

Atomic gold chain on hydrogen terminated Si(001):1×1 surface: A density functional theory study

Shyamal Konar and Bikash C. Gupta*

Department of Physics, Visva-Bharati, Santiniketan 731235, India

Inder P. Batra†

Department of Physics, University of Illinois at Chicago, 845 W. Taylor Street, Illinois 60607, USA

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The possibility for the formation of stable Au atomic wire structures on the patterned hydrogen terminated Si(001):1×1 surface is investigated using density functional theory based total energy calculations. The hydrogen terminated Si(001):1×1 surface is patterned in two different ways (pattern 1 and pattern 2) by removing desired hydrogen atoms from the surface. The adsorption of Au on such surfaces is studied at different submonolayer coverages. Eventually, it is found that at 2/3 monolayer (ML) coverage, stable Au chain structure is obtained on both the patterned hydrogen terminated Si(001):1×1 surfaces. The reason for the stability of the wire structures at 2/3 ML coverage is explained. Most importantly, the Au chain on the patterned hydrogen terminated Si(001):1×1 surface having pattern 1 may be metallic in nature, and therefore, experiments may be designed in this direction to produce metallic wires supported by semiconducting substrates. However, beyond 2/3 ML coverage, the additional Au atoms may form clusters due to the lack of dangling bonds on the surface. Hence, Au coverage should be controlled at 2/3 ML for the formation of Au chain on the patterned hydrogen terminated Si(001):1×1 surface.

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I. INTRODUCTION

Due to tremendous interest in nanotechnology, the physics of metal adsorption on semiconducting surface is heralding a technological revolution and opening new research avenues of low dimensional physics, such as atomic wires, i.e., the ultimate thin wires. With the help of scanning tunneling microscopy (STM), it has been possible to manipulate surface atoms and thus modify the semiconducting surfaces to construct atomic scale structures like quantum nanowires on semiconducting surfaces.¹⁻⁵ These wires have the vital importance because of its possible application as metallic interconnect in nanodevices.⁶

There is much activity in bottom up approach where freestanding atomic chains for a variety of metal atoms have been studied. For this, one must first compute the total energy and determine the possible stable structures. Such calculations have indeed been carried out for nanowires consisting of a wide variety of atoms, e.g., K, Al, Cu, Ni, Au, and Si.⁷⁻¹⁴ A general finding is that a zigzag structure in the form of an equilateral triangle is the most stable.^{7,8,12,14} This can be understood as arising primarily due to the maximization of coordination number for each atom in a quasi-one-dimensional structure. Another structure which also has a local minimum, but not terribly stable, is a wide angle isosceles triangle, which somehow is reminiscent of the bulk environment. In general, freestanding nanowires tend to be metallic (have bands crossing the Fermi level), but these nanowires in practice are to be supported. Silicon is the most widely used substrate for practical applications and the low index surfaces, Si(001), is the surface of choice. The interaction of metal nanowires with substrate can significantly alter the electronic properties and not always in the desired direction.

The bare Si(001) surface has dangling bonds all over the surface, and therefore, metals on Si(001) surface generally do not tend to form stable wire structures. However, hydrogen termination of Si substrate makes the surface a rigid ground for placing nanostructure because the termination prevents the chemical binding between surface and nanostructures. Thus, currently, the hydrogen terminated Si(001) surface has become one of the surface of choice for growing nanostructures. Hydrogen terminated Si(001) surface have various reconstructed patterns, such as 1×1, 2×1, and 3×1, depending on the hydrogen coverage and the experimental environment.¹⁵⁻²⁰ Experimentally, it has been shown that an ideal hydrogen terminated Si(001):1×1 surface can be achieved by wet chemical etching.²¹ However, with the use of STM tip, a hydrogen terminated Si(001) surface may be patterned according to our desire by removing the desired hydrogen atoms from the hydrogen terminated Si(001) surface and these are named as patterned hydrogen terminated Si(001) surface. Watanabe *et al.*^{22,23} explored the growth of Ga on such patterned monohydride Si(001):2×1 surface and found that the Ga atoms dimerize and tend to form clusters on the surface. As a result, a good atomic Ga wire is not obtained on the hydrogen terminated Si(001):2×1 surface. The possible wire formation of metals, such as Al, Ga, and In on patterned hydrogen terminated Si(001):1×1, has been studied recently and it was concluded that a metallic In atomic wire on the patterned hydrogen terminated Si(001):1×1 surface may be formed.²⁴

Recently, a variety of one-dimensional chain structures for gold on silicon surfaces have been observed experimentally. These are mostly on the vicinal high indexed silicon surfaces, i.e., Si(335)-Au, Si(557)-Au, Si(553)-Au, Si(775)-Au, etc.²⁵⁻²⁹ However, our interest lies on the formation of wire structures on the stable Si(001) surface. Although gold

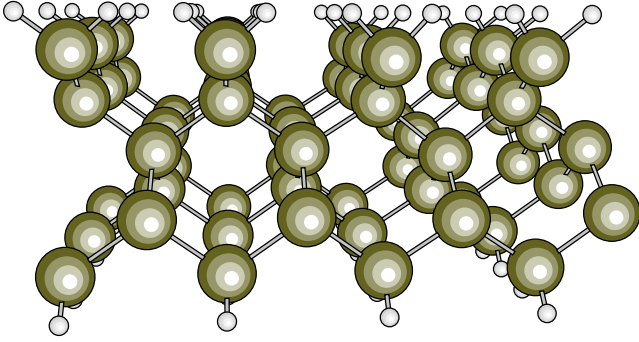


FIG. 1. (Color online) Hydrogen terminated Si(001): 1×1 surface within the 4×3 supercell. The bigger spheres correspond to the Si atoms and the hydrogen atoms are represented by the smaller spheres.

is the noblest of all metals and it interacts strongly with silicon,^{30,31} there has been no attempt to date to explore the possible formation of Au wire structure on the patterned hydrogen terminated Si(001) surface. We, therefore, perform systematic theoretical study for the adsorption of Au on the patterned hydrogen terminated Si(001): 1×1 surface and search for possible formation of metallic Au wire structures on the patterned hydrogen terminated Si(001): 1×1 surface. Our results reveal that metallic Au chain on such patterned hydrogen terminated Si(001): 1×1 surface may be obtained.

This paper is organized as follows. The method of our calculations, the description of the hydrogen terminated Si(001): 1×1 surface, and the patterned hydrogen terminated Si(001): 1×1 surfaces are presented in Sec. II. The results and discussions are presented in Sec. III, and finally, we summarize our findings in Sec. IV.

II. METHOD

First principles total energy calculations were carried out within the density functional theory at zero temperature using the VASP code.^{32–34} The wave functions are expressed by plane waves with the cutoff energy $|k+G|^2 \leq 300$ eV. The Brillouin zone integrations are performed by using the Monkhorst–Pack scheme with $4 \times 4 \times 1$ k -point meshes for 2×3 primitive cells. Ions are represented by ultrasoft Vanderbilt-type pseudopotentials and results for fully relaxed atomic structures are obtained using the generalized gradient approximation. The preconditioned conjugate gradient method is used for the wave function optimization and the conjugate gradient method for ionic relaxation. The convergence criteria for energy are taken to be 10^{-5} eV and the systems are relaxed until the forces are below 0.005 eV/Å.

The hydrogen terminated Si(001): 1×1 surface is represented by a repeated slab geometry. Each slab contains five Si atomic planes with hydrogen atoms passivating both the top and bottom layers of Si atoms of the slab (see Fig. 1). The consecutive slabs are separated by a vacuum space of 10 Å, which is sufficient to avoid the interaction from its repeating image.^{35–38} The Si atoms of the top four layers of the slab along with the hydrogen atoms attached to the top layer Si atoms are allowed to relax. The Si atoms of bottom

TABLE I. The total energies of the fully hydrogen terminated Si(001): 1×1 surface within the 2×3 supercell are given for different k -point meshes. There are 30 Si atoms and 24 H atoms within the 2×3 supercell. The cutoff energy is kept fixed at 300 eV.

k -point mesh	Total energy (eV)
$2 \times 2 \times 1$	-331.926
$3 \times 3 \times 1$	-332.339
$4 \times 4 \times 1$	-332.388
$5 \times 5 \times 1$	-332.391
$6 \times 6 \times 1$	-332.393

layer and the hydrogen atoms passivating the bottom silicon layer are kept fixed to simulate the bulklike termination. The convergence with respect to the number of Si layer of the slab has already been examined earlier (see Table I of Ref. 35) and it was found that five Si layers are sufficient to realize the Si(001) surface. From Tables I and II, we find that the convergence of the total energy is achieved with the $4 \times 4 \times 1$ k -point mesh and with the cutoff energy of 300 eV.

The hydrogen terminated Si(001): 1×1 surface may be patterned various ways by removing the selected hydrogen atoms from the top of the surface. Here, we consider two possible patterns: (i) remove the hydrogen atoms located between two consecutive rows of Si atoms along the y [$1\bar{1}0$] direction, and we name it as pattern 1 (see Fig. 2) (in this case the 2×3 supercell contains 30 Si atoms and 18 hydrogen atoms), and (ii) remove all the hydrogen atoms from a single row of Si atoms along the y [$1\bar{1}0$] direction, and we name it as pattern 2 (see Fig. 3). Here, also the 2×3 supercell contains 30 Si atoms along with 18 hydrogen atoms. Note that the total energy calculations for all the systems are done by relaxing all the atoms, except the bottom layer Si atoms and the hydrogen atoms passivating the bottom Si layer.

III. RESULTS AND DISCUSSIONS

We will first discuss the Au adsorption on the patterned hydrogen terminated Si(001): 1×1 surface having pattern 1 followed by the discussions for the Au adsorption on the patterned hydrogen terminated Si(001): 1×1 surface having pattern 2.

TABLE II. The total energies of the fully hydrogen terminated Si(001): 1×1 surface within the 2×3 supercell are given for different cutoff energies. There are 30 Si atoms and 24 H atoms within the 2×3 supercell. The $4 \times 4 \times 1$ k -point mesh is considered here.

Cutoff energy (eV)	Total energy (eV)
200	-332.063
250	-332.342
300	-332.388
350	-332.390

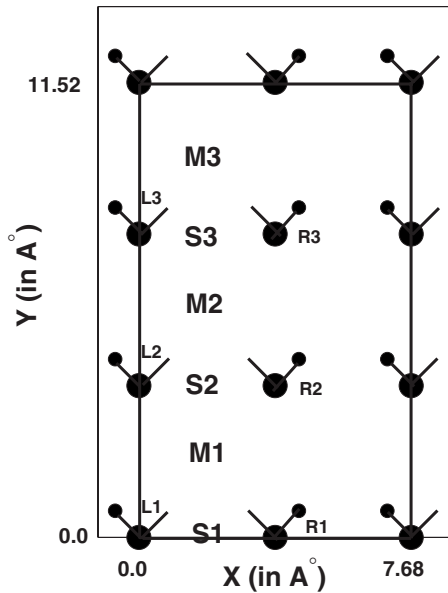


FIG. 2. Top layer of the patterned hydrogen terminated Si(001):1×1 surface having pattern 1. The 2×3 supercell closed by thick borders is shown here. Two adjacent dangling bond wires extending along the $[1\bar{1}0]$ direction is visible. The possible adsorption sites are denoted as M and S. The bigger filled circles correspond to the surface Si atoms and they are denoted by L1, L2, L3, R1, R2, and R3, while the surface hydrogen atoms are represented by the smaller filled circles.

A. Patterned hydrogen terminated Si(001):1×1 surface: Pattern 1

The patterned hydrogen terminated Si(001):1×1 surface having pattern 1 has two adjacent dangling bond wires ex-

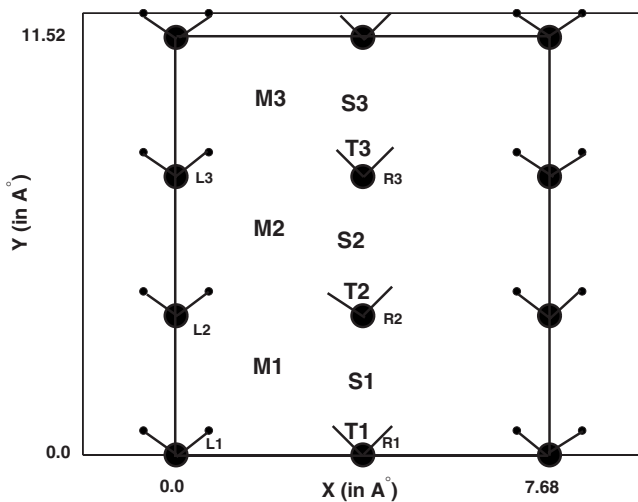


FIG. 3. Top layer of the patterned hydrogen terminated Si(001):1×1 surface having pattern 2. The 2×3 supercell closed by thick borders is shown here. The dangling bond wire extending along the $[1\bar{1}0]$ direction is visible. The possible adsorption sites are denoted as M, S, and T. The bigger filled circles correspond to the surface Si atoms and they are denoted by L1, L2, L3, R1, R2, and R3. The surface hydrogen atoms are represented by the smaller filled circles.

TABLE III. BE per gold atom, Au-Si bond length $d(\text{Au-Si})$, and the height of Au with respect to the top Si layer are tabulated for the case of 1/6 ML coverage on the patterned hydrogen terminated Si(001):1×1 surface having pattern 1. The reference energy, i.e., the energy after relaxation of the patterned hydrogen terminated Si(001):1×1 surface having pattern 1, is -210.64 eV.

Site	BE (eV)	$d(\text{Au-Si})$ (Å)	Height (Å)
S1	4.94	2.37	≈1.30
M1	5.39	2.55	≈0.65

tending along the $[1\bar{1}0]$ direction. However, the band structure calculation reveals that the surface is semiconducting in nature. The electronic structure and energetics for the adsorption of Au at different submonolayer coverages are discussed in Secs. III A 1–III A 4. Here, one monolayer (ML) is defined as one atom per surface Si atom. For example, in the 2×3 supercell, the adsorption of six Au atoms corresponds to one ML coverage.

1. 1/6 monolayer Au on patterned hydrogen terminated Si(001):1×1 surface: Pattern 1

Adsorption of one Au atom on the patterned hydrogen terminated Si(001):1×1 surface (pattern 1) within the 2×3 supercell corresponds to 1/6 ML coverage. The underlying symmetry of the surface indicates that there are two possible sites for the adsorption of a gold atom in the 2×3 supercell. As shown in Fig. 2, the adsorption sites are denoted as M1 site and S1 site, respectively. The binding energy (BE) per Au atom, the Au-Si bond length, as well as the height of the Au layer on the Si surface are given in Table III. We find that the M1 site is most favorable and has a binding energy of 5.39 eV/Au atom, which is favorable by 0.45 eV compared to the S1 site. Therefore, the Au atoms binds strongly on the Si surface.^{30,31} Even though the Au-Si bond length when the Au atom is at M1 site (≈2.55 Å) is larger compared to that when Au atom is at S site (≈2.37 Å), the M1 site is more favorable. This is because the Au atom at M1 site has more Si neighbors compared to the S1 site. In fact, as the height of the Au atom at M1 site is small, it also has an opportunity to share the electronic charges with the Si atoms lying below the top layer Si atoms. To understand the nature of the bonding between Au and surface Si atoms, the total charge density is plotted along the line of a Au-Si bond and it is shown in Fig. 4. The charge distribution shown in Fig. 4 reveals that the Au-Si bonds are mostly covalent in nature.

2. 1/3 monolayer Au on patterned hydrogen terminated Si(001):1×1 surface: Pattern 1

Two gold atoms are adsorbed on the patterned hydrogen terminated Si(001):1×1 (pattern 1) surface within the 2×3 supercell to have 1/3 ML coverage. From Fig. 2, we notice that there are three reasonable choices for the adsorption sites, namely, S1S2 (one Au at S2 site and the other on

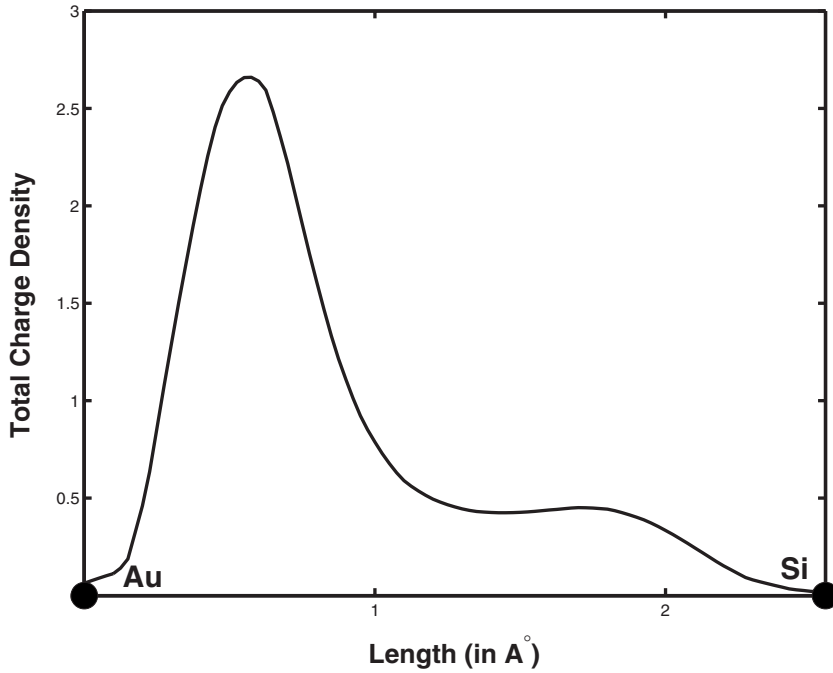


FIG. 4. The total charge density is plotted along the line of Au-Si bond when the Au atom is adsorbed at the M site corresponding to 1/6 ML coverage (see Fig. 2) on the patterned hydrogen terminated Si(001):1×1 surface having pattern 1. The Au and Si atoms are indicated in the figure.

the S2 site), M1M2 (one Au at M1 site and the other at M2 site), and S1M1 (one Au at S1 site and the other at the M1 site). Based on the physical ground, we understand that the BE for the S1M1 configuration should be between the values for S1S2 and M1M2 configurations, and therefore, the calculation for the S1M1 configuration is not done. Also, by close inspection of the results for 1/6 ML coverage, we expect that the M1M2 configuration should be most favorable. As the adsorption of the second Au atom at the M2 site in the presence of the first Au atom at the M1 site may induce strain in the surface, the net binding energy depends on the competition between the energy gain due to bonding of Au with Si atoms and the energy cost for the produced strain on the surface. The binding energy per Au atom, the Au-Si bond length, Au-Au distance, and the height of the Au layer from the top Si layer are given in the Table IV. In fact, our calculations reveal that the M1M2 configuration is most favorable and the binding energy per Au atom is ≈ 4.10 eV, which is less by ≈ 1.3 eV compared to the case of 1/6 ML coverage. This reduction in BE is for the fact that an added strain is induced due to the adsorption of the second Au atom at the M1 site and also due to the reduction of number of effective Si neighbors. For the S1S2 configuration, the Au atoms at S1 and S2 sites approach each other and eventually form a

TABLE IV. BE per Au atom, Au-Si bond length $d(\text{Au-Si})$, Au-Au distance $d(\text{Au-Au})$, and the height of the Au atoms with respect to the top Si layer are tabulated for the case of 1/3 ML coverage on the patterned hydrogen terminated Si(001):1×1 surface having pattern 1.

Configuration	BE (eV)	$d(\text{Au-Si})$ (Å)	$d(\text{Au-Au})$ (Å)	Height (Å)
S1S2	3.96	2.3	2.9	≈ 2.2
M1M2	4.10	2.6	4.02	≈ 0.7

dimer. In the M1M2 configuration, the Au atoms do not form dimer; however, due to small distance between the Au layer and the top Si layer, the Au atoms have an opportunity for sharing its charge with the Si atoms lying below the top Si layer. This could be a possible reason for favoring the M1M2 configuration over the S1S2 configuration. The charge distribution along the direction of the Au-Si bonds is similar to that shown in Fig. 4, and hence, the Au-Si bonds are mostly covalent in nature. We note that at 1/3 ML coverage, the adsorbed Au atoms form doubly periodic linear chain structure extending along the $[1\bar{1}0]$ direction on the patterned hydrogen terminated Si(001):1×1 surface having pattern 1. However, as the interatomic distances in the Au chain are ≈ 4.02 and 7.5 Å, the chain is not expected to be metallic.

3. 1/2 monolayer Au on patterned hydrogen terminated Si(001):1×1 surface: Pattern 1

Here, three atoms are adsorbed within the 2×3 supercell on the patterned hydrogen terminated Si(001):1×1 surface having pattern 1, which corresponds to the 1/2 ML coverage. Two distinct possible configurations are S1S2S3 and M1M2M3, as shown in the Fig. 2. The BE per Au atom, the Au-Si bond length $d(\text{Au-Si})$, the Au-Au distance $d(\text{Au-Au})$, and the height of the Au layer with respect to the top Si layer are given in Table V. The S1S2S3 configuration turns out to be most stable configuration with BE=3.8 eV, which is favorable by 0.16 eV compared to the M1M2M3 configuration. We see that with the increase in the coverage, the favorable sites change from M sites to S sites. As the coverage increases, the number of effective nearest neighbors of the Au atom at the M sites decreases, and in addition, the Au atoms at M sites do not form bonds with each other. On the other hand, the Au atoms when at S sites, not only make strong

TABLE V. BE per gold atom, Au-Si bond length $d(\text{Au-Si})$, the Au-Au distance $d(\text{Au-Au})$, and the height of Au layer with respect to the top Si layer are tabulated for the case of 1/2 ML coverage on the patterned hydrogen terminated $\text{Si}(001):1 \times 1$ surface having pattern 1.

Configuration	BE (eV)	$d(\text{Au-Si})$ (Å)	$d(\text{Au-Au})$ (Å)	Height (Å)
S1S2S3	3.80	2.44	2.05	1.7
M1M2M3	3.64	2.64	3.84	0.75

bonds with the surface Si atoms (bond length ≈ 2.44 Å) but they also make strong bond with themselves (bond length of ≈ 2.05 Å). This is the reason why S1S2S3 configuration is superior to the M1M2M3 configuration. Due to the formation of strong bonds between the Au atoms, we obtain a linear chain consisting of Au dimers on the patterned hydrogen terminated $\text{Si}(001):1 \times 1$ surface (pattern 1) extending along the $[1\bar{1}0]$ direction. Consequently, the interatomic distances in the Au chain are ≈ 2.05 and ≈ 6.3 Å. Hence, we do not expect the chain to be metallic in nature. The charge density along the line of the Au-Si bonds and the Au-Au bonds reveal that the bonds are mostly covalent in nature.

4. 2/3 monolayer Au on patterned hydrogen terminated $\text{Si}(001):1 \times 1$ surface: Pattern 1

The 2/3 monolayer coverage of Au on the patterned hydrogen terminated $\text{Si}(001):1 \times 1$ surface having pattern 1 corresponds to the adsorption of four Au atoms within the 2×3 supercell. There are various possible configurations for Au adsorption. However, we are interested to investigate the possibility of the formation of the stable chainlike structure of Au on the patterned hydrogen terminated $\text{Si}(001):1 \times 1$ surface. One interesting thing we note here is that four periods of a straight Au chain exactly match with the three periods of the hydrogen terminated $\text{Si}(001)$. The interatomic distance in the Au chain is assumed to be 2.88 Å, which is the Au-Au bond length in the bulk. We also note that the interatomic distance between Au atoms in the freestanding Au atomic chain varies from 2.7 to 3.04 Å.^{7,39,40} Therefore, the interatomic distance (2.88 Å) in the Au chain considered here is on the average same as that for a freestanding Au atomic wire observed experimentally. We therefore expect that the strain on the surface due to the arrangement of four Au atoms on a line along the Y $[1\bar{1}0]$ direction will be less compared to any other configuration. We first consider the periodic straight chain configuration, A1A2A3A4 as the initial configuration (as shown in the Fig. 5) and then let the system relax. We observe that a zigzag chainlike structure is obtained after complete relaxation of the system. However, the interatomic distance (Au-Au distance along the chain) varies from 2.73 to 3.07 Å, which is similar to the case of freestanding Au atomic chain.^{7,39,40} In this case, the BE per Au atoms is 3.72 eV, which is a substantial amount. The details of the Au-Au distance, the Au-Si distance, and the average height of the Au chain with respect to the top Si layer are given in Table VI. To conclude about the stability of

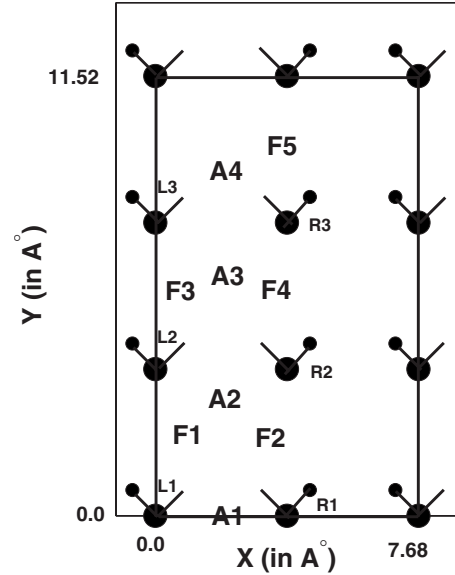


FIG. 5. The patterned hydrogen terminated $\text{Si}(001):1 \times 1$ surface having pattern 1. The possible adsorption sites of Au at 2/3 ML coverage are shown. The surface Si atoms within the 2×3 supercell are represented by the larger filled circles and they are denoted as L1, L2, L3, R1, R2, and R3. Here, each Si atom has a dangling bond, as shown in the figure. Note that small filled circles represent the hydrogen atoms on the surface.

the chain structure, we also considered the configurations (deviations from chain configuration): F1F2F3F4 and A1A2A3F5 (see Fig. 5). The BE for the F1F2F3F4 and A1A2A3F5 configurations are 2.47 and 3.55 eV, respectively. Again, the details for these configurations are given in Fig. 5 and Table VI. It is interesting to note that although the Au atoms in the F1F2F3F4 configuration form two parallel dimers, this configuration is energetically least favorable. These results indicate that the zigzag chain structure is the most favorable structure. The total charge density plot in the X - Y plane (coinciding the Au layer) is shown in Fig. 6. The formation of the Au chain is clear from the charge density plot in Fig. 6. The zigzag pattern of the chain is not apparent in the figure because the wire has zigzag pattern in the Y - Z plane. To conclude about the electrical nature of the Au wire, we have plotted the band structure in Fig. 7. It shows that a single band crosses the Fermi level. We may thus conclude that the Au zigzag chain may be metallic in nature. The geometric structure of the Au chain on the patterned hydrogen terminated $\text{Si}(001):1 \times 1$ surface having pattern 1 is shown in the Fig. 8. It is worth mentioning that the zigzag pattern of Au atomic chain was found to be most stable for the freestanding case. However, relevant experiments are desirable to see if metallic Au chain can be produced on the patterned hydrogen terminated $\text{Si}(001):1 \times 1$ surface having pattern 1.

B. Patterned hydrogen terminated $\text{Si}(001):1 \times 1$ surface: Pattern 2

The patterned hydrogen terminated $\text{Si}(001):1 \times 1$ surface having pattern 2 has dangling bond rows extending along the

TABLE VI. At 2/3 ML coverage of Au on the patterned hydrogen terminated Si(001):1×1 surface having pattern 1, the BE per gold atom, Au-Si distance $d(\text{Au-Si})$, Au-Au distance $d(\text{Au-Au})$, and height of the Au layer with respect to the top Si layer are given. In addition, the height differences among the Au atoms in the A1A2A3A4 configuration are displayed to understand the zigzag nature of the Au chain. The Au atoms at A1, A2, A3, and A4 sites are denoted as Au₁, Au₂, Au₃, and Au₄, respectively.

Configuration	BE (eV)	$d(\text{Au-Si})$ (Å)	$d(\text{Au-Au})$ (Å)	Height (Å)
A1A2A3A4 (Chain configuration)		$d(\text{Au}_1-L_1\text{Si})=2.40$	$d(\text{Au}_1-\text{Au}_2)=2.73$	$h(\text{Au}_1-\text{Au}_2)=0.20$
		$d(\text{Au}_1-R_1\text{Si})=2.40$	$d(\text{Au}_2-\text{Au}_3)=3.07$	$h(\text{Au}_1-\text{Au}_3)=0.47$
		$d(\text{Au}_2-L_2\text{Si})=2.48$	$d(\text{Au}_3-\text{Au}_4)=3.07$	$h(\text{Au}_1-\text{Au}_4)=0.20$
		$d(\text{Au}_2-R_2\text{Si})=2.48$		
	3.72	$d(\text{Au}_3-L_2\text{Si})=2.677$		
		$d(\text{Au}_3-R_2\text{Si})=2.692$		$h(\text{Au-Si}) \approx 1.35$
		$d(\text{Au}_3-L_3\text{Si})=2.677$		
		$d(\text{Au}_3-R_3\text{Si})=2.677$		
		$d(\text{Au}_4-L_3\text{Si})=2.476$		
	$d(\text{Au}_4-R_3\text{Si})=2.483$			
A1A2A3F5 (Deviation from chain)	3.55	$d(\text{Au-Si})=2.44-2.82$	$d(\text{Au-Au})=2.82-3.43$	$h(\text{Au-Si}) \approx 1.5$
F1F2F3F4 (Deviation from chain)	2.47	$d(\text{Au-Si})=2.63-2.64$	$d(\text{Au-Au}) \approx 2.6$	$h(\text{Au-Si}) \approx 1.8$

[110] direction. The surface consists of alternate dangling bond rows and dihydride Si rows. Along the dangling bond rows, each Si atom has two dangling bonds and two adjacent dangling bond rows are separated by 7.68 Å (see Fig. 3). The band structure calculation reveals that the surface is semiconducting in nature. The electronic structure and energetics for the adsorption of Au at different submonolayer coverages are discussed in Secs. III B 1–III B 4. The definition of one monolayer is same as defined earlier.

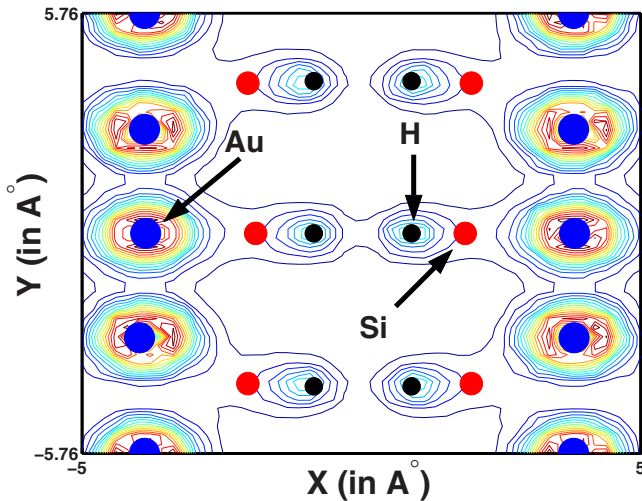


FIG. 6. (Color online) This shows the total charge density in the X-Y plane (the plane coincides with the Au layer) for the case of 2/3 ML coverage of Au on the patterned hydrogen terminated Si(001):1×1 surface having pattern 1. The Au, Si, and H atoms are indicated in the figure. The formation of Au chain is clear from the figure.

1. 1/6 monolayer Au on the patterned hydrogen terminated Si(001):1×1 surface: Pattern-2

Adsorption of one Au atom on the patterned hydrogen terminated Si(001):1×1 surface (pattern 2) within the 2×3 supercell corresponds to 1/6 ML coverage. The underlying symmetry of the surface indicates that there are three possible sites for the adsorption of a gold atom in the 2×3 supercell. As shown in Fig. 3, the adsorption sites are denoted as T1 site, S1 site, and M1 site, respectively. The BE per Au atom, the Au-Si bond length [$d(\text{Au-Si})$] as well as the height of the Au layer with respect to the top Si layer is given in Table VII. We find that the S1 site is most favorable and has binding energy of 3.72 eV/Au atom, which is favorable by 0.35 eV compared to the T1 site. Therefore, the Au atoms bind strongly on the Si surface. The M1 site is highly un-

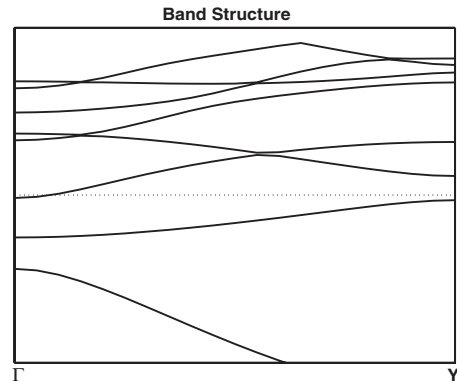


FIG. 7. This shows the band structure for the case of 2/3 ML coverage of Au on the patterned hydrogen terminated Si(001):1×1 surface having pattern 1. The Fermi level is indicated by a dotted line.

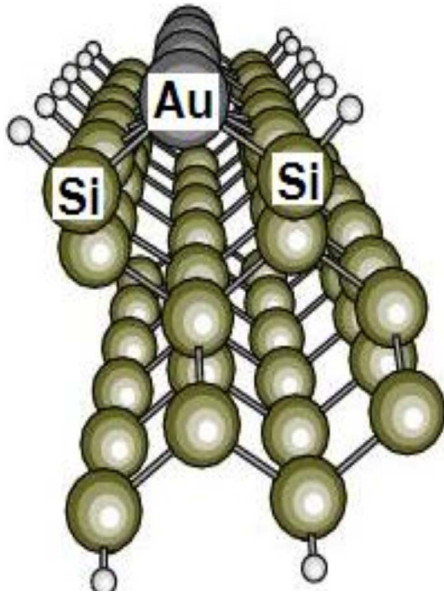


FIG. 8. (Color online) This shows the most favorable geometrical structure when 2/3 ML of Au is adsorbed on the patterned hydrogen terminated Si(001):1×1 surface having pattern 1. The gold and silicon atoms are indicated in the figure. The smallest spheres indicate the hydrogen atoms

stable and the Au atom placed at M1 site readily moves to the S1 site. Although the Au-Si bond length when the Au atom is at S1 site (≈ 2.42 Å) is larger compared to that when Au atom is at T1 site (≈ 2.29 Å), the S1 site is more favorable. This is because, the Au atom at S1 site has more Si neighbors compared to the T1 site. Furthermore, when the Au atom occupies the S1 site, the Au-Si bond orientation is more favorable and this may be another cause for favoring S1 site over the T1 site. To understand the nature of the bonding between Au and surface Si atoms, the total charge density is plotted along the line of a Au-Si bond and it is shown in Fig. 9. The charge distribution in Fig. 9 reveals that the Au-Si bonds are mostly covalent in nature.

2. 1/3 monolayer Au on patterned hydrogen terminated Si(001):1×1 surface: Pattern 2

Two gold atoms are adsorbed on the patterned hydrogen terminated Si(001):1×1 surface (pattern 2) within the 2×3 supercell to have 1/3 ML coverage. There are three pos-

TABLE VII. BE per gold atom, Au-Si bond length $d(\text{Au-Si})$, and the height of Au with respect to the top Si layer are tabulated for the case of 1/6 ML coverage on the hydrogen terminated Si(001):1×1 surface having pattern 2. The reference energy, i.e., the energy after relaxation of the patterned hydrogen terminated Si(001):1×1 having pattern 2, is -211.42 eV.

Site	BE (eV)	$d(\text{Au-Si})$ (Å)	Height (Å)
T1	3.37	2.29	≈ 2.2
S1	3.72	2.42	≈ 1.5

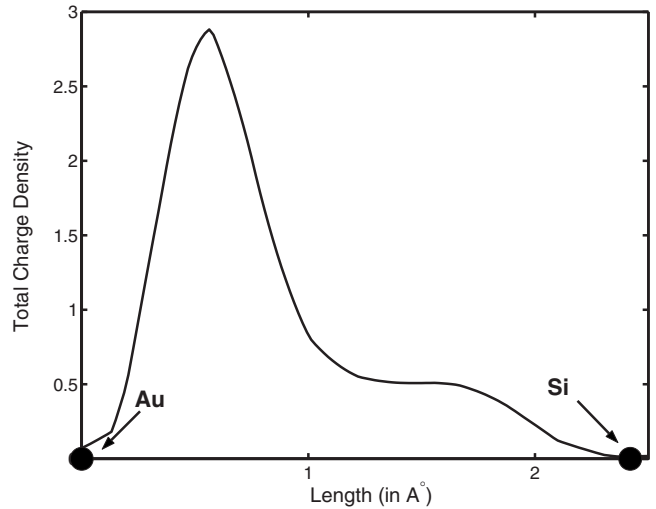


FIG. 9. The total charge density is plotted along the line of Au-Si bond when the Au atom is adsorbed at the S1 site corresponding to 1/6 ML coverage (see Fig. 3) on the patterned hydrogen terminated Si(001):1×1 surface having pattern 2. The Au and Si atoms are indicated in the figure.

sible choices for the adsorption sites, namely, T1T2 (one Au at T1 site and the other on the T2 site), S1S2 (one Au at S1 site and the other at S2 site), and M1M2 (one Au at M1 site and the other at the M2 site). Based on the results for 1/6 ML coverage, we may expect that S1S2 configuration should be the most favorable configuration. However, as the adsorption of the second Au atom at the S2 site in the presence of the first Au atom at the S1 site may cause strain in the surface, the net binding energy may depend on the competition between the energy gain due to bonding of Au with Si atoms and the energy cost for the produced strain on the surface. The binding energy per Au atom, the Au-Si bond length, Au-Au distance, and the height of the Au layer with respect to the top Si layer are given in the Table VIII. From the results given in Table VIII, we find, although the BE for all the configurations are close to each other, the M1M2 configuration is the most favorable configuration with binding energy of 3.25 eV/Au atom. We note that as the coverage increases, the BE decreases. This reduction in BE may be due to an added strain induced when the second Au atom is adsorbed at the M2 site and also due to the fact that the available dangling bonds within the supercell are now shared by two Au atoms. For the T1T2 configuration, the Au atoms

TABLE VIII. BE per Au atom, Au-Si bond length $d(\text{Au-Si})$, Au-Au distance $d(\text{Au-Au})$, and the height of the Au atoms with respect to the top Si layer are tabulated for the case of 1/3 ML coverage on the patterned hydrogen terminated Si(001):1×1 surface having pattern 2.

Configuration	BE (eV)	$d(\text{Au-Si})$ (Å)	$d(\text{Au-Au})$ (Å)	Height (Å)
T1T2	3.18	2.30	2.71	≈ 1.8
S1S2	3.20	2.45	3.41	≈ 1.2
M1M2	3.25	2.50	4.05	≈ 0.6

TABLE IX. BE per gold atom, Au-Si bond length $d(\text{Au-Si})$, the Au-Au distance $d(\text{Au-Au})$, and the height of Au layer with respect to the top Si layer are tabulated for the case of 1/2 ML coverage on the patterned hydrogen terminated $\text{Si}(001):1 \times 1$ surface having pattern 2. The Au atoms at T1, T2, and T3 sites are denoted by Au_1 , Au_2 , and Au_3 , respectively. We use the same convention for the Au atoms at S and M sites.

Configuration	BE (eV)	$d(\text{Si-Au})$ (Å)	$d(\text{Au-Au})$ (Å)	Height (Å)
T1T2T3	3.14	$d(\text{Au}_1-R_1\text{Si})=2.42$ $d(\text{Au}_2-R_2\text{Si})=2.33$ $d(\text{Au}_3-R_3\text{Si})=2.33$	$d(\text{Au}_1-\text{Au}_2)=2.73$ $d(\text{Au}_2-\text{Au}_3)=6.07$	2.1
S1S2S3	3.06	$d(\text{Au}_1-R_1\text{Si})=2.49$ $d(\text{Au}_1-R_2\text{Si})=2.45$ $d(\text{Au}_2-R_2\text{Si})=2.51$ $d(\text{Au}_2-R_3\text{Si})=2.44$ $d(\text{Au}_3-R_3\text{Si})=2.56$	$d(\text{Au}_1-\text{Au}_2)=3.84$ $d(\text{Au}_2-\text{Au}_3)=4.34$	1.4
M1M2M3	2.99	$d(\text{Au}_1-R_1\text{Si})=2.49$ $d(\text{Au}_1-R_2\text{Si})=2.49$ $d(\text{Au}_2-R_2\text{Si})=2.49$ $d(\text{Au}_2-R_3\text{Si})=2.49$ $d(\text{Au}_3-R_3\text{Si})=2.49$	$d(\text{Au}_1-\text{Au}_2)=3.84$ $d(\text{Au}_2-\text{Au}_3)=3.84$	1.3

at the T1 and T2 sites approach each other and eventually form a dimer, while in the S1S2 and M1M2 configurations, the Au atoms do not form dimers. Note that though the Au atoms make strong bond with Si and Au neighbors for T1T2 configuration, this is not most favorable. This is because the adsorbed Au atoms at M1M2 configuration find more neighbors (including the Si atoms just below the top layer Si atoms) compared to the T1T2 configuration. The charge distribution along the direction of the Au-Si bonds is similar to that shown in Fig. 9, and hence, the nature of Au-Si bonds is mostly covalent. As far as the geometric structure is concerned, at 1/3 ML coverage, the adsorbed Au atoms form a doubly periodic linear chain structure (which corresponds to the M1M2 configuration) on the patterned hydrogen terminated $\text{Si}(001):1 \times 1$ surface having pattern 2. However, as the interatomic distances in the Au chain are 4.05 and 7.47 Å, the metallicity of the chain is not expected. This is confirmed by looking at the band structure plot, which is not presented here.

3. 1/2 monolayer Au on patterned hydrogen terminated $\text{Si}(001):1 \times 1$ surface: Pattern 2

Three Au atoms are adsorbed within the 2×3 supercell of the patterned hydrogen terminated $\text{Si}(001):1 \times 1$ surface having pattern 2, which corresponds to the 1/2 ML coverage. The reasonable initial configurations that we have considered are T1T2T3, S1S2S3, and M1M2M3, as shown in Fig. 3. The BE per Au atom, the Au-Si bond length $d(\text{Au-Si})$, the Au-Au distance $d(\text{Au-Au})$, and the height of the Au layer with respect to the top Si layer are given in Table IX. The T1T2T3 configuration turns out to be most stable configuration with BE=3.14 eV, which is favorable by 0.15 eV compared to the M1M2M3 configuration and by 0.08 eV compared to the S1S2S3S4 configuration. In this case also, we

see that with the increase in the coverage, the favorable sites change from M sites to T sites. From Table IX, we note that the Au-Si bonds are stronger for all the configurations and for the M1M2M3 configuration, we obtain a periodic linear chain extending long the $[1\bar{1}0]$ direction. However, for the most stable configuration, T1T2T3, the Au atoms form dimers, and therefore, we obtain a dimerized Au chain on the patterned hydrogen terminated $\text{Si}(001):1 \times 1$ surface (having pattern 2) extending along the $[1\bar{1}0]$ direction. Two Au dimers in the chain are separated by a distance of ≈ 6.1 Å. Thus, we do not expect the chain to be metallic in nature. The charge densities along the lines of the Au-Si bonds and the Au-Au bonds reveal that the bonds are mostly covalent in nature.

4. 2/3 monolayer Au on patterned hydrogen terminated $\text{Si}(001):1 \times 1$ surface: Pattern 2

The 2/3 monolayer coverage of Au on the patterned hydrogen terminated $\text{Si}(001):1 \times 1$ surface having pattern 2 corresponds to the adsorption of four Au atoms within the 2×3 supercell. Several initial configurations including the chainlike configuration are considered for the Au adsorption on the patterned hydrogen terminated $\text{Si}(001):1 \times 1$ surface having pattern 2. We are interested in examining the possibility for the formation of chainlike structure of Au on the patterned hydrogen terminated $\text{Si}(001):1 \times 1$ surface having pattern 2. As we mentioned earlier for pattern 1 surface that four periods of a straight Au chain exactly match with the three periods of the hydrogen terminated $\text{Si}(001):1 \times 1$ surface. The interatomic distance in the Au chain is assumed to be 2.88 Å, which is the Au-Au bond length in the bulk. We also note that the interatomic distance between Au atoms in the freestanding Au atomic chain varies from 2.7 to

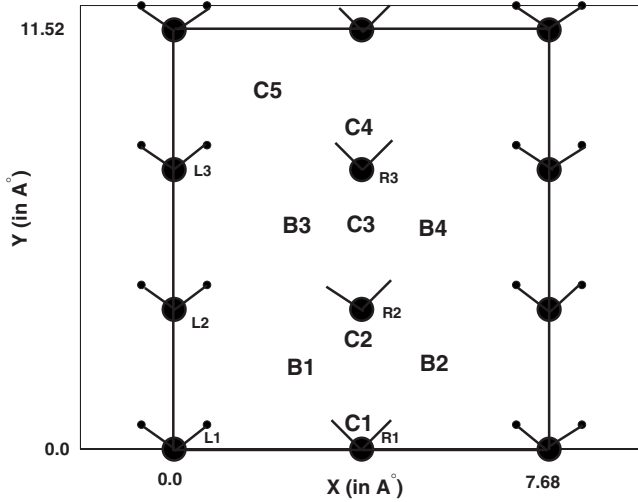


FIG. 10. The patterned hydrogen terminated Si(001): 1×1 surface having pattern 2. The possible adsorption sites of Au at $2/3$ ML coverage are shown. The surface Si atoms within the 2×3 supercell are represented by the larger filled circles and they are denoted as L1, L2, L3, R1, R2, and R3. Here, Si atoms denoted by R1, R2, and R3 have two dangling bonds each, as shown in the figure. The small circles represent the surface hydrogen atoms.

3.04 Å.^{7,39,40} Here, also we expect that the strain on the surface due to the arrangement of four Au atoms on a line

along the Y $[1\bar{1}0]$ direction will be less compared to any other configuration. We first consider the periodic straight chain configuration, C1C2C3C4 as the initial configuration (as shown in Fig. 10) and then let the system relax. After full relaxation of the system, we observe a zigzag chainlike structure of Au extending along the $[1\bar{1}0]$ direction. However, the interatomic distance (Au-Au distance along the chain) varies from 2.72 to 3.07 Å, which is similar to the case for pattern 1 surface as well as for the freestanding Au atomic chain. In this case, the BE per Au atoms is 3.07 eV, which is, however, less compared to the chain structure obtained in pattern 1 surface. The details of the Au-Au distance, the Au-Si distance, and the average height of the Au chain with respect to top Si layer are given in Table X. To conclude about the stability of the chain structure, we also considered the configurations (deviations from chain configuration): C1C2C3C5 and B1B2B3B4 (see Fig. 10). It is clear from Table X that the initial configuration, C1C2C3C5 (deviation from chain), is highly unstable and eventually merges to the C1C2C3C4 configuration after full relaxation. The BE for the B1B2B3B4 configurations is 2.9 eV, which is less favorable by 0.17 eV compared to the chain configuration. After full relaxation of the B1B2B3B4 configuration, we find strong Au-Au bonds within the supercell, and in addition, apart from the fact that the Au atoms form bonds with the top layer Si atoms, some Au atoms form bonds with the Si atoms lying just below the top Si layer. Even then, the B1B2B3B4

TABLE X. At $2/3$ ML coverage of Au on the patterned hydrogen terminated Si(001): 1×1 surface having pattern 2, the BE per gold atom, Au-Si distance $d(\text{Au-Si})$, Au-Au distance $d(\text{Au-Au})$, and height of the Au layer with respect to the top Si layer are given. In addition, the height differences among the Au atoms in the C1C2C3C4 configuration are displayed to understand the zigzag nature of the Au chain. The Au atoms at C1, C2, C3, and C4 sites are denoted as Au₁, Au₂, Au₃, and Au₄, respectively. We use the same convention for Au atoms in the configurations B1B2B3B4 and C1C2C3C5.

Configuration	BE (eV)	$d(\text{Si-Au})$ (Å)	$d(\text{Au-Au})$ (Å)	Height (Å)
C1C2C3C4 (Chain configuration)	3.074	$d(\text{Au}_1 - \text{R}_1\text{Si}) = 2.38$	$d(\text{Au}_1 - \text{Au}_2) = 2.72$	$h(\text{Au}_1 - \text{Au}_2) = -0.19$
		$d(\text{Au}_1 - \text{R}_2\text{Si}) = 4.48$	$d(\text{Au}_2 - \text{Au}_3) = 3.07$	$h(\text{Au}_1 - \text{Au}_3) = -0.65$
		$d(\text{Au}_2 - \text{R}_2\text{Si}) = 2.38$	$d(\text{Au}_3 - \text{Au}_4) = 3.07$	$h(\text{Au}_1 - \text{Au}_4) = -0.19$
		$d(\text{Au}_3 - \text{R}_2\text{Si}) = 2.51$		$h(\text{Au} - \text{Si}) \approx 2.2$
		$d(\text{Au}_3 - \text{R}_3\text{Si}) = 2.51$		
		$d(\text{Au}_4 - \text{R}_3\text{Si}) = 2.38$		
C1C2C3C5 (Deviation from chain)	3.070	$d(\text{Au}_1 - \text{R}_1\text{Si}) = 2.37$	$d(\text{Au}_1 - \text{Au}_2) = 2.60$	$h(\text{Au}_1 - \text{Au}_2) = -0.17$
		$d(\text{Au}_1 - \text{R}_2\text{Si}) = 4.48$	$d(\text{Au}_2 - \text{Au}_3) = 3.09$	$h(\text{Au}_1 - \text{Au}_3) = -0.57$
		$d(\text{Au}_2 - \text{R}_2\text{Si}) = 2.39$	$d(\text{Au}_3 - \text{Au}_4) = 3.06$	$h(\text{Au}_1 - \text{Au}_4) = -0.15$
		$d(\text{Au}_3 - \text{R}_2\text{Si}) = 2.50$		$h(\text{Au} - \text{Si}) \approx 2.2$
		$d(\text{Au}_3 - \text{R}_3\text{Si}) = 2.53$		
		$d(\text{Au}_4 - \text{R}_3\text{Si}) = 2.38$		
B1B2B3B4 (Deviation from chain)	2.901	$d(\text{Au}_1 - \text{R}_1\text{Si}) = 2.57$	$d(\text{Au}_1 - \text{Au}_2) = 2.98$	$h(\text{Au}_2 - \text{Au}_1) = 1.00$
		$d(\text{Au}_1 - \text{R}_2\text{Si}) = 2.58$	$d(\text{Au}_3 - \text{Au}_4) = 2.98$	$h(\text{Au}_4 - \text{Au}_3) = 1.00$
		$d(\text{Au}_2 - \text{R}_1\text{Si}) = 2.57$	$d(\text{Au}_1 - \text{Au}_3) = 2.94$	$h(\text{Au}_1 - \text{Au}_3) = 0.00$
		$d(\text{Au}_2 - \text{R}_2\text{Si}) = 2.58$	$d(\text{Au}_2 - \text{Au}_4) = 4.07$	$h(\text{Au}_2 - \text{Au}_4) = 0.00$
		$d(\text{Au}_3 - \text{R}_2\text{Si}) = 2.58$		$h(\text{Au} - \text{Si}) \approx 0.50$
		$d(\text{Au}_4 - \text{R}_2\text{Si}) = 2.57$		
		$d(\text{Au}_4 - \text{R}_3\text{Si}) = 2.58$		

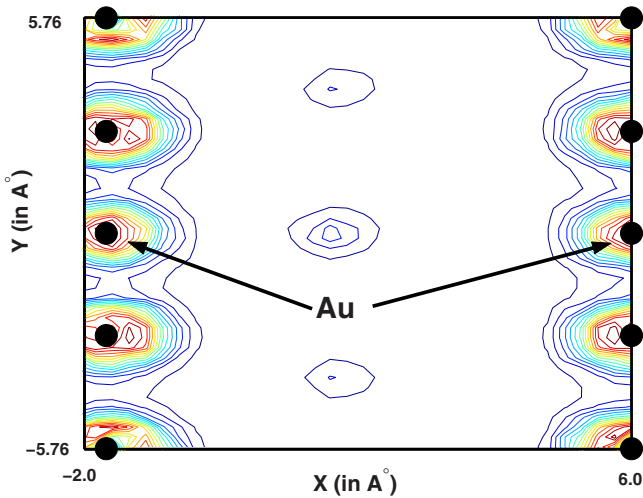


FIG. 11. (Color online) This shows the total charge density in the X-Y plane (the plane coincides with the Au layer) for the case of 2/3 ML coverage of Au on the patterned hydrogen terminated Si(001):1×1 surface having pattern 2. The Au atoms are indicated in the figure. The formation of Au chain is clear from the figure.

configuration is not most favorable. The results indicate that the zigzag chain structure is the most favorable structure. The total charge density plot in the X-Y plane (coinciding the Au layer) is shown in Fig. 11. The formation of the Au chain is clear from the charge density plot in Fig. 11. The zigzag pattern of the chain is not visible in Fig. 11 because the wire has zigzag pattern in the Y-Z plane. However, the band structure plot in Fig. 12 shows that the wire is not metallic in nature. The geometric structure of the Au chain on the patterned hydrogen terminated Si(001):1×1 surface having pattern 2 is shown in Fig. 13.

IV. SUMMARY

The electronic structure calculations are done for the adsorption of Au on the patterned hydrogen terminated Si(001):1×1 surfaces. The calculations are done within

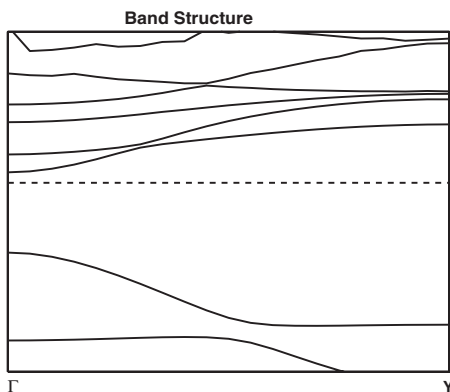


FIG. 12. This shows the band structure for the case of 2/3 ML coverage of Au on the patterned hydrogen terminated Si(001):1×1 surface having pattern 2. The Fermi level is indicated by a dotted line.

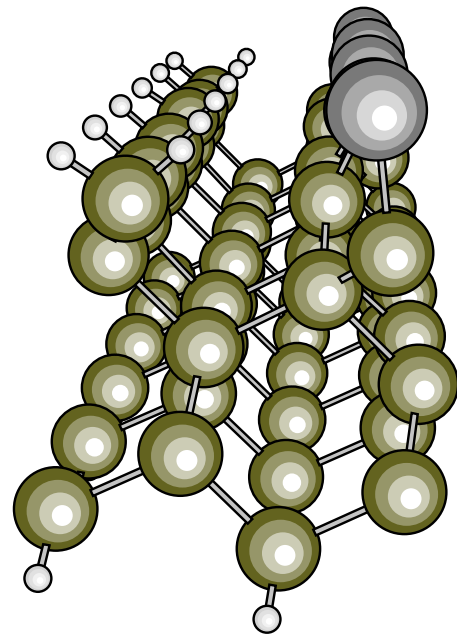


FIG. 13. (Color online) This shows the most favorable geometrical structure when 2/3 ML of Au is adsorbed on the patterned hydrogen terminated Si(001):1×1 surface having pattern 2. The smallest spheres indicate the hydrogen atoms, the medium sized spheres correspond to Si atoms, and the gold atoms are indicated by the topmost biggest spheres.

pseudopotential approximation under the density functional approach. The hydrogen terminated Si(001):1×1 surface is patterned in two different ways. On the one hand, within the 2×3 supercell, the hydrogen atoms lying between two Si rows along the [11̄0] direction are removed and the corresponding patterned surface is named as the patterned hydrogen terminated Si(001):1×1 surface having pattern 1. On the other hand, within the 2×3 supercell, the hydrogen atoms attached to the Si atoms in a single Si row along the [11̄0] direction are removed and the corresponding patterned surface is named as the patterned hydrogen terminated Si(001):1×1 surface having pattern 2. The stable sites for the adsorption of Au on such patterned surfaces are studied for various submonolayer coverages (1/6, 1/3, 1/2, and 2/3 ML) and the stable Au structures are analyzed. We find that the preference for adsorption sites changes with the increase in the coverage. The reason for such happenings is explained. Most interestingly, it is found that for such patterned surfaces, the chainlike structures of Au atoms are preferable. In particular, at 2/3 ML coverage, the zigzag Au chains with an interatomic spacing ranging between 2.72 and 3.07 Å becomes most stable on both the patterned hydrogen terminated Si(001):1×1 surfaces. These supported Au chains also resemble the freestanding Au chains obtained experimentally. The chain at 2/3 ML coverage on the patterned hydrogen terminated Si(001):1×1 surface having pattern 1 may be metallic in nature. However, the same on the patterned hydrogen terminated Si(001):1×1 surface having pattern 2 is semiconducting in nature. It is worthy of mentioning that beyond 2/3 ML coverage, the additional Au atoms may form clusters on the Si surface due to the lack of

dangling bonds.⁴¹ Therefore, the Au coverage should be maintained at 2/3 ML for the formation of Au chain on the patterned hydrogen terminated Si(001):1×1 surface. We believe that this study will encourage experimentalists to design experiments on the patterned hydrogen terminated Si(001):1×1 surface having pattern 1 and pattern 2 for obtaining atomic Au chains (metallic and/or nonmetallic) supported by semiconducting substrate. If the atomic chain structures supported by substrates are produced experimen-

tally, they will be useful for atomic scale devices and also may be used as metallic interconnects in circuit devices.

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*bikashc.gupta@visva-bharati.ac.in

†Deceased.

- ¹S. Hosoki, S. Hosaka, and T. Hasegawa, *Appl. Surf. Sci.* **60-61**, 643 (1992).
- ²M. F. Crommie, C. P. Lutz, and D. M. Eigler, *Science* **262**, 218 (1993).
- ³T.-C. Shen, C. Wang, G. C. Abeln, J. R. Tucker, J. W. Lyding, Ph. Avouris, and R. E. Walkup, *Science* **268**, 1590 (1995).
- ⁴*Advances in Scanning Probe Microscopy*, edited by T. Sakurai and Y. Watanabe (Springer-Verlag, Berlin, 1989).
- ⁵T.-C. Shen, C. Wang, and J. R. Tucker, *Phys. Rev. Lett.* **78**, 1271 (1997).
- ⁶Y. Wada, T. Uda, M. Lutwyche, S. Kondo, and S. Heike, *J. Appl. Phys.* **74**, 7321 (1993).
- ⁷D. Sanchez-Portal, E. Artacho, J. Junquera, P. Ordejon, A. Garcia, and J. M. Soler, *Phys. Rev. Lett.* **83**, 3884 (1999).
- ⁸D. Sanchez-Portal, E. Artacho, J. Junquera, A. Garcia, and J. M. Soler, *Surf. Sci.* **482-485**, 1261 (2001).
- ⁹J. A. Torres, E. Tosatti, A. D. Coros, F. Ercolessi, J. J. Kohanoff, F. D. Di Tolla, and J. M. Soler, *Surf. Sci.* **426**, L441 (1999).
- ¹⁰M. Okamoto and K. Takayanagi, *Phys. Rev. B* **60**, 7808 (1999).
- ¹¹H. Hakkinen, R. N. Barnett, and U. Landman, *J. Phys. Chem. B* **103**, 8814 (1999); H. Hakkinen, R. N. Barnett, A. G. Scherbakov, and U. Landman, *ibid.* **104**, 9063 (2000).
- ¹²P. Sen, S. Ciraci, A. Buldum, and I. P. Batra, *Phys. Rev. B* **64**, 195420 (2001).
- ¹³P. Sen, O. Gülseren, T. Yildirim, I. P. Batra, and S. Ciraci, *Phys. Rev. B* **65**, 235433 (2002).
- ¹⁴I. P. Batra, T. Ciani, D. Boddupalli, and L. Soberano, Technical Proceedings of the 2003 Nanotechnology Conference and Trade Show, San Francisco, USA, 2003, Vol. 2, p. 206.
- ¹⁵J. J. Boland *Adv. Phys.* **42**, 129 (1993).
- ¹⁶F. S. Tautz and J. A. Schaefer, *J. Appl. Phys.* **84**, 6636 (1998).
- ¹⁷Y. J. Chabal and K. Raghavachari, *Phys. Rev. Lett.* **54**, 1055 (1985).
- ¹⁸J. J. Boland, *Phys. Rev. Lett.* **65**, 3325 (1990).
- ¹⁹J. J. Boland, *Surf. Sci.* **261**, 17 (1992).
- ²⁰Y. J. Chabal and K. Raghavachari, *Phys. Rev. Lett.* **53**, 282 (1984).
- ²¹Y. Morita and H. Tokumoto, *Appl. Phys. Lett.* **67**, 2654 (1995); *J. Vac. Sci. Technol. A* **14**, 854 (1996).
- ²²S. Watanabe, Y. A. Ono, T. Hashizume, and Y. Wada, *Phys. Rev. B* **54**, R17308 (1996).
- ²³S. Watanabe, M. Ichimura, T. Onogi, and Y. Ono, *Jpn. J. Appl. Phys., Part 2* **36**, L929 (1997).
- ²⁴B. C. Gupta and I. P. Batra, *Phys. Rev. B* **71**, 165429 (2005).
- ²⁵J. N. Crain, J. L. McChesney, F. Zheng, M. C. Gallagher, P. C. Snijders, M. Bissen, C. Gundelach, S. C. Erwin, and F. J. Himpsel, *Phys. Rev. B* **69**, 125401 (2004).
- ²⁶R. Losio, K. N. Altmann, A. Kirakosian, J. L. Lin, D. Y. Petrovykh, and F. J. Himpsel, *Phys. Rev. Lett.* **86**, 4632 (2001).
- ²⁷M. Krawiec, T. Kwapinski, and M. Jalochoowski, *Phys. Rev. B* **73**, 075415 (2006).
- ²⁸H. Okino, R. Hobara, I. Matsuda, T. Kanagawa, S. Hasegawa, J. Okabayashi, S. Toyoda, M. Oshima, and K. Ono, *Phys. Rev. B* **70**, 113404 (2004).
- ²⁹H. Okino, I. Matsuda, S. Yamazaki, Rei. Hobara, and S. Hasegawa, *Phys. Rev. B* **76**, 035424 (2007).
- ³⁰Q. Sun, Q. Wang, Y. Kawazoe, and P. Jena, *Eur. Phys. J. D* **29**, 231 (2004).
- ³¹Q. Sun, Q. Wang, G. Chen, and P. Jena, *J. Chem. Phys.* **127**, 214706 (2007).
- ³²G. Kresse and J. Hafner, *Phys. Rev. B* **47**, R558 (1993); **49**, 14251 (1994).
- ³³G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).
- ³⁴G. Kresse and J. Furthmüller, *Comput. Mater. Sci.* **6**, 15 (1996).
- ³⁵P. Sen, S. Ciraci, I. P. Batra, C. H. Grein, and S. Sivananthan, *Surf. Sci.* **519**, 79 (2002).
- ³⁶C. Hobbs, L. Kantorovich, and J. D. Gale, *Surf. Sci.* **591**, 45 (2005).
- ³⁷M. W. Radny, P. V. Smith, T. C. G. Reusch, O. Warschkow, N. A. Marks, H. F. Wilson, S. R. Schofield, N. J. Curson, D. R. McKenzie, and M. Y. Simmons, *Phys. Rev. B* **76**, 155302 (2007).
- ³⁸M. Ceriotti and M. Bernasconi, *Phys. Rev. B* **76**, 245309 (2007).
- ³⁹M. Okamoto and K. Takayanagi, *Phys. Rev. B* **60**, 7808 (1999).
- ⁴⁰F. D. Novaes, A. J. R. da Silva, E. Z. da Silva, and A. Fazzio, *Phys. Rev. Lett.* **96**, 016104 (2006).
- ⁴¹Q. Sun, Q. Wang, B. K. Rao, and P. Jena, *Phys. Rev. Lett.* **93**, 186803 (2004).