Adsorption and spin-related properties of multi-Co atoms assembled in the half unit cells of Si(111)-(7 × 7)

Qin Liu, Xiji Shao, Fangfei Ming, Kedong Wang and Xudong Xiao

Abstract
Multiple Co atoms were assembled in the half unit cells (HUCs) of a Si(111)-(7 × 7) surface via vertical atom manipulation at room temperature. Combining scanning tunneling microscopy and first-principles calculations, we have determined the adsorption sites and spin-related properties of six Co atoms assembled in both faulted HUCs (FHUCs) and unfaulted HUCs (UHUCs). These multi-Co atoms do not form metal clusters, which usually have a definite adsorption configuration, because of the strong interaction between Si and Co atoms. Both the adsorption properties and magnetic moments of six Co atoms show strong HUC dependence. The six Co atoms in UHUC retain the adsorption sites of isolated single Co atoms, whereas the Co atoms in FHUC interact with each other via the mediation of Si atoms, leading to a deviation from the adsorption sites of single Co atoms. Around the suggested $U_{\text{eff}}$ value, the six-Co-atom configuration in UHUC is calculated to have a large magnetic moment of 11.78 $\mu_B$, while the six-Co-atom configuration in FHUC only has a magnetic moment of 1.02 $\mu_B$ because of the anti-ferromagnetic-like coupling between the Co spins.

1. Introduction
Investigating the properties of atoms or clusters with net electrons or nuclear spins on a semiconductor surface has significant importance for the implementation of various atomic-scale spin-based devices, such as Si-based nuclear quantum computers [1], single atom transistors [2–4], quantum-dot cellular automata [5], and other technologies [6–8]. In our previous work, we showed that single Co atoms adsorbed on Si(111)-(7 × 7) have remnant spins and that the spin states of single Co atoms can be controllably adjusted via tuning their adsorption configuration [9]. These properties make Co/Si(111)-(7 × 7) a potential system for implementation in those atomic-scale spin-based devices [1–8]. However, to further explore the potential application of a Co/Si(111) system, it is also important to find the adsorption and magnetic properties of multiple Co atoms in a given half unit cell (HUC) on Si(111)-(7 × 7). Although a large number of investigations of Co reactions on a Si surface at high coverage and high temperature have previously been carried out [10–14], both the initial Co adsorption stage and spin-related properties of multi-Co-atom configurations adsorbed on Si(111)-(7 × 7) at room temperature (RT) have been rarely investigated [10].

It is well known that the surface of Si(111)-(7 × 7) has a large unit cell, consisting of a faulted HUC (FHUC) and an unfaulted HUC (UHUC) [15]. These two HUCs can trap metal atoms inside using a high inter-HUC barrier and thus provide a template for the formation of various metal or silicide clusters [12, 16–20]. As a 3d ferromagnetic metal, cobalt atoms are highly reactive with silicon. Deposition of cobalt atoms on Si(111)-(7 × 7) at high temperatures or annealing the Si substrate after Co deposition [10–14] leads to the formation of Co silicide compounds or clusters [12]. Both theoretical and experimental studies indicate that cobalt silicides...
are non-magnetic [9, 21, 22]. This unfortunately makes those Co silicide clusters formed at high temperatures useless for fabricating atomic-scale spin-based devices for quantum computation [1–8] or ultrahigh-density magnetic devices [23–25]. Pan et al grew Co nanoplatelets on Si(111)-(7 × 7) pre-patterned by Al cluster arrays instead of directly on the Si surface and this method preserves the magnetic moments of the Co nanoplatelets and makes them suitable for implementing various applications in information technology [26]. The cobalt silicidation process even occurs at RT when Co coverage reaches a certain threshold [10]. Bennett et al speculated that silicide compounds began to form at a nominal coverage of ∼0.04 ML at RT, where all HUCs were occupied by one Co atom [10]. They also proposed that there was a net repulsive interaction between Co atoms to prevent multi-Co atoms simultaneously adsorbing in the same HUCs [10]. However, the initial nucleation reaction at RT is hard to directly observe since the initial silicidation reaction will be quite localized because of the finite mobility of Co atoms on Si(111) [9, 10]. The transition coverage (∼0.04 ML) proposed in the literature [10] lacks direct experimental verification. Apparently, scanning tunneling microscope (STM)-based atom manipulation may provide a straightforward method to find the answer. However, repositioning highly reactive metal atoms on the corrugated Si(111)-(7 × 7) surface is difficult, and until now only a few successful atom manipulation experiments have been achieved on a silicon surface at RT by atomic-force microscopy [27] and at 79 K by STM [28]. Fortunately, an STM-based vertical atom manipulation method has been proven to be useful for repositioning of Ag, Au [18] and highly reactive Co [9] atoms on a Si(111)-(7 × 7) surface, even at RT, by our group. Thus, this provides a good opportunity to directly observe the phenomena after setting more than one Co atom in the same HUC. It can also provide us an opportunity to study the adsorption and spin-related properties of multi-Co atoms formed in an HUC and to straightforwardly observe the initial stage of Co silicidation on Si(111)-(7 × 7).

In this work, we have successfully assembled multi-Co atoms in the same HUCs on Si(111)-(7 × 7) at RT by STM atom manipulations. Through combining first-principles calculations, and STM observations and manipulations we have obtained the adsorption and spin-related properties of multi-Co atoms in the HUCs. Previous studies have shown that, at high temperatures, six Co atoms adsorbed in the same HUC will react with three Si atoms to form magic clusters [12]. However, our manipulation experiment demonstrates that, at RT, multi-Co atoms with Co atom numbers smaller than or equal to six will not form silicide or metal clusters. Instead, the six Co atoms adsorbed in UHUC maintain the adsorption sites of isolated single Co atoms, while some Co atoms in the six-Co-atom configuration in FHUC slightly deviate from the adsorption sites of single Co atoms, indicating that Si-mediated indirect interactions existed among those Co atoms. Despite the observed HUC dependence of adsorption properties, the multi-Co-atom configurations adsorbed in both HUCs do not show any apparent signs of silicidation as long as the number of Co atoms is smaller than or equal to six. Moreover, the spin-related properties of six-Co-atom configurations also show HUC dependence when the effective Hubbard parameter $U_{eff}$ used in the calculation is near a suggested value for the Co/Si(111) system [9]. Theoretical calculations indicate that the six-Co-atom configuration in both HUCs have finite magnetic moments within a wide range of $U_{eff}$ while the magnetic moment of them in UHUC is much larger, near $U_{eff} = 5.8$ eV.

2. Experiments and computational methods

Our experiments were carried out with an Omicron variable temperature STM installed in an ultrahigh-vacuum chamber with a base pressure better than $1 \times 10^{-10}$ mbar. N-type Si(111) wafers with a RT resistivity of ∼0.026 Ω cm and a doping concentration of $7.3 \times 10^{17}$ cm$^{-3}$ were used as the substrates. The substrate surface was cleaned and annealed to form Si(111)-(7 × 7) reconstruction through standard procedures [29] and about 0.01 ML (1 ML = 7.83 × 10$^{14}$ Co atoms cm$^{-2}$) of cobalt atoms were deposited onto the surface at RT by electron beam evaporation. In this work, a vertical manipulation mode was used to reposition Co atoms on the Si(111)-(7 × 7) surface and assemble multi-Co atoms in a given HUC. A specially modified tungsten tip was used for atom manipulation, and details are given in [9]. Figure S1 shows an example of moving a Co atom on Si(111)-(7 × 7) by this vertical manipulation mode and describes how to judge whether the manipulation is successful (see the supplementary material). We can use this manipulation method to freely reposition Co atoms on the Si(111) surface and then obtain different Co adsorption configurations through choosing a proper atom-dropping-off position [9, 18].

First-principles calculations based on density functional theory were performed to investigate the adsorption configurations of multi-Co atoms assembled in an HUC with the energies computed by the Vienna $ab$ initio simulation package [30]. We employed the projector augmented-wave method [31] and the exchange correlation functional with generalized gradient approximation (GGA) [32] in the configuration optimization. The supercell was a slab consisting of certain number of Co atoms, six Si layers, and one H layer passivating the bottom surface. With the initial position of the Co atom properly chosen, and the Co atom, and the upper five Si
layers were then relaxed until the residual forces became smaller than 0.02 eV Å⁻¹. The GGA+U method was further used to study the spin magnetic moment and the spin-polarized partial density of states (PDOS) of multi-Co atoms assembled in the same HUCs [33, 34]. One effective Hubbard parameter $U_{\text{eff}} = U - J$, with $U$ and $J$ representing the Hubbard repulsion and intra-atomic exchange, respectively [33, 34], was used in our calculations.

3. Results and discussion

3.1. Adsorption sites of multi-Co-atom configurations

By continually adding Co atoms one-by-one into an HUC via single Co-atom manipulation, we successfully assembled multi-Co atoms with various sizes. The manipulation method used can directly determine the number of Co atoms in the given HUC and allow us to further investigate their adsorption properties. We found that the configurations of multi-Co atoms rely greatly on the dropping position of the Co atoms in the vertical manipulation process. For instance, figure 1(a) summarizes all two-Co-atom configurations constructed by STM atom manipulations or spontaneously formed after Co deposition at RT. Apparently, the two-Co-atom configurations assembled in an HUC do not have a unique set of adsorption sites. They may appear as two strongly dimmed center adatoms with a slightly dimmed one (i) and (ii) of figure 1(a), five brighter adatoms ((ii) of figure 1(a)), or a dimmed triplet pattern ((iv) of figure 1(a)). The STM images of other configurations of multi-Co atoms are given figure S2. This phenomenon suggests that these Co atoms assembled in the same HUC do not form a metal cluster, which usually has a stable adsorption configuration [16–20]. Such a conclusion is understandable because Co atoms are highly reactive with Si atoms even at RT. The binding energies between a Co atom and the surrounding Si atoms are usually large, so it is difficult for Co atoms to bind with each other to form a metal cluster with a stable or fixed configuration.

In our previous study, we reported eight adsorption configurations of single Co atoms on a Si(111)-(7×7) surface [9]. Interestingly, by carefully comparing the STM images of the two Co atoms in figure 1(a) with the images of various single Co atoms in figure 2(b) of our previous work [9], we find that the observed STM features of two Co atoms can be well reproduced by a superposition of the STM images of some single Co atoms. Therefore, we believe that the adsorption structure of two Co atoms is a simple combination of various single Co atoms. Take the ‘triplet’ configuration, which was regarded as containing only one Co atom at the interstitial site in the middle of three dimmed adatoms by Bennett et al [10], as an example. This ‘triplet’ configuration (as shown in panel (iv) of figure 1(a) and panel (i) of figure 1(b)), consisting of three equally dimmed center adatoms in a FHUC, can be observed at negative and small positive (< +0.6 V) sample biases. Our filled state STM image shows that, in the triplet configuration, one center adatom is much dimmer than the other two center adatoms, as indicated by the green arrow in panel (i) of figure 1(b). The measured height profiles along the pair and triplet configurations (panel (ii) of figure 1(b)) also confirm this point. Consequently, we propose that the triplet configuration contains two Co atoms respectively buried under two Si rest atoms, i.e. the adsorption position of the fault pair Co in [9], as shown by the structural model below panel (iv) of figure 1(a). As a result, the superposition of two faulted pairs can lead to one center adatom much dimmer than the other two in the STM image of the faulted triplet configuration. Thus, our simple superposition model can reasonably explain the observed STM feature, which cannot be explained by the ‘one Co’ model proposed in the literature [10].

Similarly, as shown by the structural models below their STM images in figure 1(a), we also give an estimation of the Co adsorption sites for the other three two-Co-atom configurations based on this ‘superposition’ rule and also the dropping-off positions of Co atoms in the manipulation process.

To further verify our proposed model, we started with various initial Co positions, optimized the configurations by first-principles calculations, and then simulated the STM images to compare with experimental observations. Figure 1(c) shows the simulated image and optimized structural models of a clean FHUC (panel (i) of figure 1(c)), faulted pair (panel (ii) of figure 1(c)) and faulted triplet (panel (iii) of figure 1(c)), respectively. The simulated filled state ($V_{\text{sample}} = -0.5$ V) image of a faulted triplet is characterized by three unequally dimmed center adatoms. In particular, the center adatom at the bottom side is obviously dimmer than the other two. Apparently, the simulated image precisely reproduces the major features of our experimental observation and straightforwardly verifies our proposed model.

In addition to the two-Co-atom configurations, we have also successfully assembled other multi-Co-atom configurations in an HUC by vertical atom manipulation. Figure 2(a) is a series of STM images showing the process of assembling six Co atoms in a clean UHUC. We picked up single Co atoms from various places on the surface and then placed them one-by-one in the clean UHUC marked by the blue dotted triangle in figure 2(a). In panel (ii) of figure 2(a), we positioned the tip above the Si rest atom and then dropped off one Co atom. We obtained an unfaulted bright structure, consisting of three brighter Si adatoms on the right side of the UHUC [9]. In panel (iii) of figure 2(a), we placed another Co atom in the UHUC and the five Si adatoms became
Only one corner Si adatom shows normal height contrast in the upper-left corner of the UHUC. In panel (iv) of figure 2(a), we placed the third Co atom in the UHUC and all the six Si adatoms became brighter. In panel (v) of figure 2(a), we positioned the tip above one center Si adatom and dropped off the fourth Co atom, making one Si center adatom appear dim. Similarly, we set two more Co atoms in the UHUC one-by one in panels (vi) and (vii) of figure 2(a), also making the remaining two center Si adatoms dim. To highlight the change in the STM images from panel (ii) to (vii), we subtracted the image of the clean Si surface (panel (i)) from the images with Co atoms (panels (ii)–(vii)) and the results are shown in figure S3. The maximum Co number achieved by atom manipulation in the UHUC is six. When we attempted to bring the seventh Co atom into this UHUC, it jumped into the nearby FHUC and formed a faulted corner, as indicated by the green arrow in panel (i) of figure 2(b).

Similarly, we also assembled multi-Co atoms in the FHUC. Figure 2(b) shows the process of moving six Co atoms in the FHUC to a clean FHUC one-by one. The chosen clean FHUC is indicated by a green dotted triangle in panel (i) of figure 2(b). As shown in panel (ii) of figure 2(b), we first picked up one Co atom in the UHUC and placed it in the chosen FHUC to form a faulted center configuration. Next, we picked up another Co atom and still positioned the tip above a Si center adatom and then dropped it off, leading to another dimmed Si center adatom (panel (iii) figure 2(b)). Then, we placed the tip above one rest atom site and dropped off the third Co atom, which made one Si center adatom on the right side of the FHUC become brighter, as shown in panel (iv)
In panels (v)–(vii) of figure 2(b), we placed three more Co atoms in the FHUC by positioning the tip above three Si adatoms in turn. As a result, three Si adatoms became dimmed in sequence. We found that the observed STM features of multi-Co atoms, like two Co atoms, can be well reproduced by a superposition of the STM images of single Co atoms. Therefore, we speculate that the adsorption structure of these multi-Co atoms is also a simple combination of various single Co atoms. Based on this point and the known adsorption configurations of single Co atoms [9], we estimated the adsorption sites of those multi-Co atoms, as shown by the structural models in figures 2(a) and (b). To verify our proposed models for these multi-Co atoms, we performed first-principles calculations to optimize the adsorption configurations of six Co atoms in both UHUC and FHUC and then simulated their STM images. The optimized structures and simulated images are shown in figure 3. In the UHUC, three Co atoms near the Si center adatoms are buried under the upper Si layer and make all center adatoms dim in the simulated images. Meanwhile, the rest of the Co atoms near the Si corner adatoms lead to a charge transfer to Si dangling bonds, making the three corner adatoms brighter. These features together produce the simulated image, which precisely reproduces the experimental observed features shown in figure 3(a) and panel (vii) of figure 2(a). The optimized model of the FHUC shows that five of the Co atoms stay deeply below the outermost Si layer and only one Co adatom is adsorbed shallowly near the upper corner adatom. The five deeply buried Co atoms make the five nearby Si adatoms dim in the filled state images. The shallowly adsorbed Co atom makes a charge transfer to the dangling bond of its neighboring Si corner adatom, resulting in a brighter Si corner adatom. These features of the simulated image agree well with the major features of the measured STM images shown in figures 2(b) and 3(b). Even the faint details in the lower part of the FHUC are well reproduced in the simulated image. Thus, we conclude the optimized models in figures 3(a) and (b) give good descriptions of the adsorption structures of six Co atoms in both HUCs.

Previously, people believed that co-adsorption of several Co atoms in the same HUC of Si(111)-(7 × 7) was almost inhibited by a net repulsive interaction between Co atoms [10]. They proposed that cobalt silicidation occurs at a transition coverage of ~0.04 ML, which corresponds to a full occupation of all HUCs on Si(111)-
Figure 3. Filled state STM image, simulated image, and optimized structural models (top view and side view) of six Co atoms assembled in (a) a clean UHUC and (b) a clean FHUC. The structural models of the adsorption configurations were obtained by first-principles calculations. The filled state STM images were taken at $V_{\text{sample}} = -0.5$ V and $I = 5$ pA. The simulated images were also taken at $-0.5$ V. We have numbered each Co atom in the two HUCs for clarity.

(7 × 7), i.e. each HUC is occupied by one Co atom [10]. Here, our manipulation results suggest a larger transition coverage because silicidation does not occur, even when six Co atoms are assembled in the same HUC. Via carefully comparing the calculated models given in figure 3 with the estimated models given in figure 2, we find that for six Co atoms in an UHUC the calculated model (figure 3(a)) is just the same as the estimated one (the structural model below panel (vii) of figure 2(a)), whereas for six Co atoms in an FHUC the calculated structure slightly deviates from our estimation. The good agreement between our estimation based on single Co atom adsorption sites and the calculation for UHUC indicates that each Co atom in the UHUC of figure 3(a) still keeps the adsorption property of single Co atoms. An important point to notice is that the UHUC remains intact after all the six Co atoms were removed from it to the FHUC, as shown in panel (vii) of figure 2(b). This demonstrates that cobalt silicidation has not occurred in the UHUC. Since the silicidation process of transition metal atoms on silicon surfaces is inevitably accompanied by remarkable Si atom displacing [10, 12, 13], the intact UHUC indicates that the Si atoms have not been displaced from their original sites (also confirmed by the optimized structural model in figure 3(a)), supporting the viewpoint that no silicidation compounds (or cobalt silicide cluster) are formed. In addition, we investigated the number of Co–Si bonds formed for each Co atom in the six-Co-atom configuration and obtained the bond length of those Co–Si bonds through first-principles calculations (table S1). For comparison, we also calculated the Co–Si bond lengths in bulk CoSi$_2$ and CoSi. The former has a CaF$_2$ structure with a lattice constant of 5.365 Å, while the latter has a FeSi structure with a lattice constant of 4.438 Å [35]. The coordination number of a Co atom in CoSi$_2$ is eight, and the Co–Si bond length is 2.321 Å. In CoSi, one Co atom is bonded with seven surrounding Si atoms. The bond lengths are 2.335 Å for three bonds, 2.431 Å for another three bonds and 2.319 Å for the last one. As shown in table S1, Co atoms form six, seven or eight Co–Si bonds with surrounding Si atoms in the six-Co-atom configuration in the UHUC. The bond lengths are unequal even for the same Co atom and most of those bonds are longer than the Co–Si bond lengths formed in the cobalt silicide compounds. The significant differences between the Co–Si bond lengths and adsorption geometry of Co atoms in the six-Co-atom configuration and those in cobalt silicides also indicate that no silicidation compounds are formed.

By contrast, in the FHUC shown in figure 3(b), four (marked as Co 1, 2, 4 and 5 in the structural model of figure 3(b)) out of the six Co atoms deviate from their estimated adsorption positions depicted in the inset of panel (vii) of figure 2(b). This phenomenon implies that the six Co atoms in the FHUC interact with each other to slightly adjust their adsorption sites via the mediation of Si atoms among them. Thus, their structure is no longer a pure combination of isolated single Co adsorption configurations. Yet, we still do not believe that they form any silicidation compounds because the calculated structural model shows that remarkable Si atom displacing does not occur. In addition, similar to the case in UHUC, the identified Co–Si bonds and their calculated bond lengths in this FHUC six-Co-atom configuration are obviously different from the values in cobalt silicide compounds. Our manipulation experiment also suggests that the silicidation process may occur after assembling eight or nine Co atoms in the FHUC (figure 4). A large bright protrusion, which may be the
Table 1. The calculated spin magnetic moments (M) of six Co atoms assembled in both a UHUC and FHUC. Here, we show both the magnetic moments of six Co atoms (denoted as ‘6 Co’) in the table and the magnetic moments of the whole system, i.e. six Co atoms with the Si(111)-7 × 7 unit cell (denoted as ‘total’).

|          | M (µB) |          |          |          |          |          |          |          |          |
|----------|--------|----------|----------|----------|----------|----------|----------|----------|----------|
|          | U_{eff} (eV) | 0.0 | 2.0 | 3.0 | 4.0 | 4.2 | 4.5 | 5.0 | 5.8 | 7.0 | 8.0 |
| UHUC     | 6 Co   | 1.54 | 2.85 | 3.26 | 1.03 | 7.65 | 7.56 | 11.65 | 11.79 | 11.88 | 11.96 |
|          | Total  | 1.54 | 3.04 | 3.01 | 0.81 | 7.78 | 7.66 | 12.04 | 12.16 | 12.2  | 12.31 |
| FHUC     | 6 Co   | 1.64 | 2.43 | 2.94 | 0.96 | 1.00 | 1.02 | 5.27 | 7.42 | 8.62 | 11.70 |
|          | Total  | 1.64 | 2.34 | 2.72 | 0.45 | 0.66 | 0.62 | 4.33 | 7.16 | 8.10 | 11.68 |

nucleus of silicide compounds at RT, appeared when we added another three Co atoms to the six Co atoms in the FHUC (figure S4).

Through comparing the manipulation experiments and theoretical calculations in the two HUCs, we found that the FHUC has a larger Co capacity and displays a higher reactivity with Co atoms. These features are consistent with the reported strong Co preference for FHUC at elevated temperatures [10–13]. At RT, Co atoms do not have enough kinetic energy to overcome the inter-HUC barrier and thus have almost equal populations in the two HUCs. At relatively higher temperatures, the Co atoms can gain enough energy from the environment to cross the boundary and reach the preferred HUCs. In our experiments, with the assistance of atom manipulations, these Co atoms do not need to overcome inter-HUC barriers. Thus their preference for the FHUC can be clearly exhibited at RT.

3.2. Spin properties of multi-Co-atom configurations

To study the spin-related properties of multi-Co-atom systems, direct experimental observation by STM-based methods turns out to be impractical at the current stage because our instruments cannot provide an external magnetic field. Even a magnetic tip cannot provide additional information since there should be no alignment of the spins of Co atoms at RT. Thus, we rely on theoretical calculations to explore the spin properties of the multi-Co-atom systems on Si(111)-7 × 7.

Because of the strong correlation arising from the localized 3d electrons in Co atoms, we have to apply the GGA+U method to investigate the spin-related properties of multi-Co-atom systems and their spin magnetic moments (M) [33, 34]. Here, we focus on the results of six Co atoms. We used various $U_{eff}$ to calculate the magnetic moments and the PDOS for the six-Co-atom configurations in both HUCs. As shown in table 1, if we neglect the correlation effect ($U_{eff} = 0$ eV), the six Co atoms in the two HUCs have small and similar magnetic moments. If we gradually increase $U_{eff}$, the magnetic moment of the six-Co-atom configuration in the UHUC increases from $U_{eff} = 0$ eV to 3.0 eV, decreases from $U_{eff} = 3.0$ eV to 4.0 eV, and then undergoes a drastic increase from $U_{eff} = 4.0$ eV to 5.0 eV, and finally falls in a smoothly increasing stage when $U_{eff}$ is above 5.0 eV. By contrast, the magnetic moment of the six-Co-atom configuration in the FHUC goes up and down when $U_{eff}$ increases from 0.0 eV to 4.0 eV, then remains almost unchanged in the range $U_{eff} = 4.0$–5.8 eV, and finally drastically increases when $U_{eff}$ is larger than 5.8 eV.

Although the exact value of $U_{eff}$ for our system is unknown, we have used a simple model of Co on Si(111)-1(× 1) for the estimation, as discussed in our previous work [9]. This simplified model suggests a value of $U_{eff} \sim 5.8$ eV, which may serve as a reference [9]. At $U_{eff} = 5.8$ eV, the six-Co-atom configuration in the UHUC has a large magnetic moment of 11.78 µB, whereas the six-Co-atom configuration in the FHUC has a small magnetic moment of 1.02 µB. The reason for this large difference between two HUCs will be discussed later. If we compare the magnetic moments of six Co atoms and the whole system (containing six Si layers, on a H layer and six Co atoms) as shown in table 1, we find their trends are consistent and only their values are slightly different. The slight difference in magnetic moment originates from the small difference between the occupied minority and majority Si-p orbitals, which is caused by their exchange interaction with the spin-polarized, partially filled 3d states of Co atoms with the introduction of $U_{eff}$. The existence of finite spin magnetic moments for the six-Co-atom configuration at various $U_{eff}$ values is in strong contrast to the bulk CoSi, and CoSi, for which a null spin magnetic moment was always found by calculations independent of $U_{eff}$. This is consistent with the experimental results for 1.4–2.1 ML Co films on Si(111) where cobalt disilicide forms at the interface [21, 22]. Therefore, we can confirm that the use of $U_{eff}$ in our theoretical calculations does not introduce artificial effects [9].

To elaborate the origin of spin magnetic moments and the effectiveness of varying $U_{eff}$, we plot the calculated PDOS for the spin-polarized d orbitals of the six-Co-atom configurations at $U_{eff} = 0$ eV, 3.0 eV,
5.8 eV, 8.0 eV in figures 4(a) and (b). As demonstrated by the spin-polarized PDOS curves, it is the exchange splitting in Co-3d orbitals, instead of Co-s or Co-p orbitals, which gives rise to the magnetic moments. At $U_{\text{eff}} = 0$ eV, the occupations of majority (spin-up) and minority (spin-down) states are slightly different in both HUCs. By checking the PDOS of each Co atom, we find that the magnetic moment mainly originates from the spin splitting in $d_{xz}$ and $d_{yz}$ orbitals of Co 2 and the spin splitting in $d_{x^2-y^2}$ and $d_{xy}$ orbitals of Co 3 in the UHUC, whereas the magnetic moment in the FHUC originates from Co 3 and Co 6. Here, the labels of Co atoms are those in the structure model of figures 3(a) and (b), and $x$, $y$ and $z$ represent, respectively, the [$\bar{1}$ 1 0], [0 $\bar{1}$ 0] and [1 1 1] directions of the Si crystal. When $U_{\text{eff}}$ is increased to 3.0 eV, the majority d states are pushed to the lower energy region and broadened via p–d hybridization in both HUCs. The Si delocalized p states located in the energy range $-5$ eV to $-1$ eV and do not suffer any obvious shifts when $U_{\text{eff}}$ is increased from 0 eV to 8 eV. Thus, once the d states of the six-Co-atom configurations are pushed into the energy range $-5$ eV to $-1$ eV, they will hybridize with the Si-p states and become broadened irrespective of the value of $U_{\text{eff}}$. However, while the magnetic moment in the FHUC still originates only from Co 3 and Co 6 at $U_{\text{eff}} = 3.0$ eV, nearly all the six Co atoms in the FHUC contribute to the total magnetic moment. When $U_{\text{eff}}$ reaches 5.8 eV, the majority d states of the six-Co-atom configuration in UHUC become almost fully occupied, meanwhile half of the minority d states shift above the Fermi energy, resulting in a large magnetic moment. By contrast, both the majority and minority d states in the FHUC are strongly broadened and there is no significant difference between their occupation, leading to a small magnetic moment. The difference between the two HUCs is caused by the different alignment of the magnetic moments of Co atoms. At $U_{\text{eff}} = 5.8$ eV, each Co atom in the two HUCs has a large magnetic moment. In the UHUC, the magnetic moments are parallel to each other. In the FHUC, however, the magnetic moments of Co 3 and Co 6 align in the same direction, whereas the magnetic moments of the remaining four Co atoms are aligned in the opposite direction. The anti-ferromagnetic-like coupling of the spin moments of six Co atoms in the FHUC results in a small value of total magnetic moment. We have also displayed the computed spin-polarized density of states for d five-orbitals for two HUCs at $U_{\text{eff}} = 5.8$ eV in figures 4(c) and (d). While all the d five-orbitals contribute to the magnetic moment in the UHUC, only $d_{xy}$ and $d_{yz}$ orbitals make a contribution to the small magnetic moment of the FHUC. In the UHUC, the majority d
states are pushed to an even lower energy region while the minority d states only slightly shift when \( U_{\text{eff}} \) is increased from 5.8 eV to 8.0 eV. Since the majority d states are already fully occupied at \( U_{\text{eff}} = 5.8 \) eV, the magnetic moment only slightly increases when \( U_{\text{eff}} \) reaches 8.0 eV. In the FHUC, when \( U_{\text{eff}} \) is increased to 8.0 eV, the magnetic moments of the six Co atoms align in the same direction, leading to a large magnetic moment. As shown by the PDOS, the majority d states of six Co atoms become fully occupied while the minority d states become less occupied because of the obvious shifts in the minority d\(_{\text{xy}}\) and d\(_{\text{zr}}\) states.

In conclusion, we states are pushed to an even lower energy region while the minority d states only slightly shift when \( U_{\text{eff}} \) is increased from 5.8 eV to 8.0 eV. Since the majority d states are already fully occupied at \( U_{\text{eff}} = 5.8 \) eV, the magnetic moment only slightly increases when \( U_{\text{eff}} \) reaches 8.0 eV. In the FHUC, when \( U_{\text{eff}} \) is increased to 8.0 eV, the magnetic moments of the six Co atoms align in the same direction, leading to a large magnetic moment. As shown by the PDOS, the majority d states of six Co atoms become fully occupied while the minority d states become less occupied because of the obvious shifts in the minority d\(_{\text{xy}}\) and d\(_{\text{zr}}\) states.

In short, the six-Co-atom configuration in both HUCs of Si(111)-(7 \times 7) have finite magnetic moments within a wide range of \( U_{\text{eff}} \) while the magnetic moments and spin states of the six-Co-atom configurations adsorbed in the two HUCs show significant difference near the suggested value of \( U_{\text{eff}} = 5.8 \) eV. Considering the obviously different Co adsorption configurations in the two HUCs, this result is quite rational. The Co atoms in the FHUC indirectly interact with each other to slightly adjust their adsorption sites through the mediations of the Si atoms among them. This indirect interaction among Co atoms leads to an anti-ferromagnetic-like coupling between the six Co atoms, resulting in a small \( M \) in the FHUC around the suggested value of \( U_{\text{eff}} = 5.8 \) eV. By contrast, such anti-ferromagnetic coupling does not exist among the six Co atoms in the UHUC and the magnetic moment of six Co atoms in the UHUC is a summation of the absolute value of \( M \) of six Co atoms when \( U_{\text{eff}} \) is in the range 4.2 eV–8.0 eV. This identified HUC-dependent magnetic property no doubt provides important information for constructing atomic-scale spin-based devices using a Co/Si(111) system. However, further experimental measurements are required to confirm these theoretical results. Low temperature spin-polarized STM [36] and electron spin resonance STM [37] may be suitable tools to detect the spin-related properties of our system and we hope corresponding works can be performed in the future.

4. Conclusion

In conclusion, we investigated the adsorption and spin-related properties of multi-Co atoms assembled in the UHUCs of Si(111)-(7 \times 7) via a combination of STM and first-principles calculations. We successfully generated multi-Co-atom configurations in an UHUC and an FHUC by vertical manipulation. By comparing the STM observations and image simulations, we determined the adsorption configurations of a faulted triplet pattern and the six Co atoms assembled in both HUCs. Interestingly, multi-Co atoms assembled in the same HUC do not form any metal clusters because of their strong attractive interactions with surrounding Si atoms. Furthermore, they do not form any silicide clusters or compounds when the number of Co atoms is smaller than or equal to six. The six Co atoms in the UHUC retain the adsorption positions of single Co atoms, whereas the six Co atoms in the FHUC indirectly interact with each other via the mediation of Si atoms, leading to a deviation from the adsorption sites of single Co atoms. Theoretical computations suggest that the six-Co-atom configuration in both HUCs have finite magnetic moments within a wide range of \( U_{\text{eff}} \), while near the suggested value of \( U_{\text{eff}} = 5.8 \) eV, the magnetic moment of the six Co atoms in the FHUC is much larger than that in the FHUC because of the different Co spin orientations in the two HUCs. We believe that our studies can provide useful information for realizing the potential applications of a Co/Si(111) system and demonstrate that the HUC effect on spin-related properties of multi-Co atoms must be considered before implementing atomic-scale spin-based devices in the Co/Si(111) matrix.

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