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# First-principle study of Mg adsorption on Si(111) surfaces

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We have carried out first-principle calculations of Mg adsorption on Si(111) surfaces. Different adsorption sites and coverage effects have been considered. We found that the threefold hollow adsorption is energy-favoured in each coverage considered, while for the clean Si(111) surface of metallic feature, we found that 0.25 and 0.5 ML Mg adsorption leads to a semiconducting surface. The results for the electronic behaviour suggest a polarized covalent bonding between the Mg adatom and Si(111) surface.

**Keywords:** electronic materials, electronic structure
**PACC:** 7115M, 7320A

## 1. Introduction

Metal/Si systems have been studied extensively for not only industrial purposes but also scientific interest. Among these studies the interaction of alkali metals and a clean Si(111) surface has attracted specific attention.[1−5] Adsorption of Mg atoms on silicon surfaces has attracted growing interest for the past few years because of the possible use of Si substrates for the growth of $Mg_2Si$ films, which is an important narrow band gap semiconductor with potential applications in optoelectronics.[6,7] More recently, much attention has been paid to the wide band gap semiconductor ZnO as a promising material for the fabrication of ultraviolet detectors.[8,9] In our previous work, by using Mg pre-growth deposition followed by oxidation to form a thin single-domain MgO interface layer, high quality ZnO has been obtained on (La, Sr) (Al, Ta)$O_3$ substrate.[10] Our further study reveals that this special interface control technique could also be applied to ZnO/Si epitaxial system, as direct deposition of ZnO or MgO buffer layer always results in the oxidation of the silicon substrate. For better control of the interface formation, it is of great importance to understand the initial growth process of Mg on Si surface. From the theoretical viewpoint, in addition, one of the basic problems that needs comprehensive understanding is how the dangling bonds of a clean Si(111) surface interact with metal atoms such as Mg, which has two valence electrons. Although the Mg/Si system has been studied experimentally by a number of groups,[6,7,11,12] only a few works have been reported in theoretical investigations. Recently, Shaltaf *et al* presented *ab initio* calculations of Mg adsorption on Si(001).[13] The atomic geometry of Mg-adsorbed on Si(001) surface for 1/4, 1/2, and 1 monolayer (ML) coverages have been given. This is the first detailed work to theoretically investigate the Mg/Si(001) system for different coverages by first principles method. Miyoshi *et al* gave a molecular orbital study on Na, Mg and Al atoms adsorbed on the Si(111) surface using cluster model calculations.[14,15] Three possible sites for Mg adsorption on Si(111), i.e. on-top ($T_1$), bridge ($B_2$) and 3-fold filled ($T_4$) sites were considered. It was revealed that the adsorption at bridge site is the most favourable. Since the adsorption energy largely depends on the cluster size used if the clusters are small, only relative stability could be obtained for different adsorption sites from the cluster model. Moreover, coverage effect and the electronic properties of the

Mg/Si(111) system were not considered at all. Thus, more precise calculation with further information of electronic properties are highly needed for better understanding of the Mg adsorption process on Si(111) surface and the mechanism for interface formation.

In this paper, we present a detailed first-principles study of the adsorption of Mg on Si(111) surfaces with different coverages, i.e. 1/4, 1/2, and 1 ML, with the aim to gain a clear understanding of the adsorption mechanisms. Various adsorption sites, including $T_1$, $B_2$, $T_4$ and 3-fold hollow ($H_3$) (see Fig.1), are considered. The band structure and the Mg–Si bond properties are also studied. To the best of our knowledge, this is the first detailed study on the coverage effects and the electronic properties of Mg/Si(111) system from first-principles calculation.

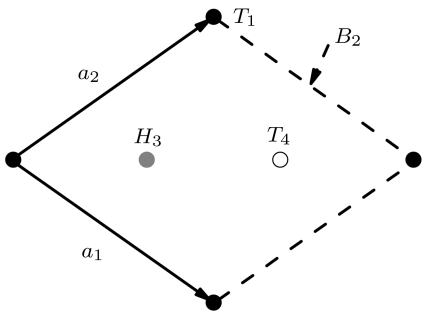



**Fig.1.** Top view of the four different adsorption sites for Mg adatoms on Si(111) surface.

This paper is organized as follows. The computational details are described in Section 2. The structure properties of the Mg/Si(111) system with different coverages and the corresponding electronic properties, including the band structure and the nature of the Mg–Si bonds, are presented in Section 3. Also, the results of work function and thermodynamic stability of Mg/Si(111) system with different coverages are given and discussed. A summary of this work and our conclusion are given in Section 4.

## 2. Computational method

Calculations were carried out with the Vienna *ab initio* simulation package (VASP) based on density functional theory. In the calculations, the projector augmented-wave (PAW) pseudopotential[16,17] with the generalized gradient approximation (GGA) was adopted. Si(111) surfaces were modelled by a supercell that contains a slab of 12 layers of silicon atoms and a vacuum region of 2 nm between neighbouring layers. Each Si atom at the bottom surface is saturated with one hydrogen atom to prevent charge transfer between the surfaces. Mg atoms are put on the top side of the slab to simulate the adsorption systems. Brillouin-zone integration was performed using Monkhorst–Pack scheme[18] with a $6 \times 6 \times 1$ $k$-point grid, and the plane-wave energy cutoff was set at 250 eV. The use of larger $k$-point meshes does not alter these values significantly. A Fermi broadening of 0.05 eV was chosen to smear the occupation of the bands around $E_{\mathrm{F}}$ by a finite-temperature Fermi function and extrapolated to $T = 0$ K.

Basically, we may consider that Mg atoms are absorbed on a Si(111) surface at four most possible adsorption sites: the onefold-coordinated top site ($T_1$), the twofold-coordinated bridge site ($B_2$), the threefold coordinated filled site ($T_4$) with a second-layer Si atom below the considered site; and the threefold-coordinated hollow site ($H_3$) without second-layer Si atoms below the considered site. These adsorption sites are schematically illustrated in Fig.1.

The nudged elastic band method[19] is used to calculate the energy barriers for Mg adsorption on Si(111) at different sites. The band structure and the electronic density of states (DOS) are obtained to characterize the bonding properties between Mg and the Si(111) surface.

## 3. Results and discussion

We first calculate the total energy of the bulk silicon to obtain the host lattice constant. The calculated bulk lattice constant for silicon is 0.5472 nm, in good agreement with the value of 0.54307 nm as given in Ref.[20]. The adsorption energy, which is the negative of the binding energy of the adatom, is defined as

$$E_{\mathrm{ad}} = [(E_{\mathrm{Si}(111)} + nE_{\mathrm{Mg}}) - E_{\mathrm{Mg/Si}(111)}]/n, \quad (1)$$

where $E_{\mathrm{Mg/Si}(111)}$ is the total energy of the Mg/Si(111) system, $E_{\mathrm{Si}(111)}$ is the total energy of the clean surface, $n$ is the number of Mg adatoms, and $E_{\mathrm{Mg}}$ is the total energy of a single Mg atom obtained in a separate calculation using the same pseudopotential and the same kinetic energy cutoff with a larger unit cell of a size 2 nm×2 nm×2 nm.

### 3.1. Structural properties for different coverages

We have studied the adsorption of Mg atoms on the Si(111) surface for 1/4, 1/2, and 1 ML starting with the unreconstructed $2 \times 2$ surface unit cell. The calculated adsorption energies as well as bond lengths for different adsorption sites are shown in Table 1.

One can see that in the case of 1/4 ML coverage, the adsorption of Mg atom on $H_3$ site is the most favourable compared to the other three adsorption sites shown in Fig.1. The $T_1$ and $T_4$ site occupations are also locally stable. However, the adsorbed Mg atom on $B_2$ site is not stable and it will migrate to the lower energy $H_3$ site during the zero-temperature relaxation process. The adsorption energy of Mg on $H_3$ site is 3.05 eV and those for $T_1$ and $T_4$ sites are found to be 1.81 eV and 0.14 eV lower, respectively. Therefore, a natural pathway for surface diffusion might be $T_1 \rightarrow T_4 \rightarrow H_3$ in addition to $B_2 \rightarrow H_3$. The height of Mg atom on $H_3$ site is 0.145 nm above the Si surface, while those for Mg on $T_4$ and $T_1$ sites are 0.162 nm and 0.233 nm, respectively.

**Table 1.** The adsorption energy $E_{\mathrm{ad}}$(eV) and structure parameters for Mg-adsorbed on Si(111) surface with three different coverages; $h$ is the distance between the Mg adsorption layer and the top layer silicon, $d$ is the Mg–Si bond length.

| coverage | adsorption site | $E_{\mathrm{ad}}$(eV) | $h$/nm | $d_1$/nm | $d_2$/nm | $d_3$/nm |
|---|---|---|---|---|---|---|
| 1/4 ML | $T_1$ | 1.24 | 0.233 | 0.259 | | |
| | $B_2$ –$H_3$ | 3.05 | 0.146 | 0.266 | 0.266 | 0.266 |
| | $B_2$ –$H_3$ | 3.05 | 0.146 | 0.266 | 0.266 | 0.266 |
| | $H_3$ | 3.05 | 0.145 | 0.266 | 0.266 | 0.266 |
| | $T_4$ | 2.91 | 0.162 | 0.267 | 0.267 | 0.267 |
| 1/2 ML | $T_1 - T_4$ | 2.49 | 0.170 | 0.284 | 0.284 | 0.284 |
| | $B_2$ –$H_3$ | 2.58 | 0.157 | 0.260 | 0.274 | 0.274 |
| | $H_3$ | 2.56 | 0.157 | 0.260 | 0.274 | 0.274 |
| | $T_4$ | 2.50 | 0.171 | 0.263 | 0.284 | 0.284 |
| 1 ML | $T_1$ | 1.47 | 0.266 | 0.266 | | |
| | $B_2$ | 1.56 | 0.201 | 0.279 | 0.314 | |
| | $H_3$ | 1.65 | 0.170 | 0.281 | 0.281 | 0.281 |
| | $T_4$ | 1.62 | 0.188 | 0.292 | 0.292 | 0.292 |

In the case of 1/2 ML coverage, we find that the most energetically favourable adsorption site is $H_3$. The $T_4$ site is stable with the adsorption energy a little lower (by 0.06 eV) than that of $H_3$. However, the adsorption of Mg atom at $T_1$ and $B_2$ is unstable and they will migrate to $T_4$ and $H_3$ sites with lower energies, respectively. For the most stable $H_3$ site, it is further found that the three Mg–Si bond lengths are not equal, which is caused by the interaction between the Mg adsorbates.

For 1 ML coverage, the $H_3$ is still the most stable adsorption site. The $T_1$, $B_2$, and $T_4$ sites are also locally stable, and the atomic migration of Mg on Si(111) surface is suppressed by the full coverage effect. Furthermore, the kinetic barriers for migration of Mg adatom among the various adsorption sites are calculated and the results are shown in Fig.2.

Again, one can see that the adsorption at $H_3$ site is the most favourable. It should be pointed out that our present observation is inconsistent with the results given by Miyoshi *et al*[15] who used a single cluster model ($Mg–Si_4H_7$), that the $B_2$ adsorption site is the

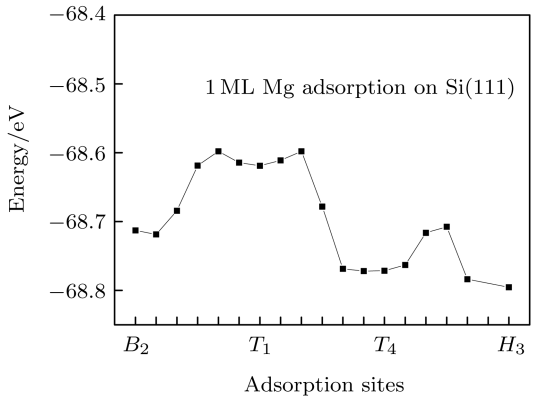



**Fig.2.** Energy barriers for Mg migration on Si(111) surface with 1ML coverage.

most stable. This inconsistency indicates the necessity of a full first-principles treatment of the Mg/Si(111) system beyond the cluster model calculation. The less favourable site is $T_4$. There is a local energy minimum between the $H_3$ and $T_4$ sites. Also it should be noticed that the energy barrier for Mg migration from the $T_1$ site to $T_4$ or $B_2$ site is very small, implying that $T_1$ could not be a locally stable adsorption site.

## 3.2. Thermodynamic stability

The thermodynamic stability for Mg adsorption on Si(111) surface with different coverages can be studied by calculating the formation energy of Mg/Si(111) system as a function of chemical potential for each case, so as to investigate the stability of the Si(111) surface with different coverages of Mg adatoms.

The formation energy of a Si(111) surface with specific Mg coverage can be expressed as[21]

$$E_{\mathrm{f}} = E_{\mathrm{Mg/Si(111)}} - E_{\mathrm{Si(111)}} - n_{\mathrm{Mg}}\mu_{\mathrm{Mg}}, \qquad (2)$$

where $n_{\mathrm{Mg}}$ is the number of the Mg adatoms and $\mu_{\mathrm{Mg}}$ is the chemical potential, $E_{\mathrm{Mg/Si(111)}}$ and $E_{\mathrm{Si(111)}}$ are total energies of the Mg-covered and clean Si(111) surfaces, respectively. The chemical potential $\mu_{\mathrm{Mg}}$ of Mg is limited in a range that cannot exceed the $\mu_{\mathrm{Mg}}^{\mathrm{bulk}}$, which was obtained from a separate calculation for Mg in its crystal phase.

Calculations are performed for 0, 1/4, 1/2, and 1 ML coverages with Mg adsorption at $H_3$ site which is the most stable for each coverage. The calculated results of formation energy as a function of the difference of chemical potentials, $\Delta\mu_{\mathrm{Mg}} = \mu_{\mathrm{Mg}} - \mu_{\mathrm{Mg}}^{\mathrm{bulk}}$, is presented in Fig.3. It shows that for $\Delta\mu_{\mathrm{Mg}} < -1.57\,\mathrm{eV}$, the clean Si(111) surface has a lower energy than the surface with any amount of Mg adsorption. For $-1.57\mathrm{eV} < \Delta\mu_{\mathrm{Mg}} < -0.62\,\mathrm{eV}$, the most stable structure is the 1/4 coverage of Mg adsorption. When $-0.62\mathrm{eV} < \Delta\mu_{\mathrm{Mg}} < 0\,\mathrm{eV}$, it is revealed that the half coverage occupation has the lowest formation energy. It is interesting that the full 1 ML coverage is thermodynamically unstable in the whole range of variation of the relative chemical potential. To explore the possibility of stable configurations with more coverages, combinations of different adsorption sites must be considered. This is now under investigation.

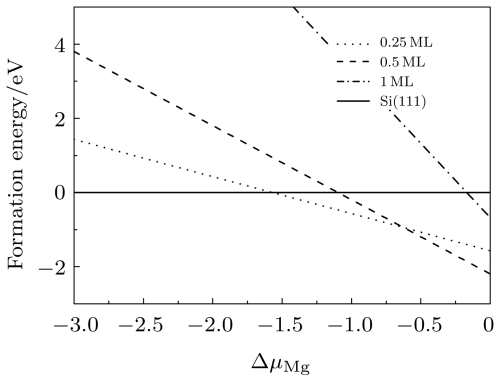



**Fig.3.** Formation energy as function of the relative chemical potential of Mg.

## 3.3. Electronic properties

Figure 4 shows the band structures for a clean Si(111) surface and the Mg-adsorbed at $H_3$ site on Si(111) surface with different coverages. For the clean surface (Fig.4(a)), one can see that three noticeable surface-state bands (attributed to a filled $S_3$, a partially filled $S_2$, and an empty state $S_1$), occur in the fundamental gap of the projected bulk band structure, causing a metallic behaviour of the Si(111) surface. These states are mainly related to $\pi$ bonding or $\pi^*$-antibonding combinations of $p$-like hybrids parallel to the surface normal. In the case of 1/4 ML coverage of Mg adsorption on Si(111) surface, as seen in Fig.4(b), the partially filled Si dangling-bond surface states are saturated by electrons donated from Mg adatoms. Thus the 1/4 ML Mg adsorption produces a semiconducting band structure. Also Fig.4(b) is featured by a direct gap at $\Gamma$ with a band gap value of 0.2 eV. When the Mg coverage increases to 0.5 ML, as shown in Fig.4(c), the empty surface state is pulled significantly into the gap due to the participation of more Mg 3s electrons and the consequent saturation of Si dangling bonds. In this case, the band structure displays almost semi-metal behaviour. The band structure for the 1 ML Mg-adsorbed Si(111) surface is given in Fig.4(d), which shows clearly a metallic feature. The cause of this metallicity is attributed to the hybridization of the Si dangling states and the Mg delocalized 3s state which is partially filled in the case of full coverage. This metallic adsorption of Mg is unstable against lowering the energy by the surface reconstruction. This is consistent with the energetic result in Fig.3 which shows that full Mg coverage on Si(111) is thermodynamically unstable even in the extreme Mg-rich condition.

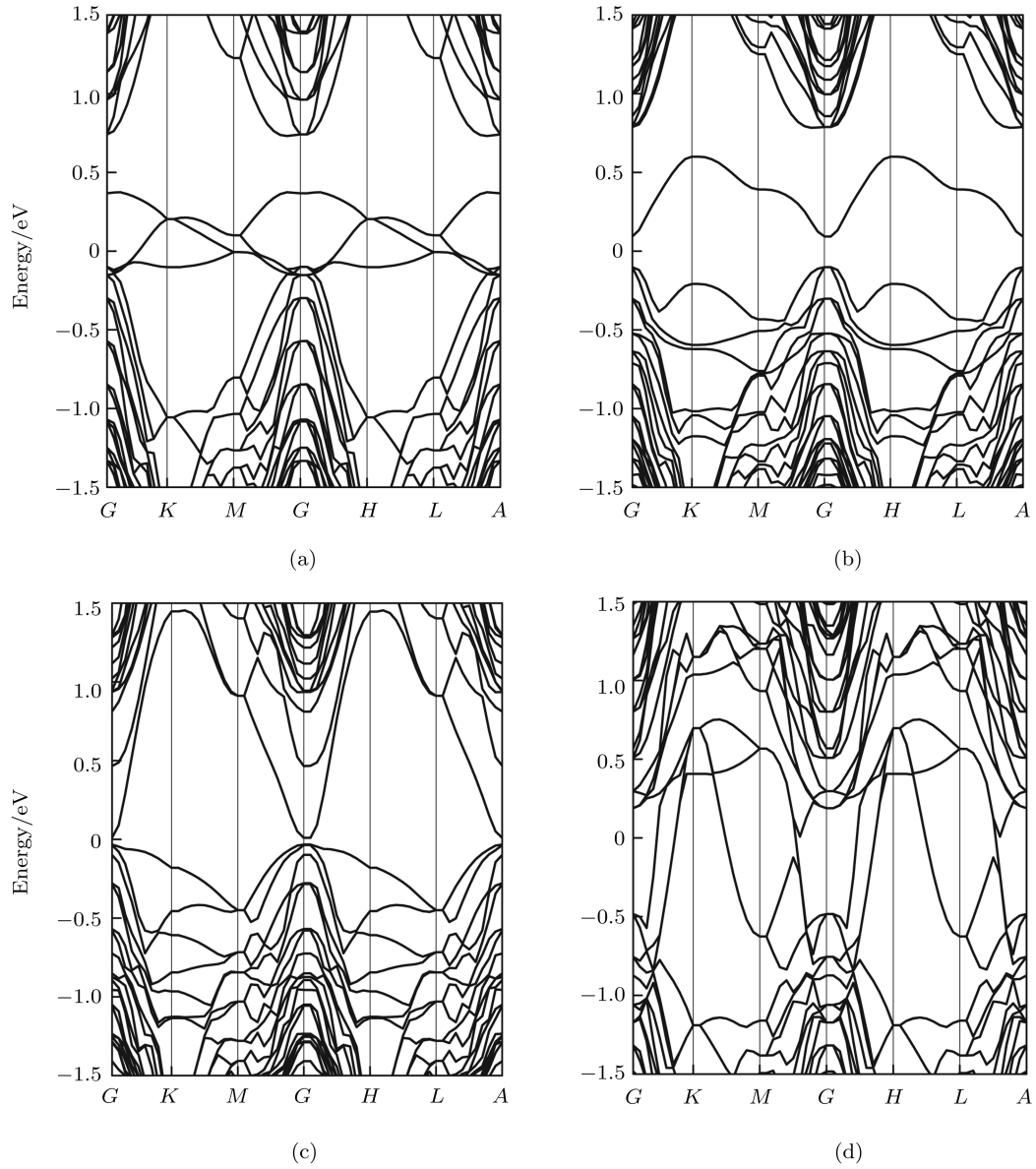



**Fig.4.** Electron band structure of the clean Si(111) surface (a) and these covered with 0.25 ML (b), 0.5 ML (c) and 1 ML (d) Mg adatoms.

The nature of chemical bonding between metals and a clean Si(111) surface has been controversial. The conclusion depends strongly on the method used for analysis of the chemical bonding.[22] To fully understand the surface electronic structure of Mg-covered Si(111), we calculate the local density of states (LDOS) through projections of the total wavefunction onto atoms of interest within the Wigner–Seitz spheres around them. Figure 5 gives a series of LDOS for different coverages of Mg/Si(111) systems of Mg adatom and the topmost Si atom forming bond with Mg. It shows a strong hybridization between the Mg 3s and Si 3p orbitals. In the case of 1/4 and 1/2 coverages, the Fermi level is pinned on top of the valence band. Also it should be noticed that with 1/4 or 1/2 ML Mg coverage, the DOS near the Fermi energy is very low, implying a semiconducting feature of the Mg/Si(111) system. With a 1 ML Mg coverage, the Fermi level shifts upward to the broad DOS peak, resulting in an obvious enhancement of the DOS at Fermi level compared with the low Mg adsorption case.

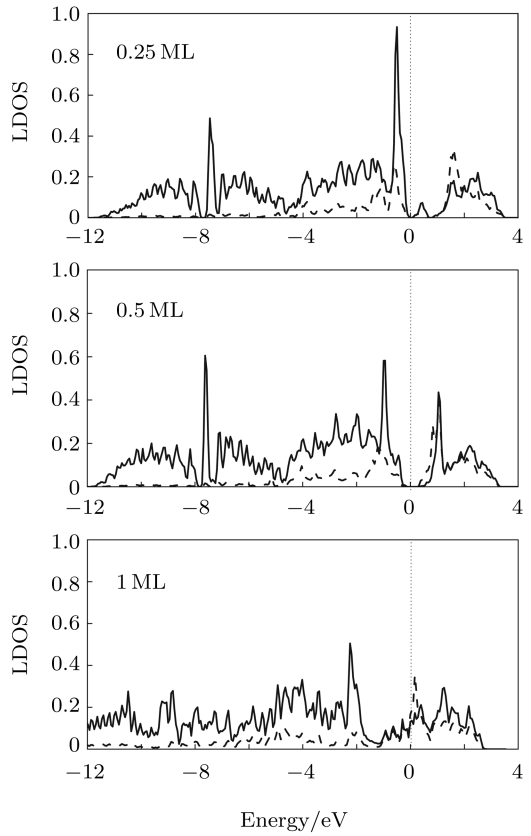



**Fig.5.** Local density of states of the Mg/Si(111) system as a function of the Mg coverage.

### 3.4. Work function

The work function is calculated as the difference between the vacuum level and the Fermi energy. For a clean relaxed Si(111) surface the calculated value is 4.51 eV. Figure 6 presents the calculated results for the work function shifts with respect to the clean surface. The work function of the Mg-adsorbed Si(111) surface decreases monotonically with the increase of the Mg coverage. Since the work function is reduced, charge is transferred from Mg to Si, leading to a polarization of electronic charge away from the Mg adlayer towards the Si surface. This behaviour in the work function shift is different from the calculated results for Cs/Si(001), where the work function shifts reach the maximum at 0.5 ML coverage before it rises again at 1 ML coverage.[23]

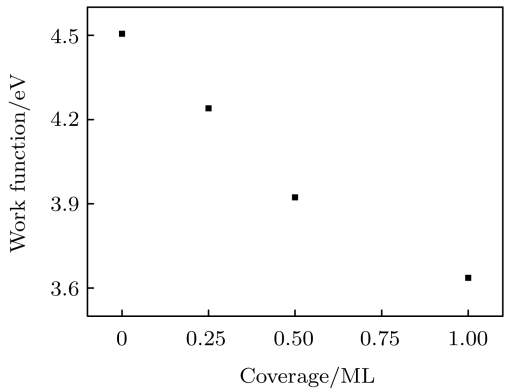



**Fig.6.** Calculated work function of the Mg/Si(111) system as a function of the Mg coverage.

## 4. Summary and conclusion

We have performed first-principles total energy calculations and geometry optimization for a clean Si(111) surface and the one adsorbed with Mg overlayer of different coverages. Different adsorption sites have been considered and we found that the threefold hollow site is energy favoured. Band structure calculation shows that the clean Si(111) surface is of metallic feature, while the surfaces covered with 0.25 and 0.5 ML Mg are of semiconducting characteristic. The calculated LDOS results suggest a polarized covalent Mg–Si bonding.

## References

[1] Clotet A, Ricart J M, Rubio J, Illas F and Moscardo E 1995 *Phys. Rev.* B **51** 19981

[2] Jeon D, Hashizume T, Sakurai T and Willis R F 1992 *Phys. Rev. Lett.* **69** 1419

[3] Reihl B, Sorensen S L, Dudde R and Magnusson K O 1992 *Phys. Rev.* B **46** 1838

[4] Fan C Y, Zhang X S, Tang J C, Sui H, Xu Y B, Pan H B and Xu P S 1997 *Acta Phys. Sin.* **46** 953 (in Chinese)

[5] Zhang X S, Fan C Y, Sui H, Bao S N, Xu Y B, Xu S H, Pan H B and Xu P S 1996 *Acta Phys. Sin.* **45** 1244 (in Chinese)

[6] Quinn J and Jona F 1991 *Surf. Sci. Lett.* **249** L307

[7] Wigren C, Andersen J N, Nyholm R and Karlsson U O 1993 *Surf. Sci.* **289** 290

[8] Chen Y F, Hong S K, Ko H J, Nakajima M, Yao T and Segawa Y 2000 *Appl. Phys. Lett.* **76** 245

[9] Look D C, Reynolds D C, Litton C W, Jones R L, Eason D B and Cantwell G 2002 *Appl. Phys. Lett.* **81** 1830

[10] Ying M J, Du X L, Liu Y Z, Zhou Z T, Zeng Z Q, Mei Z X, Jia J F, Chen H, Xue Q K and Zhang Z 2005 *Appl. Phsy. Lett.* **87** 202107
[11] Vandre D, Incoccia L and Kaindl G 1990 *Vacuum* **41** 687
[12] An K S, Park R J, Kim K S, Park C Y, Lee S B, Abukawa T, Kono S, Kinoshita T, Kakizaki A and Ishii T 1995 *J. Appl. Phys.* **78** 1151
[13] Shaltaf E, Mete E and Elliatŏglu S 2004 *Phys. Rev.* B **69** 125417
[14] Miyoshi E, Iura T, Sakai Y, Tochihara H, Tanaka S and Mori H 2003 *J. Mol. Stru. (Theochem)* **630** 225
[15] Miyoshi E, Mori H, Tanaka S and Sakai Y 2002 *Sur. Sci.* **514** 383
[16] Kresse G and Joubert J 1999 *Phys. Rev.* B **59** 1758
[17] Blochl P E 1994 *Phys. Rev.* B **50** 17953
[18] Monkhorst H J and Pack J D 1976 *Phys. Rev.* B **13** 5188
[19] Mills J, Jonsson H and Schenter G K 1995 *Sur. Sci.* **324** 305
[20] Bond W L 1960 *Acta Cryst.* **13** 814
[21] Qian G X, Martin R M and Chadi D J 1988 *Phys. Rev.* B **38** 7649
[22] Sakai Y, Miyoshi E and Katsuki S 1995 *Phys. Rev.* B **52** 14150
[23] Shaltaf E, Mete E and Elliatŏglu S 2005 *Con. Mat.* **1** 0504088