

Cs adsorption on Si(001) surface: ab initio study

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(Dated: December 22, 2018)

First-principles calculations using density functional theory based on norm-conserving pseudopotentials have been performed to investigate the Cs adsorption on the Si(001) surface for 0.5 and 1 ML coverages. We found that the saturation coverage corresponds to 1 ML adsorption with two Cs atoms occupying the double layer model sites. While the energy bands spectra of the 0.5 ML covered surface is of metallic nature, we found that 1 ML Cs adlayer leads to a semiconducting surface. The results for the electronic behavior and surface work function suggest that adsorption of Cs takes place via polarized covalent bonding. The nature of Cs-Si bond shows a hybrid character of $s - p$ type implying a limited charge transfer from the adsorbate to the substrate.

PACS numbers: 68.43.Bc, 68.43.Fg

I. INTRODUCTION

The adsorption of alkali metals on semiconductor surfaces has been the topic of interest for several decades. The experimental and theoretical studies were motivated by various technological applications as in the low-temperature and low-field electron emission sources and as for the catalyzers of silicon dioxide growth on silicon surfaces. In the latter case Cs might be a better choice because the adsorption of Cs atoms on Si surface alters the Si surface structure only a little, which enables them to be desorbed from the Si surface very easily.

First experiments on Cs/Si(001) system were performed by Goldstein¹ and Levine² in the early seventies. Using low-energy-electron-diffraction (LEED) and Auger-electron-spectroscopy (AES) they proposed a model in which Cs atoms are adsorbed on pedestal sites forming single Cs chains running along the dimer rows, hence the saturation coverage was believed to be 0.5 ML. Based on this model the electronic properties of the covered surface will have a metallic nature as can be predicted from simple electron counting. This model was generally accepted in the proceeding years until the x-ray photoelectron diffraction (XPD) results of Abukawa and Kono³ revealed that at saturation coverage, alkali adsorbent atoms, like K and Cs, will form two sets of arrays (a double layer), with a vertical separation of ~ 1 Å. Abukawa and Kono proposed a model in which the atoms get adsorbed simultaneously on two different sites, namely hollow and pedestal sites. The electronic properties of Cs/Si(001) as investigated by Enta et al.⁴ using angle-resolved ultraviolet photoemission spectroscopy (ARUPS) were consistent with the double layer model. Their results for surface state dispersion showed a semi-

conducting surface which agrees with the double layer model. Smith et al.⁵ estimated using medium energy ion scattering in conjunction with AES and LEED a saturation coverage of 0.97 ± 0.05 , a result which also supports the double layer model.

Even though Abukawa model³ was adopted and supported in many other works^{6,7,8,9,10,11,12,13}, the saturation coverage and adsorption sites of Cs/Si(001) still stay as the matter of debate. In a recent experimental work using He Rutherford backscattering, Sherman et al.¹⁴ found that saturation can not exceed 0.5 ML supporting the Levine model, they rejected the existence of DML (double monolayer) model. Kim et al.¹⁵ also arrived at the same conclusion based on their coaxial impact collision ion scattering spectroscopy. Meyerheim et al.,¹⁶ however, accepted the saturation coverage being 1 ML, but they suggested that adsorption on bridge (mid-point above the Si dimer) and hollow sites might be more stable than the Abukawa model.

The atomic reconstruction of covered surface, the bonding between the Cs atom and the Si surface, as well as the electronic properties of the covered surface still present a matter of dispute. For instance, it was suggested by various experiments^{16,17} that adsorption of Cs symmetrizes the dimers. However, Chao et al.,^{9,10,11} argued that the dimer structure is still asymmetric. On the other hand, using ARUPS⁴, extended x-ray absorption fine structure spectroscopy^{6,8} (EXAFS), and threshold photoemission spectroscopy¹² results it was concluded that the adsorption of Cs atoms on Si(001) surface takes place via covalent bonding, moreover, partially ionic bonding was suggested by synchrotron radiation photoemission by Lin et al.,⁷ and even further, a pure ionic bonding was proposed by the low energy D-scattering results of Souda et al.¹⁸

In this work, we employed ab initio total energy-pseudopotential method to study the adsorption of Cs on Si(001) surface at the previously proposed saturation coverages. We investigated the structural and electronic properties as well as the work function of the covered surface to get a better understanding of this system.

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II. METHOD

We used pseudopotential method based on density functional theory in the local density approximation. The self consistent norm conserving pseudopotentials of silicon and hydrogen were generated by using the Hamann scheme¹⁹ that is included in the fhi98PP package.²⁰ Nonlinear core corrections were included in the norm-conserving pseudopotential of Cs generated by using the Troullier-Martins scheme.²¹ In order to solve the Kohn-Sham equations, conjugate gradients minimization method²² was employed as implemented by the ABINIT code.^{23,24} The exchange-correlation effects were taken into account within the Perdew-Wang scheme²⁵ as parameterized by Ceperley and Alder.²⁶

The surface unit cell (SUC) includes a slab with 8 layers of Si atoms and a vacuum region equal to about 9 Å in thickness. Single-particle wave functions were expanded using a plane wave basis up to a kinetic energy cut-off equal to 16 Ry. The Brillouin zone integration was performed using 16 special \vec{k} -points that are sampled with the Monkhorst-Pack scheme.²⁷

We used the 2×1 unit cell for the clean Si(001) surface in our calculations, which is obtained by using the above parameters, and having the lowest two layers (out of 8) kept fixed in their ideal bulk positions while all the remaining substrate atoms were allowed to relax into their minimum energy positions.

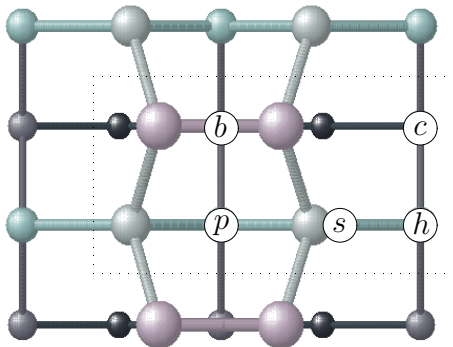


FIG. 1: Schematics of the adsorption sites for Cs atom on Si(001) surface. Surface unit cell is indicated by dashed box. The symbols stand for: b =bridge, p =pedestal, h =hollow, s =shallow and c =cave. (The dimers are shown symmetric here for visual convenience)

The resultant relaxed structure has asymmetric dimers with a dimer length of 2.27 Å and a tilt angle of 18.1°. Our result for clean Si(001) is in agreement with the theoretical results of Ramstad et al.²⁸ who found a dimer length of 2.26 Å with a tilting angle being 18.3°.

We performed separate self-consistent calculations to determine surface work function and formation energy using a symmetrical slab having a thickness equal to 10 Si layers and being separated from each other with a vacuum region of ~ 15 Å. After relaxing the clean surface into its minimum energy geometry we froze the 4 Si atoms

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

III. RESULTS AND DISCUSSION

We have studied the adsorption of Cs atoms on the Si(001) surface for 0.5 ML and 1 ML coverages, starting with the reconstructed (2×1) surface unit cell. We have chosen five different sites for the adsorption, namely, the cave, hollow, pedestal, bridge and the shallow sites. The cave site (c) is located above the fourth layer Si, hollow (h) and pedestal (p) sites are above the third layer Si, shallow site (s) is above the second layer Si between the two Si dimers, and the bridge site (b) is located above the dimer as indicated in Figure 1. The adatom and the substrate were then taken to their minimum energy configurations by performing structural optimization using the Broyden-Fletcher-Goldfarb-Shanno method²⁹ until the force on each atom reduces to a value less than 25 meV/Å.

A. Structural Properties

We have found that adsorption of Cs on h site is the most stable one with an adsorption energy per adatom, E_{ad} , equal to 2.46 eV, which is the negative of the binding energy of the adatom, and defined by the expression

$$n E_{ad} = (E_{\text{Si}(001)} + n E_{\text{Cs}}) - E_{\text{Cs/Si}(001)}. \quad (1)$$

Here, $E_{\text{Cs/Si}(001)}$ is the total energy of the covered surface, $E_{\text{Si}(001)}$ is the total energy of the clean surface, n is the number of Cs adatoms in a surface unit cell and E_{Cs} is the total energy of a single Cs atom with the spin polarization obtained in a separate ab initio calculation using the same pseudopotential and the same kinetic energy cut off, but in a larger unit cell of size ~ 26 Å.

The adsorption of Cs atom on this site symmetrizes the dimers with resulting dimer lengths equal to 2.34 Å. Other configurations of adsorption on p , c and b sites were found less stable with adsorption energies of 2.02, 1.89 and 1.46 eV, respectively, and with dimers still tilted in various angles as listed in Table I. Finally, the adsorption on s site was not found as a well defined local minimum with the adatom migrating into a neighboring h site. Our results suggest that if the saturation coverage would exist then it must contain h site as being the most probable adsorption site. Therefore, Levine's model appears to be obsolete which assumes the adsorption of Cs atom on a p site. On the other hand, our agreement is merely for the adsorption site with Kim et al.¹⁵ who found that the saturation coverage corresponds to 0.5 ML with a single Cs atom being adsorbed on h site only. The height of

TABLE I: The structural parameters for most of the stable adsorption sites for two different coverages Θ . The dimer lengths, heights of the adatoms with respect to the second silicon monolayer (all in Å) and the adsorption energies (E_{ad} in eV) for these cases are presented. The quantities in parenthesis are tilt angles (in degrees) of the corresponding dimers.

Θ	Model	dimer	d_{\perp}	E_{ad}
0.5	<i>h</i>	2.34 (0.8)	2.75	2.46
	<i>p</i>	2.39 (8.7)	3.75	2.02
	<i>c</i>	2.31 (7.5)	3.15	1.89
	<i>b</i>	2.37 (11.1)	4.30	1.46
1	<i>h-p</i>	2.46	2.67 3.86	2.39
	<i>h-b</i>	2.46	2.66 4.50	2.18

Cs atom from the second silicon layer is found to be 2.75 Å, which is smaller than their experimental value¹⁵ of 3.18 ± 0.05 Å. The distance between Cs atom and the nearest Si atom was found to be 3.58 Å which is close to their experimental value¹⁵ of 3.71 ± 0.05 Å. Hashizume et al.,³⁰ using field ion scanning tunneling microscopy, studied the adsorption at very low coverage, and suggested that adsorption takes place at the off-center hollow site (a non-symmetric site between *h* and *s* in our notation). This site has been also accepted by Gorelik et al.³¹ who made use of local surface photo voltage (SPV), current imaging, and also scanning tunneling microscopy, however, it has been rejected by a recent experimental work by Park et al.,³² who found rather the *h* site as the most stable one. While the off-center site might be stable for low coverages as reported by the references^{30,31} we did not find any theoretical evidence for this at the coverages studied in this work. Our aim being to study the cases close to the previously reported saturation coverages, this off-center site was also checked as the starting point for the 0.5 ML adsorption case and was verified that the Cs adatom migrates to the closest *h* site.

For the full coverage we have considered only the combinations that included *h* site as the starting configurations. We have four different combinations from which we found that the Abukawa model, with Cs atoms adsorbed at the *h-p* sites, was found as the most stable one with an adsorption energy of 2.39 eV. The heights of the Cs atoms as measured from the second Si ML, were 2.67 Å and 3.86 Å for *h* and *p* sites, respectively. The double layer height difference corresponds to 1.19 Å which is in excellent agreement with the experimental value³ of 1.2 Å. Meyerheim et al.¹⁶ using surface x-ray diffraction investigated the atomic structure of Cs/Si(001), and found that the saturation coverage corresponds to the combination of two adsorption sites *b* and *h*. According to our results, even though this model was found stable, it is

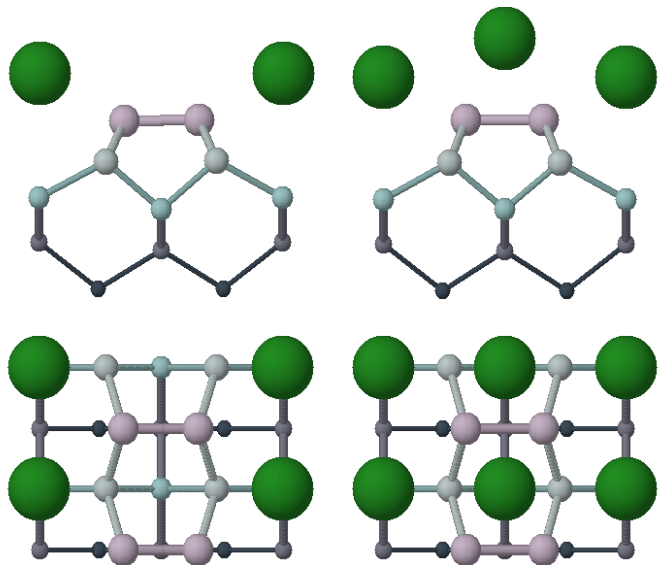


FIG. 2: Cs overlayer adsorbed on Si(001) surface (a) for 0.5 ML coverage on *h* site and (b) for 1 ML coverage on *h-p* site. Only the upper part of the slab is shown here.

less stable than the Abukawa model by 0.2 eV per Cs adatom. Figure 2 shows the most stable configurations for each coverage.

TABLE II: The structural parameters (in Å) for *h-p* model versus the previously reported experimental work. The double layer height differences, Δ_{\perp} , are also presented.

	dimer	Cs-Si ₁	Cs-Si ₂	Δ_{\perp}
This work	2.46	3.41	3.49	1.19
EXAFS ⁸	2.48 ± 0.06	3.57 ± 0.06		
Tensor LEED ¹³	2.50	3.72	3.94	0.66
XPD ³	–	–	–	1.2 ± 0.1

In Table II we tabulate our calculated structural parameters for the *h-p* case along with the experimental values. Our calculated bond lengths for Cs-Si bonds, being 3.41 Å and 3.49 Å, were in good agreement with 3.57 Å obtained from EXAFS⁸ and somewhat smaller than the tensor LEED values¹³ of 3.72 Å and 3.94 Å. We did not find that the adsorption of Cs atoms on the surface leads to significant alteration of the substrate. For the case of double layer adsorption we found that the major changes in the substrate take place in the dimer layer (Si first layer), where the upper atom in dimer gets pushed down by a distance of 0.09 Å while the lower atom is pushed up by a distance equal to 0.61 Å. In the mean time, both adatoms get displaced along $[0\bar{1}0]$ by 0.5 Å and 0.2 Å, respectively. Reconstruction in deeper silicon layers is not significant and it ranges around 0.01 – 0.06 Å only.

This result agrees well with the fact that Cs adatoms do not alter the silicon surface very much as was also suggested by Kim et al.⁶ The reconstruction of the surface leads to symmetric dimers with dimer lengths of 2.46 Å in excellent agreement with the experimental value⁸ of 2.48 ± 0.06 Å. The symmetrization of silicon dimers by Cs adsorption was found in agreement with various other experimental results^{13,16} in contrast to the high-resolution core-level spectroscopy and angle-resolved valence-band spectroscopy of Chao et al.^{9,11} who argued that the Si dimers stay asymmetric. Abukawa et al.¹⁷ studied the surface by means of core-level photoemission for the covered surface Si(001) 2×1 -Cs and found that the surface dimers are symmetric and excluded the results of Chao et al.^{9,11}

B. Electronic Properties

1. Energy Bands

In Figure 3 we show our calculated band configurations for the lowest energy structures of the 0.5 and 1 ML covered Si(001) surface. For the clean surface we have two surface states in the fundamental gap, namely S_1 and S_2 , and the S_2 state usually appears above the Fermi level. When the Cs atom gets adsorbed on h site for the half ML case, its effect will be the shifting of this state downward towards the valence bands, crossing the Fermi level and causing a metallic behavior due to the partial filling of the S_2 dangling bond band (Fig. 3(a)).

For the full ML coverage with adsorption of Abukawa type ($h-p$), the dispersion shows a semiconducting surface as expected, and in agreement with ARUPS results of Enta et al.⁴ We have a direct gap at Γ with a band gap value of 0.30 eV (Fig. 3(b)). This semiconducting nature of the surface might be due to the saturation of the dimer dangling bonds. Benemanskaya et al.¹² expected that at 1 ML coverage, the adsorbed surface will be semiconducting with two surface state bands, S_3 and S_4 , appearing in the band gap below the bottom of the conduction band which is in good agreement with our theoretical results.

The occupied band S_1 represents the π -like silicon dangling bond surface state, while S_2 corresponds to the π^* -like Si dangling bond state, which are shown in Figure 3. In order to study the nature of these states we calculated the 3D charge density distributions for these occupied surface states at 1 ML coverage at the K and J high symmetry SBZ points. These plots are given for the surface state S_1 in Figures 4(a) and 4(c), and for S_2 in 4(b) and 4(d) at K and J points, respectively. The electronic character of π and π^* Si dangling bond surface states show partial contribution from the adsorbed Cs atoms which can readily be seen in the Figures 4(c) and 4(d) at the J point of the SBZ. At J point, in Figure 4(c), the contribution to surface state S_1 comes from the upper Cs adatom while it is vice versa for S_2 , as seen in

Figure 4(d). At K point the composition of the surface states S_1 and S_2 show more contribution from the lower Cs adatom.

The unoccupied low-lying surface states originate mainly because of the adsorbed Cs atoms. They show a hybrid character as a combination of Cs atomic s -orbital and dimer Si dangling bond orbitals.

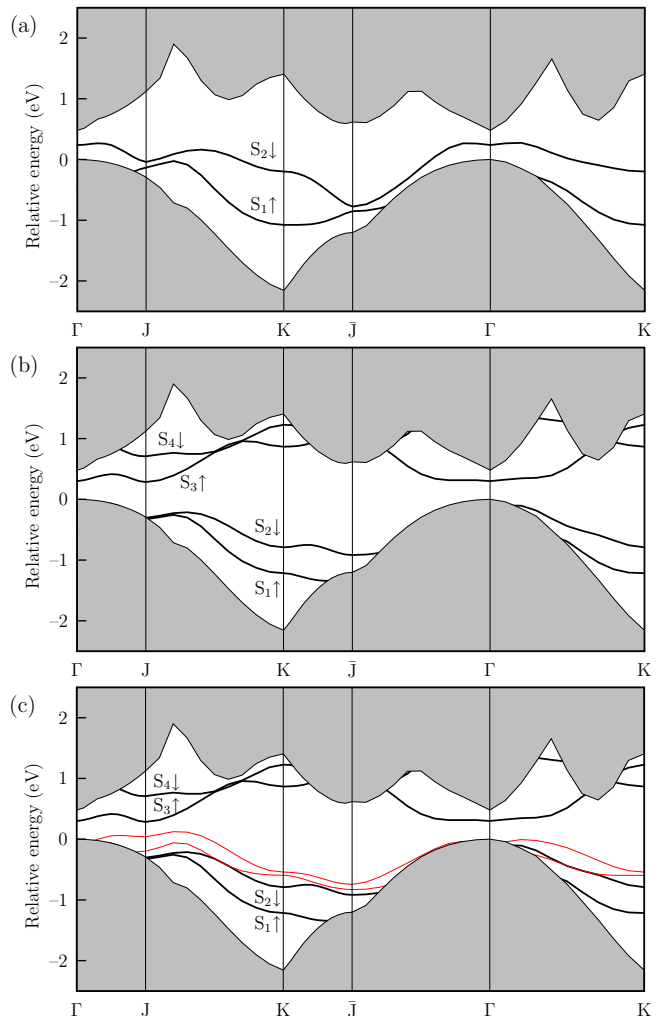


FIG. 3: Electronic band structure of the Si(001) 2×1 surface for (a) 0.5 ML Cs coverage and (b) 1 ML Abukawa model. Projected bulk continuum is shown by the shaded region. (c) Same substrate as in (b) reconstructed due to adsorption of 1 ML Cs (thick lines), but the Cs adatoms are taken away (thin lines).

The adsorption of Cs atoms causes a substantial shift in the energies of surface states S_1 and S_2 towards bulk valence band continuum over the whole SBZ as a result of the increase in the binding energies. In the case of 1 ML coverage Figure 3(b) shows maximum change in the dispersions for S_1 at J and for S_2 at K. Other significant deviations appear at \bar{J} and J for S_1 and S_2 , respectively. At K and \bar{J} points S_1 and S_2 get closer when no Cs present. This implies Cs-Cs electronic interaction is dominant at

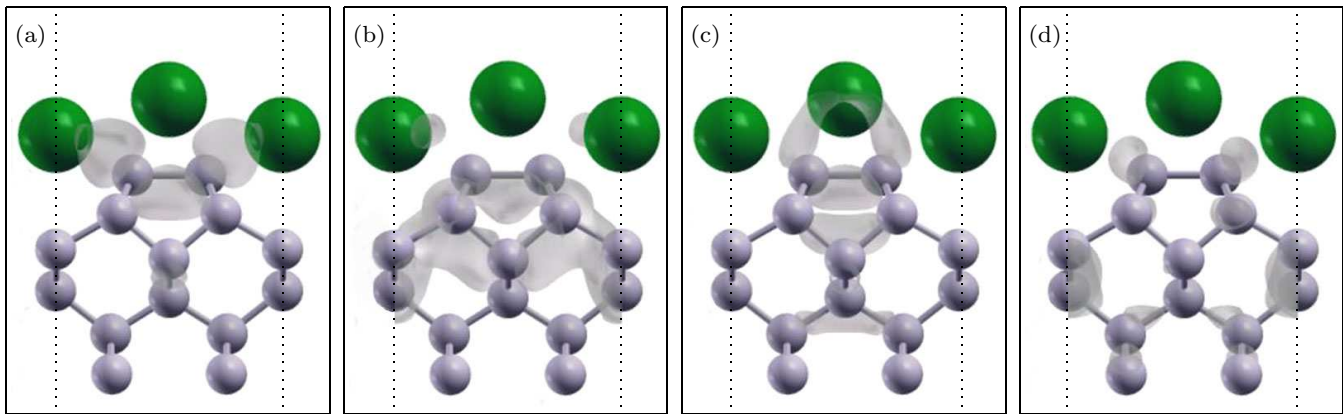


FIG. 4: h - p model 3D charge density distributions for S_1 and S_2 bands at high symmetry points K and J in the surface Brillouin zone. Dashed lines show the SUC boundaries. (a) S_1 at K, (b) S_2 at K, (c) S_1 at J and (d) S_2 at J.

K and \bar{J} . At J point, on the other hand, Cs-Si interaction seems to be more pronounced. This is because when Cs atoms are removed the electron-electron interaction around dimer Si atoms becomes more repulsive.

The shift in the energy values for the surface states S_1 and S_2 comes mainly from the lowering of kinetic energy rather than potential contribution to eigenenergies for these surface states. Ishida et al.³³ showed for K/Si(001) system that this lowering of kinetic energy increases with increasing K adsorption. This behavior can be seen as a charge localization in the vicinity of dimer Si and Cs atoms. Our results support the interpretation of Soukiasian et al.³⁵ of these shifts as being due to Si $3p$ -Cs $6s$ hybridization.

2. Nature of the Cs-Si Bond

Because the charge of Cs atom is much lower than that of Si bulk, the total charge density of the adsorbed surface will show a bare Cs atom, which makes the total charge density not meaningful in studying the charge distribution for the adsorbed surface. Hence we can not decide on the ionicity or covalency from the total charge density picture.^{33,36} This leads us to investigate the difference in charge distributions instead. Our results for the charge difference are very similar to those obtained previously.^{33,36} In Figure 5(a) and (b), we show 3D plots of the difference in charge distributions for the half and full coverage adsorption, which is defined as

$$\delta\rho(r) = \rho_{\text{Cs/Si}(001)}(r) - \rho_{\text{Si}(001)}(r) - \rho_{\text{Cs}}(r) \quad (2)$$

where $\rho_{\text{Cs/Si}(001)}(r)$ corresponds to the total charge density of the covered surface, $\rho_{\text{Si}(001)}(r)$ is the total charge density of the Si substrate with the same atomic arrangement as that of the covered surface, and $\rho_{\text{Cs}}(r)$ is the total charge density of the isolated Cs atom. We notice from Figure 5 that the strongest bonding charge is in the plane which includes the silicon dimers and not in

the plane containing the Cs atoms. We also see that the charge depletion for Cs atoms adsorbed on the surface takes place mostly along [001] direction. Another major depletion takes place in between the dimer atoms. This depletion results in favor of accumulation of the charge between the dimer and Cs atoms. Similarly, the depletion of charge around the Cs atom was found to be mainly in the dimer plane rather than in the Cs adlayer. The charge depletion around Cs atom in the vacuum direction is a little bit shrunk for 1 ML coverage which comes as a sign of weaker Cs-Si interaction and a smaller polarization of the bond. This result suggest that we have polarized covalent bonding as was suggested before by Ishida et al.³³ The bond becomes less polarized as Cs coverage increases. Our theoretical Cs-Si bond lengths for the 0.5 and 1 ML cases being 3.58 Å and 3.45 Å are close to the sum of the Cs (2.35 Å) and Si (1.17 Å) covalent radii, moreover they compare well with the minimum bond length of 3.56 Å for the CsSi compound.³⁴ The po-

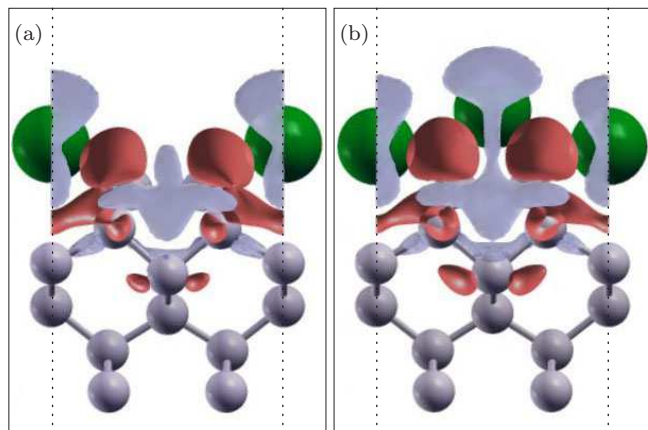


FIG. 5: Electronic charge density difference 3D plots for 0.5 ML and 1 ML coverages. Blue (bright) and red (dark) regions denote charge depleted and charge accumulated zones, respectively.

larized covalent nature of the Cs-Si bonding is also in agreement with the experimental results of Soukiassian et al.³⁵

On the basis of these results we can now interpret the symmetrization of dimers to be as result of saturation of dangling bonds via hybridization. Since the Cs 6s orbital has a largely spread wave function, Cs atom may interact with many neighboring Si atoms resulting in symmetrization of the dimers at low coverages such as 0.5 ML or even smaller, e.g., 0.3 ML as was shown experimentally.⁸ This may also explain the small reconstruction that take place in the substrate which we believe is due to the very limited charge transfer from the Cs atom to the substrate.

C. Work Function

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 perpendicular to the surfaces. It can be obtained from the Poisson's equation,

$$\frac{\partial^2}{\partial z^2} V_{av}(z) = -4\pi\rho_{av}(z) \quad (3)$$

and is given by the relation,

$$V_{av}(z) = -4\pi \int_z^\infty \rho_{av}(z') z' dz' + 4\pi z \int_z^\infty \rho_{av}(z') dz' \quad (4)$$

where

$$\rho_{av}(z) = \frac{1}{A} \iint_A |\psi(x, y, z)|^2 dx dy. \quad (5)$$

The work function for clean Si(001)-2×1 surface was reported to be 4.9 eV by Abukawa et al.³⁷ This agrees very well with our theoretical value of 4.9 eV for the clean relaxed surface. In Figure 6 we present our calculated values for the work function shifts with respect to the clean surface, which are 3.26 eV and 3.02 eV for half and full coverages, respectively. The lowering in the work function is more rapid between the clean surface and the 0.5 ML coverage before it rises again by 0.24 eV at the saturation coverage. Our calculated value for the lowering of the work function for the full coverage compares well with the other experimental values as shown in Table III. This behavior in the work function shift is consistent with experimental results^{4,38} for Cs/Si(001). It was found in most of the experimental results that work function shifts reach to some maximum value at a smaller coverage than that of saturation coverage before it backs up a little to a value for the 1 ML. Since we found that bonding between Cs atom and the silicon surface is polarized covalent, we can not explain the lowering in the work function on the basis of the classical Gurney picture³⁹ which is based on the charge transfer and ideal ionic bonding systems. Hence, we found that

TABLE III: Work function change $\Delta\Phi$ (in eV) at the saturation coverage with respect to the clean Si(001) 2 × 1 surface.

$\Delta\Phi(\text{eV})$	Reference	Method
-3.02	This work	ab initio
-3.11	Ref. [4]	ARUPS
-3.4	Ref. [35]	VBPS, CLPS
-3.2	Ref. [36]	EELS
-2.8	Ref. [37]	AES, LEED

the model suggested previously by Ishida et al.³³ might be more suitable to our results. In the initial stages of Cs adsorption, the strong modification of charge distribution around the Cs atoms will result in a polarized adlayer. Adsorbed Cs atoms, thus, can be considered as dipole moments as a result of charge depletion from the Cs adatom vacuum sides and the charge accumulation between Cs-Si atoms. This signifies a hybridization of Si 3p and Cs 6s which implies the saturation of Si dangling bonds, leading to a rapid drop of the work function. Even if the single dipole moments get weakened as a function of increasing Cs coverage, the number of dipoles on the surface increases making the overall dipole-dipole interaction significant. This raises the potential energy barrier for outgoing electrons and results in an increase in the work function by 0.24 eV as the coverage goes from 0.5 ML to 1 ML.

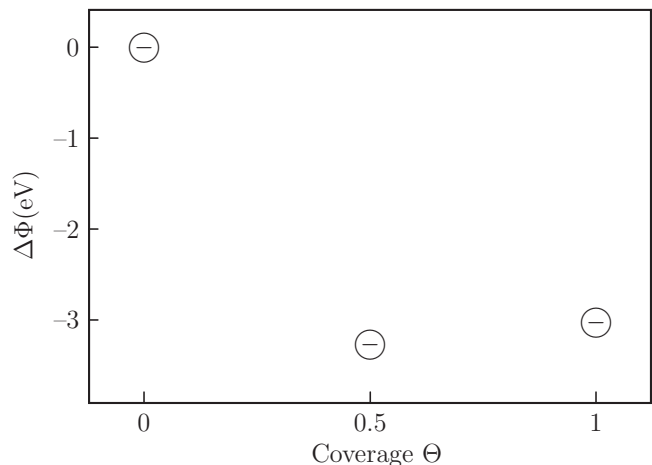


FIG. 6: Calculated shifts in the work function as a function of the coverage with respect to the clean surface

D. Thermodynamic Stability of the Phases

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

number of Cs adatoms.

The surface formation energy⁴⁰ at 0 K for a slab containing n_{Si} atoms of Si and n_{Cs} atoms of Cs adsorbed on its surface can be written as

$$\Omega = E_{\text{Cs/Si}(001)} - n_{\text{Si}} \mu_{\text{Si}} - n_{\text{Cs}} \mu_{\text{Cs}} \quad (6)$$

where μ_{Cs} and μ_{Si} are the chemical potentials of Cs and Si, respectively. $E_{\text{Cs/Si}(001)}$ is the total energy for the covered surface as obtained by the self-consistent ab initio calculations. In the usual adsorption experiments using gaseous Cs, μ_{Cs} of gaseous Cs is less than the corresponding value of bulk, and it varies with pressure and temperature. Thus surface chemical potential μ_{Cs} of Cs should be considered in some range such that it cannot exceed the $\mu_{\text{Cs}}^{\text{bulk}}$. Taking the origin as the chemical potential of bulk Cs, the calculated formation energies as a function of μ_{Cs} were presented in Figure 7.

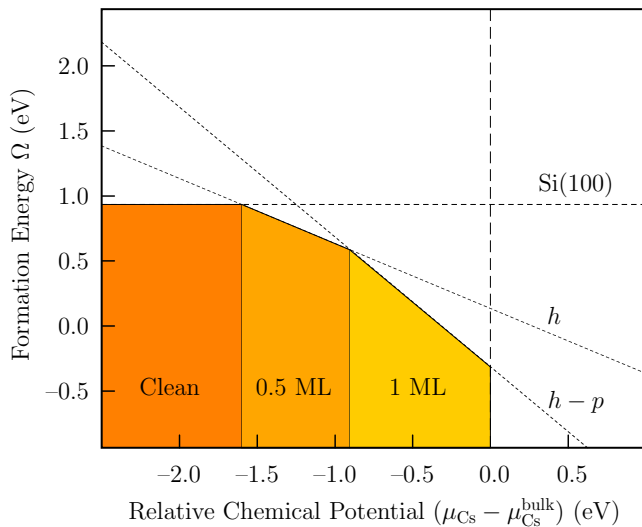


FIG. 7: The surface formation energy as a function of the relative chemical potential of Cs adsorbed on Si(001) surface per (1×1) unit cell.

It was found that for $(\mu_{\text{Cs}} - \mu_{\text{Cs}}^{\text{bulk}}) < -1.60$ eV the clean Si(001) surface has a lower formation energy than that with any amount of Cs adsorbed on it. However, in the

range -1.60 eV $< (\mu_{\text{Cs}} - \mu_{\text{Cs}}^{\text{bulk}}) < -0.90$ eV, the half coverage adsorption with a 2×1 symmetry is found to be the most stable structure. A transition to full coverage with 2×1 surface has occurred when $(\mu_{\text{Cs}} - \mu_{\text{Cs}}^{\text{bulk}}) > -0.90$ eV.

Since the half coverage is thermodynamically stable with a work function difference close to that of the saturated surface, this might be the reason why some experimental results were interpreted as the half ML being the saturation coverage.

Our results show that after the completion of the half coverage with all hollow sites occupied, if extra Cs atoms are added, they will start filling the pedestal sites until a complete 1 ML is formed. Thus, the saturation coverage for Cs/Si(001) system is 1 ML and is in agreement with the experimental results.^{6,7,8,9,10,11,12,13}

E. Conclusion

We have performed an ab initio total energy calculation and geometry optimization for a clean Si(001) surface and that with Cs overlayer for 0.5 and 1 ML coverages on it. For the 0.5 ML coverage we have found that Cs occupy the *h* site between dimer rows. The adsorption sites for 1 ML coverage agree well with the Abukawa model with *h-p* configuration. While our findings suggest that 0.5 ML is thermodynamically stable, we found that 1 ML coverage is the saturation coverage. The energy band spectra show metallic and semiconducting surfaces for the half and full ML coverages, respectively. The results for difference in charge upon Cs adsorption suggests that the nature of the Cs-Si bonding is polarized covalent. Our calculated values for the work function difference agrees well with the existing experimental results.

Acknowledgments

This work was supported by TÜBİTAK, The Scientific and Technical Research Council of Turkey, Grant No. TBAG-2036 (101T058).

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