adsorption on *b*-*b* was also found to be stable with symmetrical dimers but with an adsorption energy less than the *c*-*c* case by 0.68 eV per adatom.

The other combinations were found to be not stable and the adatom migrates to any one of the above stable configuration sites.

In all of the above stable configurations we have found that the surface dimers become symmetric [e.g., Fig. 2(b)] in contrast to the 1/4 ML adsorption case discussed before. The dimer lengths for all the stable adsorption sites are in the range 2.43–2.55 Å except for the case of *p*-*h* adsorption where the two dimers were stretched to rather long values of 2.87 and 2.91 Å, respectively. As to the Mg–Si backbonds, they are in the range of 2.53–2.93 Å. In Table I the $d_{\mathrm{Mg-Si}}$ values listed for the *p*-*h* case are for the Mg atom on *p* and *h* sites bonded to dimer Si atoms, respectively. Similarly, the $d_{\perp}$ values correspond to the heights measured from Si dimers of Mg adatoms on *p* and *h* sites, respectively.

In addition to the pathway $b \rightarrow s \rightarrow c$, we have also $b \rightarrow p \rightarrow s \leftrightarrow h \leftrightarrow c$ pathway in 1/2 ML coverage, where the backward migrations in energy take place among sites in the trough. Another rule brought by the double occupancy in this

TABLE I. The structural parameters (in Å) for most of the stable adsorption sites for three different coverages Θ. The heights of the adatom with respect to the dimers ($d_\perp$ in Å) and the adsorption energies (E_{ad} in eV) for these adsorption cases are also presented. The quantities in parenthesis are tilt angles (in degrees) of the corresponding dimers.

Θ	Model	Dimer$_1$	Dimer$_2$	$d_{\mathrm{Mg-Si1}}$	$d_{\mathrm{Mg-Si2}}$	$D_{\perp 1}$	$D_{\perp 2}$	$2\times n$	E_{ad}
1/4	*c*	2.54 (2.5)	2.28 (16.0)	2.68	2.65	0.75		2×2	2.26
	s	2.46 (5.5)	2.35 (13.0)	2.57	2.51	1.46		2×2	2.01
	b	2.51 (3.6)	2.29 (17.1)	2.54	2.49	2.08		2×2	1.58
1/2	*c-c*	2.54		2.68		0.82		2×1	2.20
	s-s	2.43		2.59		1.52		2×2	2.19
	s-s′	2.44		2.55		1.54		2×2	2.14
	p-h	2.87	2.91	2.66	2.93	1.32	0.57	2×2	2.01
	p-p	2.52		2.68		1.39		2×1	1.75
	b-b	2.55		2.53		2.18		2×1	1.52
1	*s-s-s-s*	2.38		2.73		1.49		2×1	1.98
	c-c-s-s	2.45		2.75	2.79	0.81	2.00	2×2	1.93
	p-p-h-h			2.65	2.87	0.53		(2)×1	1.91
	c-c-p-p	2.50		2.65	2.76	0.60	1.56	2×1	1.74
	c-c-b-b	2.58		2.59	2.69	0.59	2.36	2×1	1.59
	p-p-b-b	2.56		2.65	3.59	1.31	3.35	2×1	1.46

coverage is that the adatoms form chains along the dimer rows or along the dimer bonds. The *s-s*′ case looks like an exception to this, however, it is not considered to be a chain to first order. Any possible unstable combination α-β phase will diffuse into one of the stable phases listed in Table I by the adatom on either one of α or β sites migrating to a new site according to the above rules. In the case of *b-c* phase, since each Si atom of all dimers are bonded to two Mg atoms it is not stable and, consequently, both Mg atoms at *b* and *c* sites migrate to their corresponding neighbors *p* and *h* sites, respectively, to reach the stable *p-h* phase. We should emphasize here that this conclusion is not only based on the total energy calculations but also on the comparisons of the Hellman-Feynman forces and the adatom behavior in the other less stable cases.

C. 1 ML Coverage

For the full coverage adsorption, we have found six most probable configurations that are also consistent with our findings for the half coverage case. They are listed in Table I in the order of their adsorption energies.

The adsorption on *s-s-s-s* was found to be the most favorable one with an adsorption energy of 1.98 eV per adatom. In this model we have four Mg atoms occupying all four *s* sites forming Mg lines that run along the dimer rows. The surface symmetry of this structure is 2×1 with dimers shortened to 2.38 Å as compared to 2.43 Å of the *s-s* half coverage case. Such a short dimer length may be due to the shortest Mg-Mg distance along $[\bar{1}10]$ obtained in the present case than in all the other geometries considered. The Mg-Si backbond of length 2.73 Å compares well with the Mg-Si bond (of length 2.70 Å) in $\mathrm{Mg_2Si}$.

The next stable case that has less adsorption energy (by only 0.05 eV per adatom) is the *c-c-s-s* in which one has two Mg adatoms on *s-s* along the $[\bar{1}10]$ direction, while the other two Mg adatoms occupy the *c-c* sites along the [110] direction as seen in Fig. 4(b). In this case the reconstructed surface structure possesses a 2×2 symmetry with dimers of length 2.45 Å. The Mg-Si backbonds being in the range of 2.75–2.79 Å also compare well with the Mg-Si bonds in silicates.

The *p-p-h-h* combination, in which every hallow and pedestal sites are occupied, was also found to be stable with an adsorption energy differing from the *s-s-s-s* case by 0.07 eV per adatom. This phase is very interesting in its symmetry properties. Upon relaxation the dimers are removed and they approach to an almost 1×1 phase where *p* and *h* become the same. The deviation from 1×1 is very small and is due to a slight shift (0.15 Å) of only the ex-dimer-member Si atoms in the $[\bar{1}10]$ direction opposite to one another, so that the Mg adatom will only bond to two Si atoms instead of four. This symmetry breaking due to charge transfer from Mg to surface Si atoms causes the zigzag bond picture shown in Fig. 4(c).

Next combination is the *c-c-p-p* case where the adsorbed atom in *p* site is fourfold coordinated with the neighboring Si dimer atoms with a bond length of 2.65 Å while the other adatom in cave site is twofold coordinated with a bond length of 2.76 Å giving rise to an adsorption energy of 1.74 eV per adatom. This structure possesses 2×1 symmetry with a dimer length of 2.50 Å.

The combination *c-c-b-b* was also found stable with adsorption energy equal to 1.59 eV per adatom. In this model we have Mg atoms occupying all the bridge and cave sites, forming Mg lines that run orthogonal to the dimer rows and resulting in a 2×1 symmetry. The dimer length was found to be 2.58 Å. The difference in heights of the Mg adatoms on *c* and *b* sites measured from the silicon dimers corresponding to 1.77 Å undulates the Mg chains along the dimer direction.

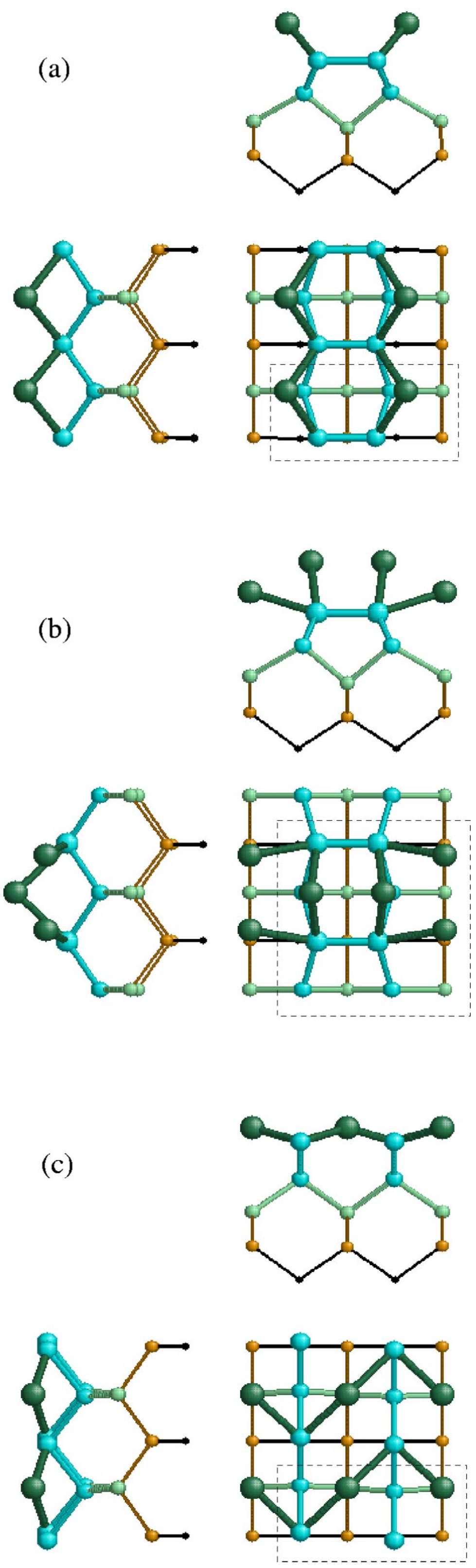

FIG. 4. Three views of the minimum energy structures (after relaxation) for (a) Mg/Si(001)-(2×1)-s-s-s-s, (b) Mg/Si(001)-(2×2)-c-c-s-s, and (c) Mg/Si(001)-(2×1)-p-p-h-h cases for 1 ML coverage.

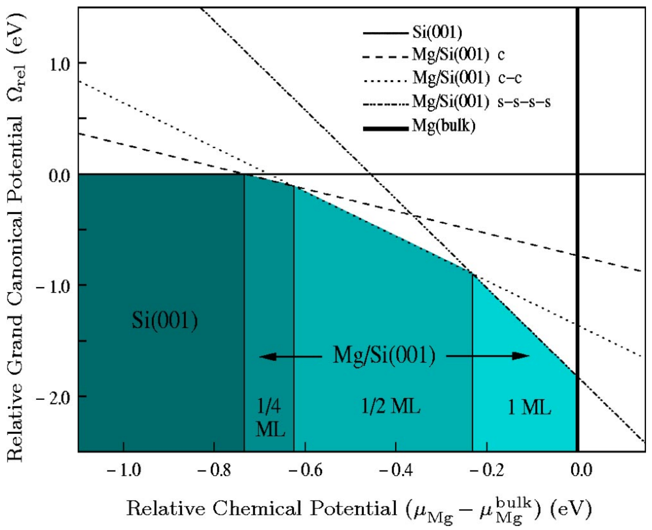

FIG. 5. The relative grand canonical potential as a function of the relative chemical potential of Mg adsorbed on Si(001) surface for the minimum energy cases of various coverages.

The configuration p-p-b-b can be described as double half monolayer where two Mg atoms occupy two pedestal sites ($d_\perp = 1.31$ Å) while the other two Mg adatoms rise further up to a height of 3.35 Å measured from the center of the dimer. This structure possesses 2×1 symmetry with a dimer length of 2.56 Å and can be described as undulated Mg wires located on the Si dimer rows, similar but orthogonal to the c-c-b-b case.

D. Thermodynamic Stability of The Phases

The thermodynamic stability for these coverages can be studied by calculating the grand canonical potential as a function of chemical potential for each case. This allows one to compare the stability of surface having different number of Mg adatoms.

The relative grand canonical potential[25] at 0 K can be written as

$$\Omega_{rel} = E - E_{clean} - n_{Mg}\mu_{Mg}, \tag{2}$$

where n_{Mg} is the number of adatoms and μ_{Mg} is the chemical potential of them, E and E_{clean} are the total energies obtained by the *ab initio* calculations for the covered and clean surfaces, respectively. The surface chemical potential $\mu_{\rm Mg}$ of Mg should be considered in some range such that it cannot exceed the $\mu_{\rm Mg}^{\rm bulk}$. The value of $\mu_{\rm Mg}^{\rm bulk}$ was obtained from a separate *ab initio* calculation for Mg in its crystal phase as described in Sec. II. Since the number of Si atoms is constant in all calculations, the relative grand canonical potential according to Eq. (2) is expected to vary linearly with Mg chemical potential for each coverage.

We have performed the calculations for 0, 1/4, 1/2, and 1 ML adsorption coverages with $p(2\times2)$, 2×2, 2×1, and 2×1 reconstructions, respectively. These reconstructions represent the most stable adsorption configurations for each coverage, i.e., c, c-c, and s-s-s-s. The relative grand canonical potential Ω_{rel} as a function of $\mu_{\rm Mg} - \mu_{\rm Mg}^{\rm bulk}$ has been calculated and presented in Fig. 5. It was found that for $\mu_{\mathrm{Mg}} - \mu_{\mathrm{Mg}}^{\mathrm{bulk}} < -0.73$ eV the clean Si(001) surface has a lower energy than that with any amount of Mg adsorbed on it. However, in the range $-0.73\ \mathrm{eV} < \mu_{\mathrm{Mg}} - \mu_{\mathrm{Mg}}^{\mathrm{bulk}} < -0.63$ eV, the quarter coverage adsorption with a 2×2 symmetry is found to be the most stable structure. A transition to half coverage with 2×1 surface has occurred when $\mu_{\mathrm{Mg}} - \mu_{\mathrm{Mg}}^{\mathrm{bulk}} > -0.63$ eV. Finally, when $\mu_{\mathrm{Mg}} - \mu_{\mathrm{Mg}}^{\mathrm{bulk}} > -0.23$ eV the full coverage occupation of the surface having the least energy is reached as explained in the *s-s-s-s* case. These findings suggest that all coverages that have been studied in the present work can be stable within the allowed chemical potential values of Mg.

IV. SUMMARY AND CONCLUSION

We have performed an *ab initio* total energy calculation and geometry optimization for a clean Si(001) surface and that with Mg overlayer of different coverages on it. For the 1/4 ML coverage we have found two favorable adsorption sites, namely *c* and *s* with a relative adsorption energy difference of only 0.25 eV per adatom. Our results agree well with the room-temperature results of Hutchison *et al.*[4] and of Cho *et al.*[7] where they have suggested that the most favorable site is the cave site. Kubo *et al.*[5] have suggested for the higher temperature adsorption that the *s* site is favorable, however, they assumed an extra Si on the surface bonding to the adatom. Even though Kubo *et al.*[5] suggested the possibility of single adatom occupation on a pedestal site at room temperature, we did not find any evidence to confirm it. Our calculations show that this site is unstable for a single adatom adsorption. Occupation of pedestal site has also been ruled out by Cho *et al.*[7] for low coverage. But we find that the argument of Hutchison *et al.*[4] that this site can be occupied by multiple atoms is in agreement with our stable *p-p* case for 1/2 ML.

Contrary to the theoretical results[11] for Ba adsorption on Si(001), we found that the Mg adsorption on *h* site is not stable. Since the total energy of this case is higher than the adsorption on *c* site by 0.85 eV per adatom, it leaves this saddle point and migrates to the neighboring cave site. We believe the reason for this disagreement with the Ba case might be due to the difference in their atomic sizes.

For the case of half monolayer coverage, our results give 2×1 reconstruction with the Mg adatoms on *c-c* sites. The high-temperature result of Kubo *et al.*,[5] for the same coverage suggested that it contains two Mg adatoms located nearly on *c-c* sites but distorted by the existence of an extra Si atom which causes the symmetry to be a 2×2. On the other hand, their 1/2 ML result for low temperature can be described as two Mg adatoms confined in every other cave site and separated towards *h* saddle to make it a 2×2. This corresponds to a distorted version of our *h-h* case. Starting from both of these geometries we have found them unstable ending up in *c-c* case with a 2×1 symmetry. Even though we have started with a 2×2 unit cell for each case in our calculations we have ended up with 2×1 reconstruction for the 1/2 ML coverage except for the *p-h* case and the *s-s* cases, which are naturally 2×2.

The bridge site *b-b* was found to be stable in accordance with the theoretical result of Khoo and Ong[8] for this coverage, even though it is the least favorable case.

For the case of full monolayer coverage, we have found that the adsorption model in which all the Mg atoms occupy all the *s* sites with 2×1 construction is more favorable than 2×2 reconstruction in which Mg atoms occupy two shallow and two cave sites having an adsorption energy difference of only 0.05 eV per adatom. The next favorable case having 0.07 eV per adatom smaller adsorption energy than the most preferable *s-s-s-s* case is the *p-p-h-h* configuration with a 2×1 symmetry, but just slightly away from 1×1 geometry as seen in Fig. 4(c). This may suggest that more than 1 ML coverage might lead to a 1×1 phase consistent with the LEED results of Kim *et al.*[6] who reported that the 1×1 phase corresponds to 2 ML coverage.

The model of adsorption that can be concluded from our theoretical results is that for the low coverage, Mg atoms will be adsorbed mostly on *c* sites and less likely on *s* sites, which continues until the coverage reaches to 1/4 ML. As the coverage exceeds 1/4 ML, the Mg atoms are adsorbed on the *c-c* sites and on the *s-s* sites along $[\overline{1}10]$ with almost equal probabilities until the surface becomes saturated at 1/2 ML, where it is going to have domains of *c-c* and *s-s* phases with 2×1 and 2×2 reconstructions, respectively. Further increase in coverage will result into *s-s-s-s*, *c-c-s-s*, and even *p-p-h-h* domains with 2×1, 2×2, and almost 1×1 reconstructions, respectively.

Using *ab initio* total energy calculations we have performed detailed investigation of the atomic geometry of Mg adsorbed Si(001) surface for 1/4, 1/2, and full monolayer coverages. We have investigated the adsorption sites, the energetics, and the reconstruction of Si(001) surface after Mg adsorption. We have found that our results agree well with the existing experimental observations.

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