Tuning of the periodicity of stable self-organized metallic templates*

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The atomic and electronic structures of Pb bilayer/Pt(111) are investigated with two theoretical calculations. We find that the stable $(2 \times 2)/(3 \times 3)$ Pb/Pt(111) structure is a promising candidate for being used as a template with self-organized ordered Pb semi-cluster array on the first Pb monolayer. This stable structure can realize the ordered Au single-atom array around the Pb semi-clusters that can cause selective adsorption of noble atoms. The size of Pb magic number semi-cluster plays a more important role in determining the periodicity of the template than the lattice constant misfit between the substrate and the overlayer. This leads to quite a different periodicity between the two stable templates, which are $(2\times2)/(3\times3)$ Pb/Pt(111) and Pb/Cu(111). Therefore, by considering the size of the stable semi-clusters and carefully selecting different substrate materials, we can tune the density of Pb semi-clusters as the nucleation points and then tune the periodicity of the stable template.

Keywords: self-organizing, template, Chen–Möbius inversion method, first-principles calculation

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1. Introduction

A periodic nano-scale structure on a simple crystal surface is of great interest not only for fundamental studies but also for applications in nanotechnology, besides the self-organized phenomena in semiconductor material surface.[1,2] For example, it can be used as a template to organize adsorbed atomic and molecular species into a nanostructure, thereby providing desired features in dimensions that cannot be achieved with lithographic techniques.[3,4] Experimentally, self-organized metallic surface templates, such as Ag/Pt,[5] Ag/Ru,[6−8] Au/Ni,[9] Ag/Cu,[10,11] and Cu/Pt,[5] are very promising candidates for controlling the nucleation and the growth of nanostructures.[11−16] The strain-relief in Ag/Pt or Cu/Pt templates occurs spontaneously when two layers of Ag or Cu atoms are deposited on the Pt(111) substrate, because of the difference in lattice constant between the overlayer and the substrate. The second monolayer of Cu or Ag forms a network of dislocations, in order to relieve the strain induced by the lattice misfit between the substrate and the overlayer. It is believed that the dislocations often repel adsorbed atoms diffusing over the surface, so they can serve as templates for the selective nucleation of nanostructures from adatoms.[5] There are only a few first-principles studies dealing with the electronic and atomic structures of these systems.[17] In our recent work,[17] it was shown that the stable $(2\times2)/(3\times3)$ Pb/Cu(111) structure was a good candidate for template formed by ordered array of identical (2×2) Pb semi-clusters. The coverage of each Pb layer was next to the Pb complete coverage on the Cu(111) surface. The strain-relief, which was induced by the lattice mismatch between the substrate and the overlayer, determined the periodicity of the template, which was similar to the other experimental results mentioned above.[5] In this work, we find that on the Pt(111) substrate, $(2\times2)/(3\times3)$ Pb/Pt(111) is a good candidate for serving as a template, but it is with a larger periodicity than the case of Cu substrate, and far from the Pb complete coverage on the Pt(111) surface. The new result reveals an additional mechanism

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that also influences the periodicity of the template.

2. Computational method

In order to find the stable interface structure of the Pb bilayer on the Pt(111) surface, with a large mismatch considered, we first develop an appropriate interfacial potential via the Chen–Möbius lattice inversion method,[18−22] and then use the potentials to relax the interface structures with the energy minimization method. The initial interface structures are modeled in super cells of $[(n-1)\times(n-1)]/(n\times n)$ Pb/Pt(111) ($n = 2, 3, \ldots, 22$) to take the mismatch into account. The $(n-1)\times(n-1)$ indicates the super cell size of the Pb bilayer that is in the plane parallel to the interface, and the $(n\times n)$ denotes the super cell size of Pt(111) substrate. In the normal direction of the interface, the repeated slabs with five Pt layers separated by a vacuum region equivalent to eleven Pt layers are used for modeling the Pt(111) surface. Both sides of the Pt slab are adsorbed symmetrically by Pb bilayer. All the Pt and Pb atoms are initially located at their bulk positions with the equilibrium lattice constants of 3.92 Å (1 Å = 0.1 nm) and 4.95 Å respectively. In order to obtain the equilibrium structure, all the Pt and Pb atoms in the unit cell except those in the central Pt layer are fully relaxed via the energy-minimization algorithm based on the interfacial potentials. The stable structures are determined by finding the structures with ordered configurations, and usually they have the lower average energies per atom than other structures with disordered configurations.

The first-principles calculations are carried out on these stable structures to investigate the electronic properties, by using the unrelaxed interface structure model mentioned above. The calculations are based on a density functional theory implemented in a projector augmented wave (PAW) representation.[23,24] The exchange–correlation effect is treated in the generalized gradient approximation (GGA).[25] The plane wave kinetic energy cutoff is 22.06 Ry, and the Monkhorst–Park k-point mesh is $2\times2\times1$.[26] Energy convergence is reached when the forces on the relaxed atoms are less than 0.03 eV/Å.

3. Results and discussion

Using the Chen–Möbius inversion method,[20,22] we extract the interaction potential $\Phi_{\mathrm{Pt-Pb}}$ from the interfacial adhesive energy calculated with the first-principles method. The potentials $\Phi_{\mathrm{Pt-Pt}}$ and $\Phi_{\mathrm{Pb-Pb}}$ are extracted from the cohesive energies of bulk Pt and Pb using the method described in Ref. [21]. All the three potentials are expressed in the form of Rahman–Stillinger–Lemberg function as

$$\begin{aligned}\Phi = {} & D_0 \exp[y(1-r/R_0)] + a_1/\{1+\exp[b_1(r-c_1)]\} \\ & + a_2/\{1+\exp[b_2(r-c_2)]\} \\ & + a_3/\{1+\exp[b_3(r-c_3)]\}. \end{aligned} \quad (1)$$

Table 1 provides the parameters for the interaction potentials $\Phi_{\mathrm{Pb-Pt}}$, $\Phi_{\mathrm{Pt-Pt}}$ and $\Phi_{\mathrm{Pb-Pb}}$. Using these potentials, the calculated lattice constants of bulk Pt and Pb are 3.92 Å and 4.95 Å, which are in good agreement with the values of 3.97 Å,[27] and 4.949 Å respectively.[28] Figure 1 shows the average energies for the $[(n-1)\times(n-1)]/(n\times n)$ Pb/Pt(111) ($n = 2, 3, \ldots, 22$) structures, which are calculated with the interfacial potentials. The average energy means that the total energy of each relaxed structure is divided by the total number of atoms in the structure. Relaxed structures show that when $7 \le n < 22$, the Pb bilayer cannot remain as a bilayer structure but it is reorganized into three or even more layers and becomes disordered, owing to the increasing of mismatch strain. For example, the disordered structures of $n = 7$ and 22 are illustrated in Fig. 1. In other words, when $n = 6$, the disorder structure means $(5\times5)/(6\times6)$ Pb/Pt(111) structure, which has (5×5) Pb bilayer and (6×6) Pt(111) substrate. For $n = 6$, each layer of the Pb bilayer can cover the Pt surface at 0.69 ML. But when $n = 12$, the disorder structure means $(11\times11)/(12\times12)$ Pb/Pt(111) structure, which has (11×11) Pb bilayer and (12×12) Pt(111) substrate. For $n = 12$, each layer of the Pb bilayer can cover the Pt surface at 0.84 ML, which is larger than that of $n = 6$ and then causes a larger mismatch strain between the Pb bilayer and Pt(111) substrate, so the Pb bilayer of the structure of $n = 12$ cannot keep stable. Therefore, these structures with $n \ge 7$ cannot be used as stable templates to support ordered arrays of atoms or clusters. However, when $n \le 6$, the relaxed structures retain the well-ordered two Pb layers on the Pt(111) substrate, although a few Pb atoms of the second layer move upward by 0.2 Å along the normal direction of the Pt(111) surface when $n = 6$ (i.e. $5\times5/6\times6$). These results suggest that there is a critical size around $n = 6$. When $n = 6$, each layer of the Pb bilayer can uniformly cover the Pt surface at 0.69 ML, where 1 ML is defined as one Pb

atom per surface Pt atom, and in fact the coverage is slightly greater than a complete coverage of 0.64 ML. When $2 \leq n \leq 6$, the relaxed structures are all stable, while the average energies of the structures increase slowly with the value of n increasing. However, when $n = 2$, the Pb surface cell has a super cell size of 1×1, so it is unsuitable for being used as a template. Therefore, the $[(n-1)\times(n-1)]/(n\times n)$ Pb/Pt(111) ($n = 3,\ 4,\ 5,\ 6$) are stable structures that can possibly be used as templates for selective adsorptions of atoms or clusters, while the coverage of each Pb layer is less than the complete coverage for the structures with $n = 3$ and 4. This is quite different from the case of Pb/Cu(111),[17] where only the structure with $n = 3$ is stable when the coverage of each Pb layer is less than complete coverage.

Table 1. Parameters of $\Phi_{\mathrm{Pb-Pt}}$, $\Phi_{\mathrm{Pt-Pt}}$ and $\Phi_{\mathrm{Pb-Pb}}$ for the Pb bilayer/Pt(111) structure.

Pb/Pt(111)	D_0/eV	R_0/Å	y	a_1/eV	b_1/Å^{-1}	c_1/Å	a_2/eV	b_2/Å^{-1}	c_2/Å	a_3/eV	b_3/Å^{-1}	c_3/Å
$\Phi_{\mathrm{Pb-Pt}}$	0.61	1.00	6.57	84.35	4.37	2.25	–60.07	1.12	0.33	0.02	2.19	7.71
$\Phi_{\mathrm{Pt-Pt}}$	11501.72	1.00	1.65	–2996.80	2.62	1.55	–3519.84	1.59	1.66	0.00	1.00	1.00
$\Phi_{\mathrm{Pb-Pb}}$	370.36	1.00	1.02	4082.02	2.64	1.09	–476.68	1.05	1.02	–669.59	1.33	0.17

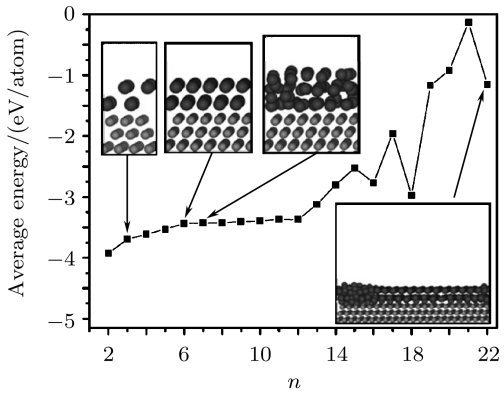
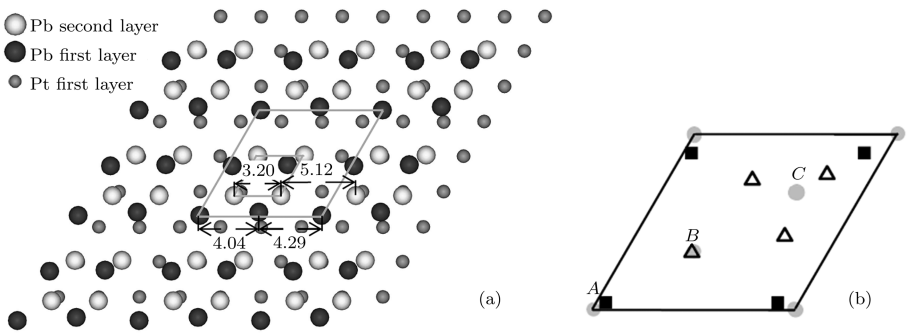


Fig. 1. Average energies for the $[(n-1)\times(n-1)]/(n\times n)$ Pb bilayer/Pt(111) ($n = 2, 3, \ldots, 22$) structures, where the dark (big) and gray (small) balls represent Pb and Pt atoms, respectively.

Next, we carry out comprehensive first-principles investigations on the atomic and electronic properties of the stable $(2\times2)/(3\times3)$, $(3\times3)/(4\times4)$, $(4\times4)/(5\times5)$ and $(5\times5)/(6\times6)$ Pb/Pt(111) structures. Figures 2(a), 2(c) and 2(e) show the top views of the relaxed $(2\times2)/(3\times3)$, $(3\times3)/(4\times4)$ and $(4\times4)/(5\times5)$ structures, which are still stable and remain the ordered configurations that accord with the above calculations. In Fig. 2(a), the four Pb atoms in the second layer form a closed packed semi-cluster structure (marked by the smaller parallelogram). We defined the semi-cluster as a kind of structure exhibiting the cluster character only in two-dimensional plane (in the (111) surface plane for this paper).[17] In the second Pb layer, the nearest distance between the Pb atoms is $d_{\mathrm{in}} = 3.20$ Å (4.04 Å for the first Pb layer) that is shorter than $d_{\mathrm{out}} = 5.12$ Å (4.29 Å for the first Pb layer) between neighbouring semi-clusters by 1.92 Å (0.25 Å). This arrangement indicates that within the semi-cluster, the Pb atoms are packed more closely with stronger interactions than those between the neighbouring semi-clusters. It is worth while mentioning that for the $(2\times2)/(3\times3)$ structure, Pb/Pt(111) has significantly smaller d_{in} and much greater d_{out} than those ($d_{\mathrm{in}} = 3.60$ Å, $d_{\mathrm{out}} = 4.06$ Å) of Pb/Cu(111).[17] These findings show that the density of the nucleation points can be tuned by varying the substrate, and the increase of the lattice constant from Cu to Pt results in the reduction of the density of the Pb semi-clusters. The binding energy (i.e., $E_{\mathrm{b}} = E_{(\mathrm{Pb_bilayer/Pt(111)})} - E_{\mathrm{Pb_bilayer}} - E_{\mathrm{Pt(111)}}$) of the Pb bilayer on the Pt(111) substrate is 8.2 eV that is significantly greater than 4.95 eV on the Cu(111) substrate. The reduction of the internal distance of the Pb atoms within one cluster and the higher binding energy of the $(2\times2)/(3\times3)$ Pb/Pt(111) indicate that the Pb semi-clusters of $(2\times2)/(3\times3)$ Pb/Pt(111) are more stable than those of $(2\times2)/(3\times3)$ Pb/Cu(111). The semi-cluster structure is induced mainly by the inherent electronic character of Pb bilayer, and partly by the mismatch strains between the Pb and Pt atoms at the interface. The difference in surface property between the covered area and the uncovered area leads to the selective adsorption of atoms or clusters. Figure 2(b) shows the relative sites of all Pb and Pt atoms in one super cell. These atoms in the $(2\times2)/(3\times3)$ Pb/Pt(111) structure are shifted into one Pt(111) (1×1) surface cell, but retain their relative positions. The '*A*', '*B*' and '*C*' points denote the Pt atoms in the third, second, and first Pt layers of the slab respectively, which are the standard fcc sites, because the Pt atoms stay more or less at the same position after relaxation. One open triangle, which corresponds to the relative positions of Pb atoms of the first Pb layer,

is located at the 'B' site that is aligned with the fcc site of the Pt layers. The other three open triangles are near the 'C' site. These indicate as follows: (i) the configuration of Pb atoms does not maintain the standard fcc stacking of the Pt substrate, but forms semi-clusters, which makes the main contribution to the periodic network of dislocations at the surface of Pb/Pt(111); (ii) the first Pb layer serves as the buffer layer between the Pt substrate and the second Pb layer. The configuration of each Pb semi-cluster in the second layer is similar to the stable freestanding Pb_4 cluster. Previous work has shown that Pb_4 cluster is a magic number cluster with two-dimensional structure.[29] Figures 2(c) and 2(e) show that the relaxed structures of $n = 4$ and 5 remain the stable Pb bilayer configurations. The Pb atom coverages of the structure with $n = 4$ is 0.56 ML that are less than the complete coverage, while the coverage of $n = 5$ is equal to complete coverage 0.64 ML with the lattice constant close to 5/4 that of the Pt. Usually, when the coverage of each Pb layer of the Pb bilayer is less than the complete coverage, the periodic network will have great opportunity to form at the surface, according to the strain-relief theory.[5] This means that the periodic network can appear at the surface of the $n = 4$ [i.e., $(3 \times 3)/(4 \times 4)$] structure. However, the relaxed $(3 \times 3)/(4 \times 4)$ Pb/Pt(111) structure does not show a periodic network, while the separation between the neighbouring Pb atoms in the first and second layer are almost equal (Fig. 2(c)). For instance, the separations are all 3.73±0.17 Å for the second layer of the $(3 \times 3)/(4 \times 4)$ structure. This indicates that the second Pb monolayer with (3×3) periodicity cannot form semi-clusters due to the inherent electric character of Pb atoms. As for the $n = 5$ structure, the difference in separation between the neighbouring Pb atoms in the second layer is very small (±0.05 Å), owing to the complete coverage of Pb atoms on Pt(111). Therefore, for both structures of $n = 4$ and 5, the surfaces of the Pb bilayer can, to some degree, be regarded as a clean Pb(111) surface with (1×1) period for the adsorption atoms. Hence, the $(3 \times 3)/(4 \times 4)$ and $(4 \times 4)/(5 \times 5)$ Pb/Pt(111) structures are unsuitable candidates for being used as templates. Furthermore, because the second Pb monolayer with (2×2) structure can form a semi-cluster but (3×3) and (4×4) cannot, we believe that the second Pb monolayer with $(l \times l)$ structure does have a magic number, such as $l = 2$, which is similar to that of a free cluster.[29] For example, the Pb semi-cluster (with the magic number $l = 2$) in the $(2 \times 2)/(3 \times 3)$ Pb/Pt(111) structure also exhibits the very stable semi-cluster character in Cu(111) surface.[17] These facts indicate that both the inherent character of the Pb semi-cluster and the lattice mismatch between the substrate and the overlayer induce the strain, thereby leading to the formation of periodic template. Besides, the size of Pb semi-cluster plays a more important role in determining the periodicity of the template than the lattice constant mismatch between the substrate and the overlayer. This mechanism is different from that of the Pb/Cu(111) case, where the periodicity of the template can be derived only from the lattice constant mismatch between Pb and Cu, because the Pb coverage of the stable template of $(2 \times 2)/(3 \times 3)$ Pb/Cu(111) is next to the complete coverage of $(3 \times 3)/(4 \times 4)$ structure.[17]

After the first-principles relaxation, the Pb atoms of the $n = 6$ structure cannot remain as the bilayer structure but becomes disordered slightly. The shifts of Pb atoms are greater than those calculated with the Chen–Möbius inversion potential. The MD method based on the Chen–Möbius inversion potential can give the possible sizes in a small range, and the first-principles calculations are needed to further examine the possible structures. Therefore, the structure of $n = 6$ is unsuitable for being used as a stable template. These mean that the critical size should be $n = 5$.



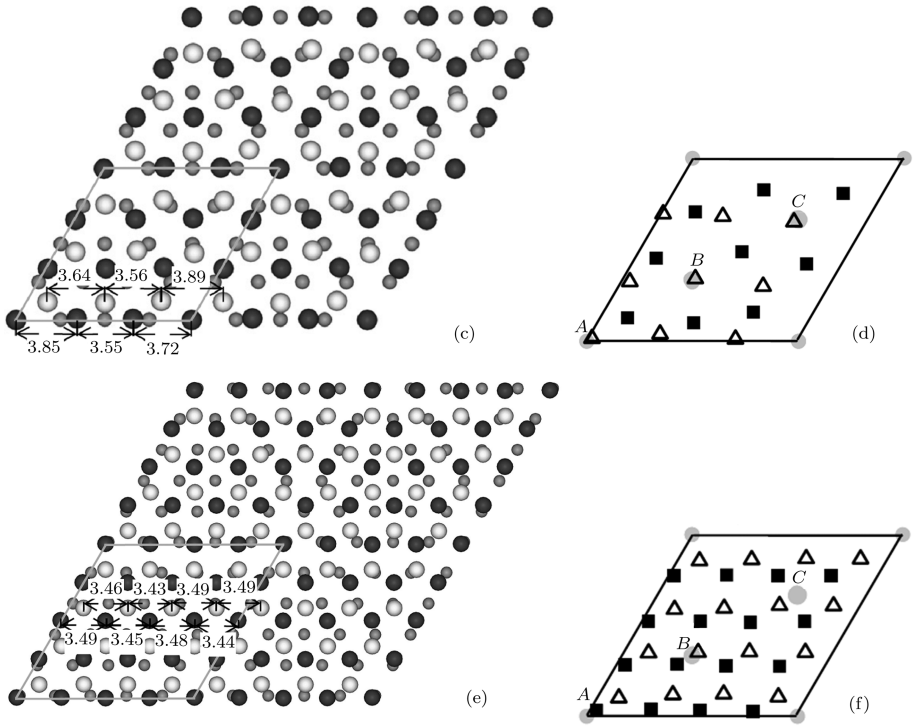


Fig. 2. (a) Top view of relaxed $(2 \times 2)/(3 \times 3)$ Pb/Pt(111) structure ($n = 3$), and the bigger parallelogram represents one super cell; (b) The relative positions of Pb and Pt atoms in Pt(111) 1×1 surface cell for the same structure as panel (a). The gray dot, open triangle and solid square are for the atoms of Pt substrate, first Pb layer and second Pb layer respectively; panels (c) and (e) are the same as panel (a), but for the $n = 4$ and 5 structures respectively; panels (d) and (f) are the same as panel (b), but for the $n = 4$ and 5 structures respectively. The distances (in Å) between some Pb atoms are also shown.

The differences of electron charge densities of the $(2 \times 2)/(3\times3)$ Pb/Pt(111) structure are calculated and shown in Figs. 3(a) and 3(b). The difference of electron charge density is defined as the difference in density between the Pb/Pt(111) structure and the superposition of atomic electron charge, i.e., $\Delta\rho(\boldsymbol{r}) = \rho(\text{Pb/Pt(111)}) - \sum_\mu \rho_{\text{atom}}(\boldsymbol{r} - \boldsymbol{R}_\mu)$. The property of the bonding between the Pb atoms in the second layer is clearly shown in Fig. 3(a). There is a high charge density area within each Pb semi-cluster, which is surrounded by the zero charge density areas between neighbouring semi-clusters. Each semi-cluster includes four Pb atoms that are congregated by the attraction due to the inherent electronic character of Pb bilayer, and one semi-cluster is marked with a parallelogram in Fig. 3(a). The semi-clusters are separated by the dipole repulsion caused by elastic interactions partly due to the strain relief of the lattice mismatch in the interface. Theoretical study reveals that the free Pb_m clusters with the magic number $m = 4$, 7, 10, and 13 have higher stabilities than the other clusters.[29] The configuration of the free stable Pb_4 cluster is two-dimensional. After the adsorption of Pb bilayer on Pt(111) surface, the (2×2) Pb semi-clusters in the Pb second layer inherit the stability of the free Pb_4 cluster. In other words, for the Pb bilayer/Pt(111) structure, the stability and the configuration of (2×2) Pb semi-clusters are similar to those of the free Pb_m cluster with magic number $m = 4$. These confirm the above judgment that $l = 2$ is a magic number for $(l \times l)$ Pb semi-cluster. This condition is difficult to realize experimentally, therefore only a few metal/metal templates have been found in experiment. However, a similar phenomenon has already appeared on the surface of semiconductor materials. For example, experimentally, the existence of magic numbers of the semiconductor clusters on semiconductor surface was shown in the reconstructed Ga/Si(111) surface.[30] For Pb/Pt(111), there are obvious covalent bonds between the Pb atoms in first Pb layer and the Pt atoms at Pt(111) surface [Fig. 3(b)], which indicates the strong interactions between them. In the second Pb layer, there are alternately high and zero electronic charge density areas between Pb atoms. Such a picture reveals that the direct interactions between these Pb atoms are alternately strong and weak.

The interactions between the two different areas and the adatoms, such as Au adatoms, will be different. Such a mechanism will help to realize the selective adsorption of adatoms on the surface of Pb/Pt(111). So the periodic $(2 \times 2)/(3 \times 3)$ Pb/Pt(111) structure with a very short periodicity (8.32 Å) will be a promising candidate for being used as a template. Based on different substrates, the periodicity of $(2 \times 2)/(3 \times 3)$ Pb/Pt(111) structure is greater than that (7.67 Å) of $(2 \times 2)/(3 \times 3)$ Pb/Cu(111),[17] although both of the two structures are good candidate for periodic template. Thus, we consider that by carefully selecting different substrate materials, we can tune the periodicity of the template, with the same material used as the adsorbed bilayer. This is useful for the nanofabrications.

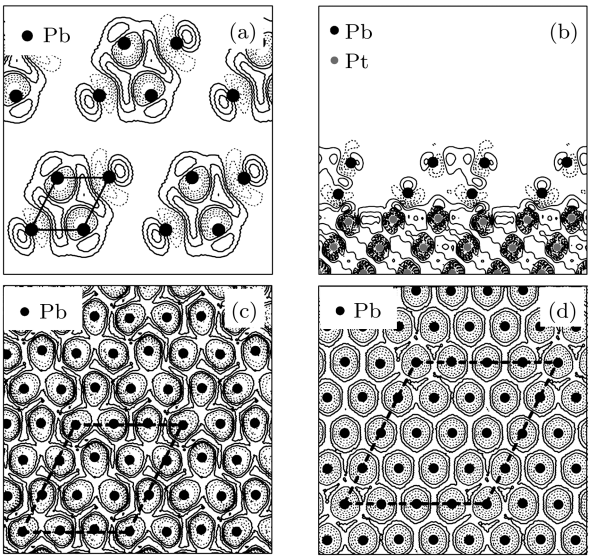
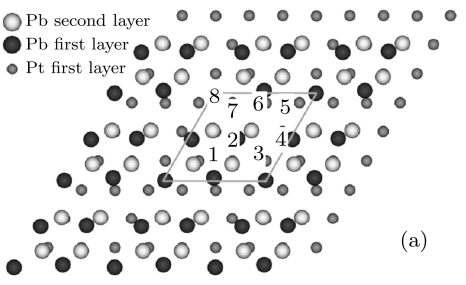


Fig. 3. (a) The $\Delta\rho(\boldsymbol{r})$ for the $(2\times2)/(3\times3)$ Pb/Pt(111) structure ($n = 3$), and the plotted plane is parallel to the Pt(111) surface and across the Pb atoms in the second layer. One semi-cluster is marked with a parallelogram; (b) the same as panel (a), but the plotted plane is perpendicular to the Pt(111) surface and along the longer diagonal of the parallelogram pattern [in Fig. 2(a)]; (c) and (d) the same as panel (a), but for $n = 4$ and 5 structures respectively, and the parallelogram in black bold dash line indicates one super cell. Solid lines and dash lines correspond to $\Delta\rho > 0$ and $\Delta\rho < 0$, respectively.

Figures 3(c) and 3(d) show the differences of electron charge densities for the $n = 4$ and 5 structures respectively. The electronic structure of the second Pb layer is very similar to that of the clean Pb (111) surface with (1×1) periodic cell, which confirms our above analysis. However, for Pb/Cu(111), when the Pb coverage is less than the complete coverage, the electronic structure of second Pb layer does not exhibit (1×1) periodic cell except the $n = 2$ structure.[17] As a result, the structures of $(3 \times 3)/(4 \times 4)$ and $(4 \times 4)/(5 \times 5)$ Pb/Pt(111) are unsuitable for being used as a template.

To understand how the Pb semi-clusters of $(2 \times 2)/(3 \times 3)$ Pb/Pt(111) realize the selective adsorption of noble metal adatoms, we perform the first-principles calculation on the system of single Au atom adsorption on the $(2\times2)/(3\times3)$ Pb/Pt(111). Au atom cannot be stably adsorbed on the top or bridge sites of the surface. The full relaxations are performed on the eight adsorption systems with eight important hollow sites [shown in Fig. 4(a)], respectively. In Fig. 4(b), the total energies and binding energies of eight adsorption systems show that only one site S5 (representing site 5 in Fig. 4(a)) has lower total energy and higher binding energy than the other sites. This implies that experimentally the Au atoms are preferentially adsorbed on the S5 site. Furthermore, the Au adatoms should be deposited on the surface of $(2 \times 2)/(3 \times 3)$ Pb/Pt(111) with a moderate coverage of about 0.11 ML (i.e., one Au atom in one super sell) in order to achieve the Au adatoms ordered array. Then, under moderate temperatures and with careful deposition, the ordered adsorptions of Au adatoms on the surface of $(2 \times 2)/(3 \times 3)$ Pb/Pt(111) should be possible. Therefore, the lowest total energy and the highest binding energy of the S5 adsorption site are conducive to the realizing of the selective adsorption of Au adatoms on $(2\times2)/(3\times3)$ Pb/Pt(111). It confirms that the $(2\times2)/(3\times3)$ Pb/Pt(111) is a promising candidate for being used as a periodic template to support ordered arrays of atoms. The identical Au single-atoms ordered array on the template of $(2\times2)/(3\times3)$ Pb/Pt(111) has important applications, for example, each Au single-adatom may offer a fixed off-centre axis for the rotation of single small molecular motor, just as Au single-adatom did for (t-Bu_4)-ZnPc molecules.[31]



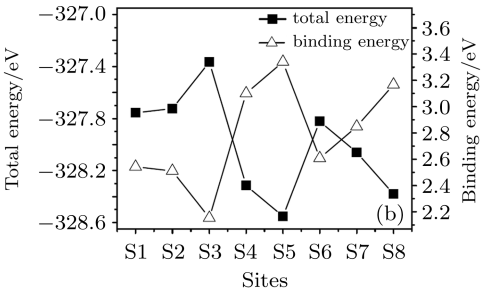


Fig. 4. (a) Eight important sites of single Au atom adsorptions on $(2 \times 2)/(3 \times 3)$ Pb/Pt(111) surface, and the gray parallelogram represents one super cell; (b) the total energies and the binding energies of the eight important adsorption systems of Au atom on $(2\times2)/(3 \times 3)$ Pb/Pt(111) surface.

4. Conclusions

Using two theoretical methods, MD calculations with the Chen–Möbius inversion potential and the self-consistent first-principles calculations, we investigated the atomic and electrical structures of the $[(n-1) \times (n-1)]/(n \times n)$ Pb bilayer/Pt(111) $(n = 2, 3, \ldots, 22)$ structures to find an appropriate template for self-organizing growth. We find that only $(2 \times 2)/(3 \times 3)$ Pb bilayer/Pt(111) is a promising candidate for stable periodic strain-relief template, although the $(2 \times 2)/(3 \times 3)$, $(3 \times 3)/(4 \times 4)$ and $(4 \times 4)/(5 \times 5)$ Pb/Pt(111) structures are all stable. It can be attributed to the formation size of Pb semi-clusters, which determines the size of the stable template. On the Pt(111) surface, the (2×2) Pb semi-clusters each have a magic number, and inherent the stability of the free magic number Pb_4 cluster. The size of Pb magic number semi-cluster plays a more important role in determining the periodicity of the template than the lattice constant mismatch between the substrate and the overlayer. Therefore, we consider that the self-organizing template should at least meet the following two conditions at the same time: (i) The adsorption metal bilayer can form the ordered array of semi-clusters with a magic number; (ii) The coverage of each layer of the adsorbed metal bilayer is less than the complete coverage. The further calculations on the eight adsorption sites of Au atoms on $(2 \times 2)/(3 \times 3)$ Pb bilayer/Pt(111) structure confirm that the $(2\times2)/(3\times3)$ Pb bilayer/Pt(111) structure is a promising candidate for being used as self-organizing template. Each Au single-adatom on the template has important applications, such as offering a fixed off-centre axis for the rotation of single small molecule rotor. Then the ordered array of many single small molecule rotors on the template can be used to realize the molecular 'gear wheel'. The $(2\times2)/(3\times3)$ Pb/Pt(111) and Pb/Cu(111) structures are both good candidates for templates, and their periodicities are quite different. As a result, by considering the sizes of the stable semi-clusters and appropriately selecting different substrate materials and meeting the two conditions mentioned above, we can tune the periodicity of the stable ordered templates and remain the same material as the adsorbed bilayer. This may have important applications, e.g., in nano-fabrications which need different stable templates with different periodicities.

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