Ab initio Study of the Si Adsorption on Mo(110)

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Abstract. The energetics and the electronic structure of the Si/Mo(110) surface have been investigated using density functional theory calculations based on the generalized gradient approximation. The calculated potential energy surface for a single Si adatom reveals that a hollow site is favored for the adsorption of Si on Mo(110). The energy barrier for hopping between the hollow sites is located at the bridge site and is found to be 0.64 eV. The electron density plot indicates that four Mo-Si covalent bonds were formed around the Si atom at the hollow site. According to the surface formation energy for different Si coverage, 1 ML Si/Mo(110)$-p(1 \times 1)$ is energetically favorable for a Si-rich environment. For the Si-poor case, the clean Mo(110) surface is the most stable structure.

Keywords: density functional theory, Si adsorption, Mo(110), EUV lithography

1. Introduction

Extreme ultraviolet lithography (EUVL) is one of the leading next-generation lithography technologies [1–3]. The high-reflectance Mo/Si multilayer used in the EUVL system consists of polycrystalline Mo and amorphous Si layers that are separated by an interfacial region [4, 5]. In order to obtain high reflectivity, a minimal thickness of Mo/Si interface is required because the intermixing region tends to reduce reflectivity [6].

In this work *ab initio* total energy calculations of Si adsorption on the Mo(110) surface has been presented in order to clarify the explanation of the formation mechanism of the interfacial layer between Mo/Si. First, the potential energy surface (PES) of the Si adatom adsorbed on Mo(110) has been obtained to find the site of the lowest adsorption energy of Si adatom on Mo(110). Next, the electron density of Si/Mo(110) has been provided to obtain the nature of Mo‐Si bonding. Finally, the surface formation energy for various Si coverages has been calculated. From the surface formation energy, the stable Si/Mo(110) structure has been

proposed for successively higher quantities of adsorbed Si.

2. Calculation Method

The Vienna *ab initio* simulation package (VASP) [7] based on density functional theory has been employed to perform the *ab initio* total energy calculations. The exchange-correlation interaction between the electrons is described within the generalized gradient approximation (GGA) scheme [8]. The electron-ion interaction is treated by the projector augmented wave (PAW) potential [9]. The electron wave functions are expanded by plane waves with a kinetic energy cutoff of 225 eV to achieve the convergence of the bulk total energy to within 0.05 eV/atom. Self-consistent solutions to the Kohn-Sham equations [10] were obtained by employing an 8×8 Monkhorst-Pack k-point grid [11] in the Brillouin zone of Mo(110) $- (1 \times 1)$. With the use of a finer 12×12 k-point mesh, the energy changes are found to be less than 0.05 eV/(1×1). We also applied Fermi-function broadening scheme with the temperature-broadening for the Brillouin zone integration at 0.02 eV. The Mo(110) surface is modeled as a periodic slab consisting of the five layers of Mo and a vacuum region of 26.7 Å [12]. All the atoms, except

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for those on the central Mo layer, are relaxed until the Hellmann-Feynman forces [13] become less than 10 meV/Å using the conjugate gradient method [14].

To determine the theoretical equilibrium lattice constant of Si and Mo bulk, a series of total energy calculations for various lattice constants has been performed. From the acquired set of total energies, lattice constants are fit to the Murnaghan formula [15] of the equation of state [16]. The calculated theoretical equilibrium lattice constant of Mo and Si are 3.152 Å and 5.470 Å, respectively. To check the convergence of the adsorption energy, we have performed the calculation for various surface cell size of the slab from $p(1 \times 1)$ to (4×4) with one Si adatom. For the case of (2×2) surface cell, the error in the adsorption energy of Si is estimated to be less than 0.1 eV/Si atom, which is small enough for our purpose. Therefore, we used (2×2) surface supercell to address the energetics and to calculate the electronic structure for a single Si atom adsorption.

3.   Results and Discussion

To construct the PES for the adsorption of atomic Si on the clean Mo surface, the total energy as a function of the adsorbate position within the surface supercell was computed using a (2×2) supercell. The PES was sampled at a real space grid with a spatial resolution of about 0.4 Å in the $[\bar{1}10]$ direction and 0.56 Å in the [001] direction. At each grid point, the in-plane

position of the adsorbate is fixed and the rest of the atomic positions are fully relaxed. Then, the adsorption energy per adatom could be obtained from

$$E_{ads} = E[Si/Mo(110)] - E[Mo(110)] - \mu_{Si} \quad (1)$$

where E[Si/Mo(110)] is the total energy of the adsorbate-substrate system, E[Mo(110)] that of the Mo(110) substrate, and μ_{Si} the chemical potential of Si, in this case the same as the calculated cohesive energy, -5.43 eV/atom. The resulting PES is shown in Fig. 1. The PES has a minimum value at the hollow site (ⓐ in Fig. 1), and the calculated adsorption energy is 0.85 eV. The surface diffusion of Si adatoms seems to follow a straight path (ⓐ–ⓑ–ⓐ in Fig. 1). The energy barrier for Si adatom hopping on Mo(110) is located at the bridge site (ⓑ in Fig. 1) and is found to be as much as 0.64 eV higher than the hollow site.

Si adsorption should induce a change in the electron distribution near the Si atom. In order to elucidate how and to what degree a Si adatom modifies the electron distribution near surface, the total valence electron density and its change upon adsorption is plotted in Fig. 2. Here, the change in electron density upon adsorption is defined as

$$\delta\rho(r) = \rho(r)^{Si/Mo(110)} - \rho(r)^{Mo(110)} - \rho(r)^{Si} \quad (2)$$

where $\rho(r)^{Si/Mo(110)}$ is the total valence electron density of the Si adsorbate-substrate system, $\rho(r)^{Mo(110)}$
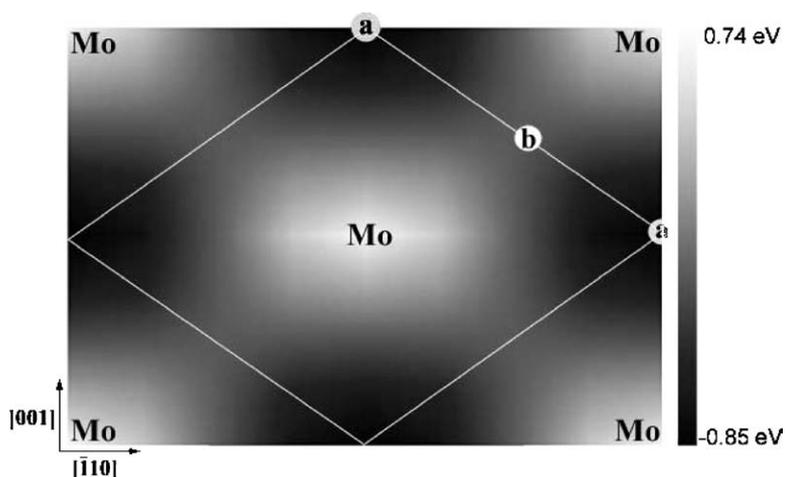
Fig. 1. The potential energy surface of a Si adatom on the Mo(110) surface. The symbol ⓐ represents a favored site, hollow site, for Si adatom. The solid white line, ⓐ–ⓑ–ⓐ, is the suggested path for surface diffusion for Si adatom.
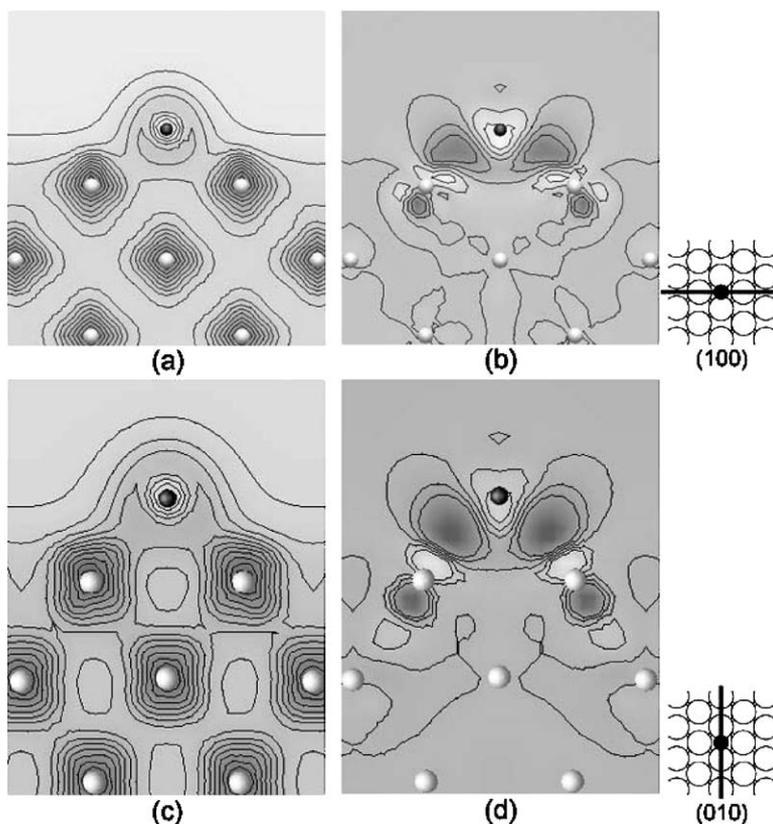
Fig. 2. Total electron density (a), (c) and its change upon Si adsorption (b), (d) plotted on the (100) and (010) plane. The contour lines are drawn for every 0.138 e/Å^3 for total electron density difference and 0.017 e/Å^3 for its change. Black and white circles represent for Si and Mo atoms, respectively. The darker shaded contour indicates the larger electron density in (a) and (c). In (b) and (d), the dark and the bright shaded contours indicate electron accumulation and depletion, respectively.

that of the clean Mo(110) substrate, and $\rho(r)^{Si}$ that of the free Si atom. The total electron density shown in Fig. 2 (a) and (c) is dominated by the localized Mo 4d electrons. However, it is evident that there is electron accumulation in-between the Si adatom and its four Mo neighbors. In other words, there are four covalent Mo—Si bonds formed per Si adatom. This is more clearly observed in the contour plots of $\delta\rho(r)$. In addition, comparison of Fig. 2(b) and (d) reveals that the Mo—Si bonds lying on the (010) plane are stronger than those in the (100) plane. This is expected since the bond length is shorter on the (010) plane.

To find the stable surface structure of Si/Mo(110), the surface formation energy for various Si coverage was calculated. The stable Si coverage (θ) is determined as the one having the lowest surface formation energy, Ω. Here, the surface formation energy is defined as

$$\Omega(\theta) = E[Si_\theta/Mo(110)] - E[Mo(110)] - n_{si}\mu_{si}$$

(3)

where $E[Si_\theta/Mo(110)]$ is the total energy of the adsorbate-substrate system with the Si coverage θ, and n_i the number of Si adatom. The value for μ_{Si} is bounded by their respective bulk values $\mu_{Si}^{(b)}$.

Figure 3 shows the calculated surface formation energy of the Si/Mo(110), as a function of the relative chemical potential of Si. The full geometry optimization has been performed for different Si coverage of 1, 1/2, 1/8, and 1/16 ML. For high values of μ_{Si}, (Si-rich environment), the surface with a 1 ML Si, Si /Mo(110)−$p(1 \times 1)$, is found to be the energetically favored structure. For low values of μ_{Si}, (Si-poor case), the clean Mo(110)
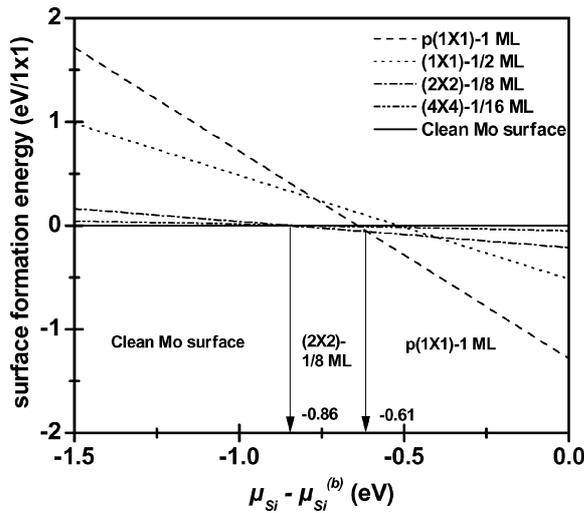
Fig. 3. Relative formation energy of the Si/Mo(110) surface, as a function of the Si chemical potential, with respect to the clean Mo(110) surface.

surface is the most stable structure. In-between, there is an interval of the Si chemical potential where 1/8 ML structure is energetically stabilized.

4.   Conclusions

The initial stage of Si deposition on Mo(110) and the subsequent formation of a Si over layer has been investigated using *ab initio* total energy calculations. The adsorption of a single Si atom is found to strongly favor the hollow site of Mo(110). According to the PES, surface diffusion of Si adatoms is realized as a series of hopping between the neighboring hollow sites, by overcoming a diffusion barrier of 0.64 eV located at the bridge site. The valence electron density reveals the formation of four Mo-Si covalent bonds per adsorbed Si atom. Analysis of the surface formation energy indicates that the stable surface structure changes from the clean Mo(110) surface to Si/Mo(110) $-$ (2×2) with

1/8 ML Si coverage and finally to Si/Mo(110) $-$ $p(1 \times 1)$ with 1 ML Si as the chemical potential of Si increases.

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