



DFT study of Rb/Si(100)-2 × 1 system

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Abstract

We have investigated Rb adsorption on the Si(100) surface for 0.5 and 1 monolayer coverages using the total energy method with norm-conserving pseudopotentials. For 2 × 1 reconstruction at 1 ML coverage symmetrized dimers are found to be energetically more favorable. On the other hand, half a ML coverage is found to have symmetrical dimers only for the most stable adsorption model. All possible surface-adatom configurations have been considered in the calculations to find which adsorption sites are energetically favored. In addition to the structural properties, the interface is investigated electronically for the work function and surface states. The results are discussed and compared with the existing experimental findings.

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1. Introduction

Silicon surfaces covered with alkali metal (AM) atoms have been investigated extensively for various coverage models [1–10]. The motivation behind these studies is to understand the metal–semiconductor junctions and to study metallization of semiconductor surfaces. In addition, from technological point of view, AM–Si interfaces are considered for possible nanoscale device applica-

tions [11]. One may expect alkali metal adsorbed silicon surfaces to exhibit similar characteristics. However, systematic differences arise as one goes from lighter atoms to heavier ones leading to different electronic behavior. The discussion, especially, on the atomic and electronic structure of alkali metal adsorbed Si(100)-2 × 1 surface is still under debate which concerns the matters such as the adsorption sites, the saturation coverage at room temperature (RT), the nature of alkali metal–Si bond and the charge transfer from the adsorbate to the substrate.

Another reason why AM adsorption on Si surfaces attracted much interest is that AM's have

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simple electronic structures and do not intermix with the surface Si atoms, except Li, allowing us to investigate a relatively simpler interface. Therefore Si–AM systems were seen as a prototype to understand the physics of AM overlayers on semiconductor surfaces. In the last years the advances in the engineering of nano scale structures allow device designs based upon these contacts on the atomic scale.

There are, fundamentally, two proposed coverage models which have been experimentally realized. These are 0.5 and 1 ML coverages. Half a ML model has been first studied by Levine for Cs/Si(100)- 2×1 system [3]. In this model alkali metal atoms are placed in the middle of neighboring dimers in the same row. This adsorption location is called as pedestal site, *p*, (see Fig. 1). Alkali metal atoms adsorbed on pedestal site form a linear chain along the dimer row preserving 2×1 surface symmetry.

In recent years, there is much interest towards larger alkali metals (Rb and Cs) [4–7]. Eteläniemi et al. studied the adsorption sites of Rb adsorbates on Si(100) surface with XSW experiments for various coverages [8]. They attempted to define the surface geometry at the saturation coverage. Castucci et al. determined AM–Si bond length and the Rb site distribution on Si(001) 2×1 surface for low (0.19 ± 0.02) coverages using XSW [9]. Chao et al. investigated the surface electronic structure and work function shifts as a function of the Rb coverage [5,10]. Johansson et al. made a systematic

study of the electronic structure for Rb adsorption on Si(100) 2×1 surface with ARUPS and IPES by comparing to the results of other AM's [4].

In this work our aim is to study Rb adsorbed Si(100) surface with 2×1 periodicity for 0.5 and 1 ML coverages which include experimentally realized adsorption sites. Main focuses of this study are to determine the atomic structure of Si surface reconstructed with Rb coverage, to discuss the saturation coverage with an emphasis on the Si dangling bonds and surface work function, and to investigate the electronic structure to identify surface states. This is, to the best of our knowledge, the first theoretical work that investigates the Rb adsorption on Si(100) surface.

2. Computational details

The calculations were performed using the plane-wave expansion approach within the local density approximation to density functional theory as implemented in the ABINIT code [12]. We generated Troullier–Martins pseudopotentials [13] using fhi98pp [14] package with PW92 [15] exchange–correlation model. We treated the true electronic valence states in the calculations. Non-linear core-valence corrections were taken into account for the case of Rb by setting the cut-off radius to 3.6 bohrs. To test Rb pseudopotential, Rb crystals having bcc structure have been reproduced with the lattice parameter 5.49 Å. This value

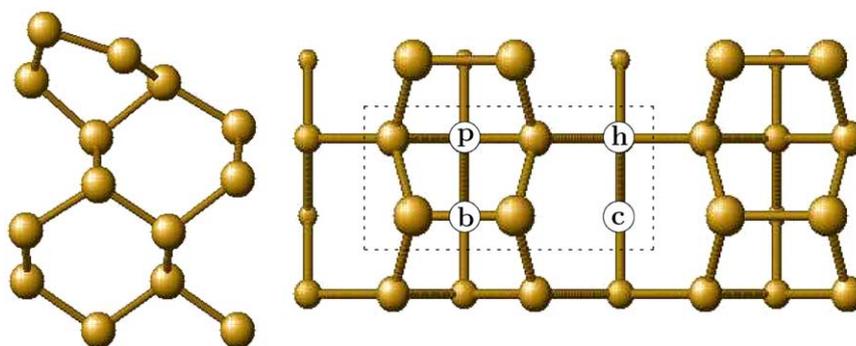


Fig. 1. On the left : schematics are shown for the side view of relaxed clean Si(100)- 2×1 surface. On the right : top view of Si(100) surface with all possible stable adsorption sites are illustrated. (Dimers are shown as symmetrical for visual convenience.) Dashed box defines the supercell boundary on the surface.

is 1.6% lower than the experimental value of 5.58 Å [16].

We carefully tested the convergence behavior of our calculations with respect both to the plane-wave cut-off and to the k -point grid. A series of tests showed that $8 \times 4 \times 1$ Monkhorst–Pack mesh [17] with 16 Ryd cut-off gives well converged results for our self-consistent calculations. In other words, any further increase in these parameters would not enhance the accuracy of the calculated values like lattice constants, band structures, etc. The convergence criterion to reach the lowest energy configuration is determined by minimizing the forces using the Hellmann–Feynman theorem.

For surface geometry and band structure calculations we have used a slab with 8 layers of Si. In order to prevent an interaction between the two surfaces, the bulk dangling bonds are hydrogenated and a vacuum region of 10 Å is used. In geometry optimization calculations, Si atoms which stay at the two bottom layers are kept frozen and all the other atoms are let relax to their minimum energy configurations. In order to observe if the surface symmetry breaks we did not impose any symmetry operations other than the identity which naturally incorporates.

We performed separate self-consistent calculations to determine surface work function using a symmetrical slab having a thickness equal to 10 Si layers and being separated from each other with a vacuum region of ~ 10 Å. After relaxing the clean surface into minimum energy geometry we

frozeed 4 Si atoms which are located in the middle of this slab. We also repeated geometry optimizations using symmetrical slab for all of the coverage models as done in the case of hydrogenated surface. These calculations produced equivalent results.

3. Results and discussion

Although a number of experimental studies are present for Rb adsorption on Si(100) surface, no first principles work has been published yet. This paper not only studies Rb adsorption on Si(100) theoretically, but also presents calculated results like Rb–Si bond length, adsorption energy, etc. which have not been measured experimentally. In a few papers these values are estimated from the theoretical studies for K/Si(001) or Cs/Si(001) systems. We tabulated our calculated results for structural properties in Table 1. For the surface energetics we used the formula as described in Ref. [18] to calculate the adsorption energies. The adsorption energy represents the negative of the binding energy.

Our calculated clean surface dimer length is 2.27 Å. It compares well with the experimental value of 2.20 ± 0.05 Å [19]. This value becomes larger because of the adsorption which causes Rb to make a charge transfer to the closest dimer Si atom. In turn, this saturation of the dangling bonds on the surface leads to a stretching of the

Table 1
Calculated parameters for the atomic structure of 0.5 ML and 1 ML coverages of Rb adsorption on Si(100) 2×1 system

θ	Model	d_{dimer}	$d_{\text{Rb-Si}}$	Δx	$\alpha_{\text{tilting}} (^{\circ})$	$E_{\text{ad}} (\text{eV})$
0.5	<i>h</i>	2.32	3.23	1.26	2.4	1.69
	<i>p</i>	2.39	3.22	2.36	8.0	1.28
	<i>c</i>	2.30	3.17	1.67	5.6	1.21
	<i>b</i>	2.37	3.26	3.01	10.4	0.74
1	<i>h-p</i>	2.49	3.20–3.24	1.11–2.32	–	1.72
	<i>b-h</i>	2.48	3.22–3.20	2.98–1.15	–	1.46
	<i>c-p</i>	2.42	3.14–3.24	1.76–2.34	–	1.39
	<i>b-c</i>	2.40	3.26–3.10	3.04–1.67	–	1.11
	<i>c-h</i>	2.34	2.94–3.31	1.30–1.27	–	0.68
	<i>b-p</i>	2.44	3.00–3.25	2.75–2.34	–	0.50

The lengths, d_{dimer} , $d_{\text{Rb-Si}}$ and Δx , are all in Å. $d_{\text{Rb-Si}}$ is the distance from Rb atom, adsorbed at the corresponding site, to the nearest Si atom. Δx is the height of the Rb atom measured from the dimer center.

dimer. When we compare the dimer lengths between 0.5 ML and 1 ML coverages, we see that the dimer is more stretched for 1 ML adsorption models.

For 0.5 ML coverage, bridge (*b*), cave (*c*), hollow (*h*) and pedestal (*p*) sites are found to be stable adsorption configurations. We tested the stability of two more sites which are the top of one of the dimer Si atoms and the site on the half way from *p* to *h*, so called the shallow site. None of these two sites were found to be stable. Each time we put an Rb atom on these locations they relaxed into the nearest stable sites. Energetically the most favorable adsorption site is *h*. The total energy of this geometry is 0.41 eV lower than the second lowest configuration *p*. This surface geometry has the dimer length of 2.32 Å with a tilting angle of 2.4°. Symmetrical dimers which correspond to a tilting angle of less than 5° are found only for this model. The other adsorption configurations—*b*, *c* and *p*—result in asymmetrical dimers.

For 1 ML coverage, we have studied all the possible adsorption configurations and have found bridge–cave (*b–c*), bridge–hollow (*b–h*), bridge–pedestal (*b–p*), cave–pedestal (*c–p*), cave–hollow (*c–h*) and hollow–pedestal (*h–p*) are the stable site combinations. Any combination with the top and/or shallow sites which are as described in the case of half ML, are energetically unstable. Based on an estimation for the Rb–Si bond distance Eteläniemi et al. [8] argue that two nearest neighbor adsorption sites cannot be occupied at the same time.

We found that these configurations (*b–p* and *c–h*) produce the lowest two adsorption energies. Therefore, they are energetically the least probable adsorption models for 1 ML coverage.

The 2×1 symmetry was found to be preserved for these 1 ML adsorption coverage models as suggested by the LEED result of Chao et al. [10,5] and ARUPS result of Johansson et al. [4]. Among these *h–p* is the energetically most favorable configuration which corresponds to PV model of Eteläniemi et al. [8]. In our calculations *h–p* has a total energy of 0.52 eV less than the second lowest energy coverage model *b–h*. Rb–Si bond length for this configuration has been found to be 3.20 Å and 3.24 Å measured from Rb atoms at *h*-site and *p*-site, respectively, to the nearest Si atom. Concerning this bond length Eteläniemi et al. [8] reported a value of 3.31 ± 0.1 Å. This was based upon an estimation expecting that the value closely reproduces the sum of covalent radii. Castrucci et al. [9], on the other hand, obtained the bond length to be 3.06 ± 0.03 Å which favors a partly ionic character for Rb–Si bonding. Our result supports the idea that the nature of Rb–Si bond is not purely covalent but is rather referred as ionic covalent. This is also suggested by our calculations for charge density which gives a small fraction of charge around Rb adatom. The effect of Rb adsorption appears to cause alteration of Si(100) surface. In this geometry symmetrically dimerized surface is energetically favored. After the relaxation the dimer length is measured to be 2.49 Å

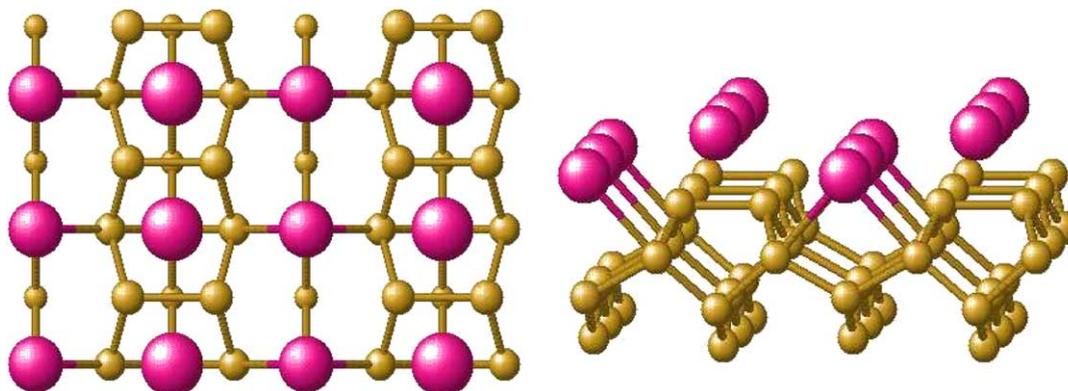


Fig. 2. On the left : Illustration for top view of *h–p* (or double layer) adsorption model on Si(100)- 2×1 surface. (Upper is shown bigger.) On the right : side view of Rb/Si(100)- 2×1 system for 1 ML *h–p* configuration.

which is close to the experimental value of 2.3–2.4 Å reported by Eteläniemi et al. [8]. This adsorption model is also referred as the double layer model. Rb atoms adsorbed at *h* and *p*-sites are separated a distance 1.21 Å along [100] as shown in Fig. 2. This difference in the heights is close to one Si layer which has the value ~1.20–1.30 Å. In this model the nearest-neighbor distances for the Rb atoms have been predicted by Johansson et al. to be 3.84–4.0 Å [4] which is in a very good agreement with our calculated values of 3.82 Å along [0 1 1] and 4.0 Å along [0 $\bar{1}$ 1].

The work function is calculated as the difference between the vacuum level and the Fermi energy (E_F). The vacuum level is determined from the self-consistent, plane-averaged potential (V_{av}) in the middle of the symmetrical slabs along the direction [100] perpendicular to the surfaces. It can be obtained from the Poisson's equation,

$$\frac{\partial^2}{\partial x^2} V_{av}(x) = -4\pi\rho_{av}(x) \quad (1)$$

and is given by the relation,

$$V_{av}(x) = -4\pi \int_x^\infty \rho_{av}(x')x' dx' + 4\pi x \int_x^\infty \rho_{av}(x') dx' \quad (2)$$

where

$$\rho_{av}(x) = \frac{1}{A} \int \int_A |\psi(x, y, z)|^2 dy dz. \quad (3)$$

Calculated values for the plane-averaged electrostatic potential and the work function corresponding to different adsorption models are shown in the Fig. 3 by setting the zero level at the Fermi energy. Fig. 3(a) represents clean surface. The work function for Si(100)-2 × 1 surface was reported as 4.9 eV by Abukawa et al. [20]. It agrees very well with our theoretical result of 4.9 eV, for the clean relaxed surface. Fig. 3(b) corresponds to the half ML model of Levine [3] which is the *h*-model in our case. For 1 ML coverage we presented the result in Fig. 3(c) which represents PV model of Eteläniemi et al. [8] which is the *h-p* model in

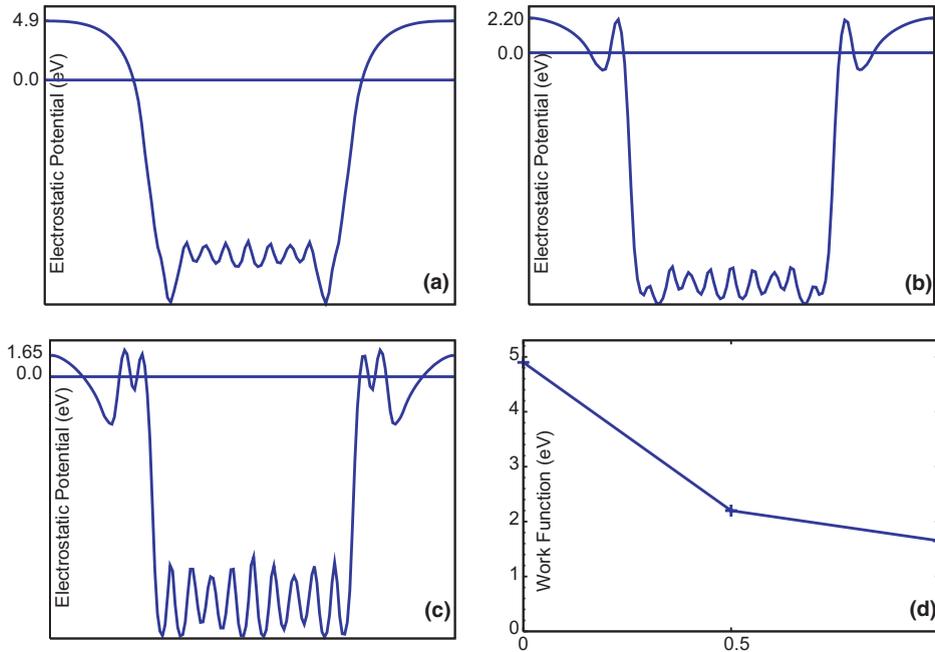


Fig. 3. Planar-averaged electrostatic potential $V(x)$: (a) for the clean relaxed geometry, (b) for *h* adsorption model, (c) for *h-p* model along [100], the direction perpendicular to the surface within the cell and (d) calculated shifts in work function as a function of the coverage.

our calculations. The zigzag regions in the middle of these figures represent Si layers in the bulk. A Si atom layer sits in each valley and a localized charge coincides with each peak in this bulk region. Each peak above the Fermi level represents the position of a Rb atom. The tails of the electrostatic potential away from the bulk region go into the vacuum regions.

The work functions were calculated as 2.20 eV and 1.65 eV for the cases of 0.5 ML and 1 ML, respectively. When compared with the results of Johansson et al. [4] and Chao et al. [5], we obtained a similar behavior for the change in the work function as Rb coverage increases. These work function shifts as a function of coverage are shown in Fig. 3(d). The lowering in the work function is more rapid between the clean surface and 0.5 ML coverage than that of between 0.5 ML and 1 ML coverages. This behavior is consistent with the experimental observations [4,5]. Moreover, they reported that the work function takes a constant value after the saturation coverage. This can be explained by the fact that there is no further lowering in the work function by Rb adsorption after the saturation reached for Si(100) surface. It appears from Fig. 3(d) that 0.5 ML cannot be the saturation coverage for Rb/Si(100)- 2×1 system since there is a shift in the work function for the coverages greater than half a ML. We calculated the change in the work function for 1 ML to be 3.25 eV. The experimental result for the saturation coverage is 3.4 eV given by Johansson et al. [4] and Chao et al. [5]. The comparison of our theoretical results with the experimental findings gives a strong evidence that the saturation coverage occurs at about 1 ML.

The bulk projected surface band structure is presented for full coverage in Fig. 4. Energy values are given relative to the valence band maximum (VBM) along high symmetry points. The direct band gap is calculated to be 0.47 eV which is underestimated by LDA as expected. The experimental value was given as 0.6 eV by Johansson et al. [4]. Conduction band minimum (CBM) and valence band maximum (VBM) both occur at Γ . The overall electronic behavior reveals similar characteristics to the Si(100)- 2×1 -AM band structure except the dispersion and location of surface

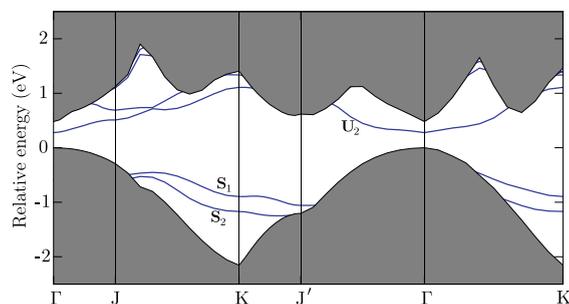


Fig. 4. Bulk projected surface energy bands for 1 ML coverage. The shaded region is the projected bulk band continuum.

states. We identified surface states which fall into the band gap. Two unoccupied and two occupied surface states are shown in Fig. 4.

Chao et al. in their ARUPS study, reported two Rb-induced surface states $C1$ and $C2$ for a RT saturated Si(100)- 2×1 surface with energies of -0.55 and -1.55 eV at Γ , respectively [5]. Their results are in favor of the proposed double-layer model which leads to a semiconducting surface. The states $C1$ and $C2$ correspond to the occupied states $S1$ and $S2$ in our case with the energies -0.35 and -0.72 eV at Γ .

Johansson et al. observed a Rb-overlayer derived empty band, $U2$, with a large isotropic dispersion [4]. They argued that even though they observed a metallization due to the large dispersion of the unoccupied band $U2$ at saturation coverage, the surface electronic behavior is expected to be semiconducting at 1 ML with a surface band gap of about 0.6 eV as they measured. The explanation of the occupation of this empty band was given by the presence of small amounts of excess charge on the surface together with the close energy position of $U2$ at VBM. The minimum of this band was reported to be about 0.2 eV above the VBM at Γ [4]. There is a good agreement with this experimental value such that we found the separation between the $U2$ minimum and the VBM to be 0.25 eV. Although they observed a metallization at saturation coverage we see from Fig. 4 that Rb/Si(100)- 2×1 system has a semiconducting electronic structure at 1 ML for the h - p -model even we see a large dispersion of 0.84 eV in the conduction band $U2$.

4. Conclusion

In the case of 0.5 and 1 ML coverages, all possible configurations were studied for Rb adsorption on Si(100) surface having $p(2 \times 1)$ symmetry. For 0.5 ML coverage, h -site and for 1 ML coverage, $h-p$ model are found to be the minimum energy configurations. Our results suggest that Rb atoms prefer to be adsorbed firstly, on h -site then on p -site as the coverage increases.

Clean surface work function was calculated to be 4.9 eV which is equivalent to the experimental value of Abukawa et al. [20]. The work functions for 0.5 ML and 1 ML are 2.20 eV and 1.65 eV, respectively. A 3.25 eV shift in the work function was found for $h-p$ model which agrees well with the experimentally observed shift of 3.4 eV for the saturation coverage at RT. Bulk-projected surface bands were calculated within the affinity of the gap for the case of $h-p$ model. Experimentally resolved S_1 and S_2 bands together with the unoccupied U_2 band are identified as surface states. 1 ML Rb adsorbed Si(100)- 2×1 surface was electronically found to be semiconducting. Being consistent with the experiments, the separation at Γ was found to be 0.25 eV between VBM and Rb driven band U_2 . When the change in work function and the energetics of the surfaces are compared, our results support the double-layer model ($h-p$) as the saturation coverage. Our theoretical results fit well to the picture drawn by the experimental findings.

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