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Structural properties of Cu clusters on Si(1 1 1):Cu_2Si magic family

A.A. Saranin [a,b,*], A.V. Zotov [a,b,c], O.A. Utas [a], V.G. Kotlyar [a], C.M. Wei [d], Y.L. Wang [d]

[a] Institute of Automation and Control Processes, 5 Radio Street, 690041 Vladivostok, Russia
[b] Faculty of Physics and Engineering, Far Eastern State University, 690000 Vladivostok, Russia
[c] Department of Electronics, Vladivostok State University of Economics and Service, 690600 Vladivostok, Russia
[d] Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 10617, Taiwan

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ABSTRACT

Basing on the results of the scanning tunneling microscopy (STM) observations and density functional theory (DFT) calculations, the structural model for the Cu magic clusters formed on Si(1 1 1)7 × 7 surface has been proposed. Using STM, composition of the Cu magic clusters has been evaluated from the quantitative analysis of the Cu and Si mass transport occurring during magic cluster converting into the Si(1 1 1)'5.5 × 5.5'-Cu reconstruction upon annealing. Evaluation yields that Cu magic cluster accommodates ~20 Cu atoms with ~20 Si atoms being expelled from the corresponding 7 × 7 half unit cell (HUC). In order to fit these values, it has been suggested that the Cu magic clusters resemble fragments of the Cu_2Si-silicide monolayer incorporated into the rest-atom layer of the Si(1 1 1)7 × 7 HUCs. Using DFT calculations, stability of the nineteen models has been tested of which five models appeared to have formation energies lower than that of the original Si(1 1 1)7 × 7 surface. The three of five models having the lowest formation energies have been concluded to be the most plausible ones. They resemble well the evaluated composition and their counterparts are found in the experimental STM images.

1. Introduction

It is known that when Cu submonolayers are deposited onto the Si(1 1 1)7 × 7 substrate held at room temperature (RT), ordered arrays of magic clusters are formed at the surface (Fig. 1). Cluster formation was first detected in the scanning tunneling microscopy (STM) studies of 1990s [1,2], but only recently these clusters have been designated as magic clusters, i.e. the clusters having identical size and structure [3,4].

Atomic structure of the surface magic clusters has attracted a considerable interest of the researchers [5] and for selected clusters (e.g., for those formed by Group III metals [6–12], by sodium [13,14] or by lead [15] on Si(1 1 1)7 × 7 surface) it has been successfully determined. Bias-dependent STM appearance of the Cu magic clusters differs qualitatively from that of the other known magic clusters, which implies that they have a different atomic structure [3,4]. Zhang et al. [3] suggested a model for the Cu magic cluster, in which six Cu adatoms form a ring-like aggregation with three sitting on the top of the Si center adatoms and three binding to the Si rest atoms. However, this model is tentative and not reliably justified. So, conclusive determination of the Cu magic cluster structure remains a challenge task for the researchers.

In the present study, we have estimated a plausible range of compositions for the Cu magic clusters and suggested a set of the structural models fitting this finding. The basic feature of these models is that they resemble fragments of the Cu_2Si-silicide monolayer incorporated into the Si(1 1 1)7 × 7 half unit cells (HUCs). Density functional theory (DFT) calculations have revealed that, at least, five models have formation energies lower than that of the original Si(1 1 1)7 × 7 surface. Three of five models seem to be the most plausible. Close inspection of the Cu magic cluster array, indeed, revealed the presence of three types of clusters at the surface.

2. Experimental and calculation details

Our experiments were performed with Omicron scanning tunneling microscope (STM) operating in an ultrahigh vacuum (~ 1×10^{-10} Torr). Atomically-clean Si(1 1 1)7 × 7 surfaces were prepared *in situ* by flashing to 1280 °C after the samples were first degassed at 600°C for several hours. Copper was deposited at a rate of about 0.5 monolayer (ML)/min by resistive heating a tungsten filament wrapped with a Cu wire. One monolayer (ML) corresponds to 7.8×10^{14} cm^{-2}, the density of the topmost Si atoms on the unreconstructed Si(1 1 1)1 × 1 surface. For STM observations, electro-chemically etched tungsten tips cleaned by *in situ*

* Corresponding author. Address: Institute of Automation and Control Processes, Science and Technology Center, 5 Radio Street, 690041 Vladivostok, Russia. Fax: +7 4232 310452.
E-mail address: saranin@iacp.dvo.ru (A.A. Saranin).

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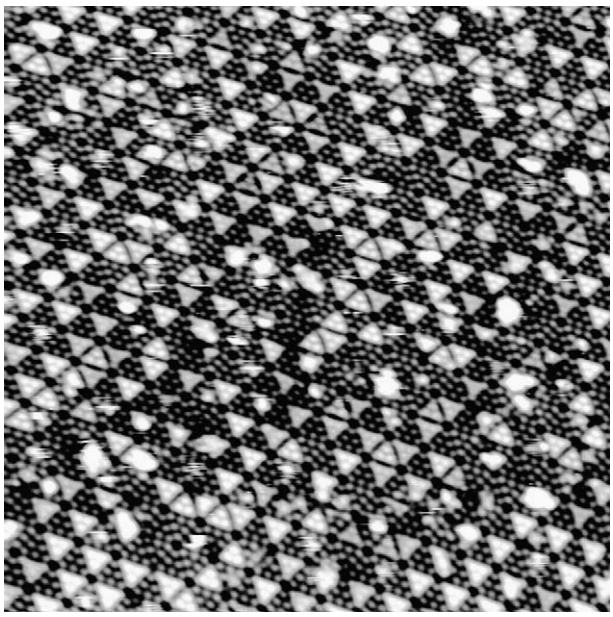

Fig. 1. (a) 420×420 Å^2 empty-state (+2.0 V) STM image of the Cu magic cluster array on the Si(1 1 1)7 × 7 surface.

heating were employed. The STM images were acquired in a constant-current mode after cooling the sample to RT.

To interpret experimental findings, we have performed plane-waves total energy calculations. The calculations reported here were done by using the Vienna *Ab Initio* Simulation Package (VASP) [16–19] based on density functional theory (DFT) [20] with projector-augmented wave (PAW) pseudopotentials [21]. The exchange-correlation functional is treated in the generalized gradient approximation of Perdew, Burke and Ernzerhof (PBE) [22]. Wave functions are represented using a plane-wave basis set with a kinetic energy cutoff of 300 eV. The supercell geometry used in this study is simulated by a repeating slab of four atomic Si bilayers and a vacuum region of 10 Å. The 7 × 7 unit cell is used to fulfill the periodic boundary condition in the lateral directions. The adsorbed Cu atoms are added on the reconstructed Si(1 1 1)7 × 7 surface, and the dangling bonds on the unreconstructed surface are saturated by the hydrogen atoms. There are totally four Si bi-layers in the supercell. The Brillouin zone integration was approximated by the Γ point. In all the calculations, the top three atomic bilayers are fully relaxed, and the bottom bilayer is kept at the bulk positions. The geometry is optimized until the total energy is converged to 10^{-4} eV. The sensitivity of total energies on slab thickness, relaxed layers, vacuum region, kinetic energy cutoff, etc., has been tested, and the values in the total-energy difference presented here are accurate to 30 meV.

To compare the structures having different number of silicon and copper atoms in the different proposed models, we have used the surface formation energy defined as [23]:

$$\Omega = E(N_{Si}, N_{Cu}) - N_{Si}\mu_{Si} - N_{Cu}\mu_{Cu},$$

where $E(N_{Si}, N_{Cu})$ is the total energy of the system, N_{Si} and N_{Cu} are the number of Si and Cu atoms, and μ_{Si} and μ_{Cu} are the energies per atom in bulk Si and Cu, respectively. There are totally nineteen models with various compositions tested (see Table 2) in this study.

3. Results and discussion

As an example, Fig. 1 shows an array of Cu magic clusters formed at Si(1 1 1)7 × 7 surface at ~40 °C. One can notice that Cu cluster array is less perfect compared to the cluster arrays formed on Si(1 1 1)7 × 7 by Group III metals, Al [24,25], In [6] and Ga [7], which demonstrate an almost ideal ordering. In the case of Cu/Si(1 1 1)7 × 7 system, ordered magic cluster arrays are depraved by a presence of the random clusters having irregular shape. Annealing of the cluster array does not improve its structural quality. Up to about 200 °C, the cluster array remains essentially unchanged, while at higher temperatures the clusters (both magic clusters and irregular ones) become unstable. As a result, the patches of the Si(111)'5.5 × 5.5'-Cu reconstruction develop at the expense of reducing Cu clusters (Fig. 2). The transition is completed at about 400 °C, when no Cu clusters are left on the surface.

The Si(1 1 1)'5.5 × 5.5'-Cu reconstruction is known to resemble a Cu_2Si-silicide monolayer residing atop a bulk-like Si(1 1 1) substrate [4,26–29]. Due to the lattice mismatch between the silicide and silicon, the layer has quasi-periodical incommensurate structure with an averaged size of the hexagonal domains of $\sim 5.5a_0$. An ideal Cu_2Si-silicide monolayer contains 1.0 ML of Si and 2.0 ML of Cu. Experimentally determined values for the Si(1 1 1)'5.5 × 5.5'-Cu phase are 0.96 [30,31] to 0.99 ML [32] of Si and 1.7 to 1.9 ML of Cu [4]. With the knowledge on the '5.5 × 5.5'-Cu composition, one could estimate the Cu content in the Cu magic clusters just by counting their number density before annealing and measuring the area occupied by the '5.5 × 5.5'-Cu phase after annealing. Note that patches of the '5.5 × 5.5'-Cu phase are formed in the form of the "hole-island" pairs (see Fig. 2d), which is a sequence of the Si imbalance between '5.5 × 5.5'-Cu and 7 × 7 reconstructions containing ~1.0 and 2.08 ML of Si, respectively. From the measured area fractions occupied by the "holes" and "islands" at the transient stages (when magic clusters and '5.5 × 5.5'-Cu patches coexist), one could also estimate the Si content in the Cu magic clusters.

Evaluation of a set of STM images with cluster arrays at various stages of annealing yields an estimation for the composition of the Cu magic cluster as follows: each cluster contains ~20 Cu atoms, while ~20 Si atoms are removed from a corresponding 7 × 7 HUC during cluster formation. It should be noted that the accuracy of the composition determination is limited by about 50%. The main obstacle is that besides the magic clusters the irregular-shaped clusters are present which composition is unknown (they might be built of either Cu or Si or both). Thus, the obtained values seem to provide only a draft hint for the range of compositions which Cu magic clusters could possess.

Comparing the estimated composition of the Cu magic clusters with the composition of the known magic clusters (Table 1), one can clearly see that the Cu clusters stand apart all other magic clusters. The number of metal atoms in the Cu cluster far exceeds their typical numbers in other magic clusters (~20 versus 6 to 11). Furthermore, while for the other magic clusters all Si atoms remain within a given 7 × 7 HUC, about 20 Si atoms are expelled from the 7 × 7 HUC in the course of Cu cluster formation.

To adopt the above extensive substitutional incorporation of Cu in the Cu magic cluster, we have suggested that the cluster is essentially a patch of the Cu_2Si monolayer developed in the rest-atom layer within a 7 × 7 HUC. Thus, upon the Cu_2Si-cluster formation, no Si adatoms are left and a certain portion of Si rest-atoms becomes replaced by Cu atoms. An extremely high chemical reactivity of Cu with respect to Si and the fact that Cu_2Si monolayer on Si(1 1 1) (i.e., a '5.5 × 5.5'-Cu phase) is a stable configuration of the Cu/Si(1 1 1) interface seem to be supportive arguments for this suggestion. Nineteen structural models have been constructed and their stability has been tested using DFT calculations (Table 2). As one can see, five configurations (the models 10, 14, 15, 17, and 19) have formation energies lower than that of the original adsorbate-free Si(1 1 1)7 × 7 surface. Three of these five models, namely the models 14, 15, and 17, have the lowest energies and

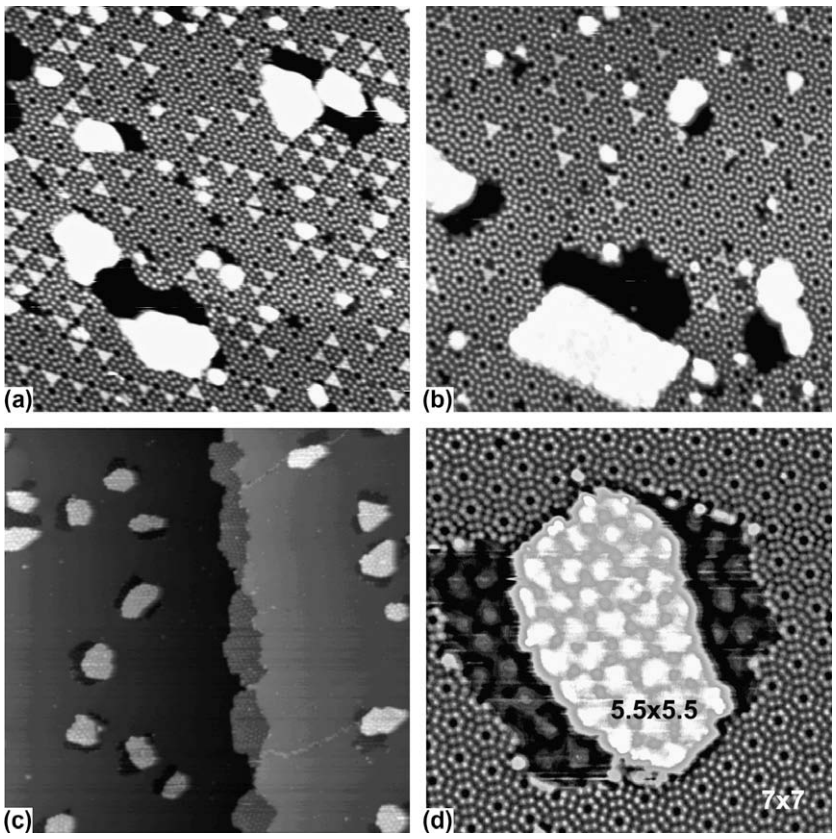

Fig. 2. Annealing-induced transition of the Cu magic clusters to the domains of the '5.5 × 5.5'-Cu reconstruction. STM images illustrating evolution of the magic cluster array like that in Fig. 1 upon annealing at (a) 250 °C, (b) 270 °C, and (c) 400 °C. (d) STM image showing "hole-island" pair of the forming '5.5 × 5.5'-Cu reconstruction at a greater magnification. Scale: (a) and (b) 420 × 420 Å^2, (c) 1500 × 1500 Å^2, and (d) 320 × 320 Å^2. Sample bias voltage: (a) and (b) +2.0 V, (c) and (d) +2.5 V.

Table 1
Composition of the magic clusters formed by various metal adsorbates on the Si(1 1 1)7 × 7 surface [5].

Metal adsorbate	Number of metal atoms per HUC	Number of Si atoms removed from HUC
Al, In, Ga	6	0
Na	6	0
Pb	6	0
Sn, Ge, Mn, Tl, Ag, Cr	9–11	0
Cu	~20	~20

Table 2
Results of the DFT calculations for the models of the $CuSi_2$-like Cu magic clusters on the Si(1 1 1)7 × 7 surface with various compositions. The Si(1 1 1)7 × 7 formation energy is set zero.

Model	Number of Cu atoms per HUC	Number of Si atoms removed from HUC	Energy (eV)
1	7	0	8.19
2	13	0	0.20
3	3	3	2.46
4	6	3	5.34
5	7	3	4.75
6	9	6	4.53
7	10	6	1.08
8	10	6	3.05
9	12	9	0.65
10	13	9	−0.43
11	13	9	8.85
12	15	12	1.27
13	16	12	0.01
14	18	14	−0.71
15	19	15	−1.27
16	22	12	4.86
17	22	15	−1.00
18	31	24	0.96
19	37	24	−0.59

the compositions which are the closest to that estimated in the experiment. Fig. 3 shows these models together with the model 10 given for comparison. The models are apparently similar differing only by the extent to which the Si rest-atom layer in the 7 × 7 HUC is replaced by the Cu_2Si monolayer. Thus, the clusters constitute a "Cu_2Si-cluster family", of which selected (magic) clusters have the lowest formation energies.

Taking into account a similar structure and close formation energies of the models 14, 15, and 17, one could expect that the clusters of all these three types have a chance to occur at the surface. Indeed, close inspection of the STM images with Cu magic cluster arrays reveals a presence of the clusters of three types. This is illustrated by the Fig. 4, where one can see the clusters having similar appearance but different contrast. They are labeled in Fig. 4 as "Normal" (the cluster outlined by a solid frame), "Bright" (the cluster in a dashed frame), and "Dark" (the cluster in a dotted frame). Statistical analysis reveals that the "Normal" clusters are the most abundant and constitute 76% of all clusters, while the fraction of the "Bright" and "Dark" clusters is 14% and 10%, respectively. Thus, it seems reasonable to attribute the model 15 to the "Normal" clusters, the model 17 to the "Bright" clusters and the model 14 to the "Dark" clusters. However, the further experimental and theoretical efforts are apparently required for the conclu-

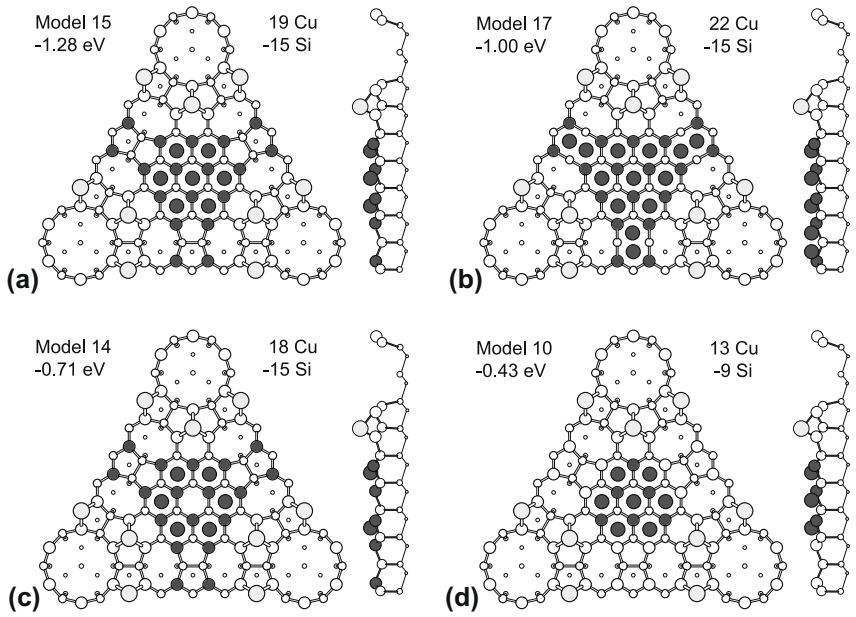

Fig. 3. Structural models of the Cu_2Si-like Cu clusters on Si(1 1 1)7 × 7 surface (front and side views): (a) model 15, (b) model 17, (c) model 14, and (d) model 10 (according to the notation of the Table 2). Si atoms are shown by white and light gray circles (the latter for Si adatoms), Cu atoms are shown by dark gray circles. The models show the clusters occupying the faulted 7 × 7 half unit cell (HUCs). The models for clusters in the unfaulted 7 × 7 HUCs are similar.

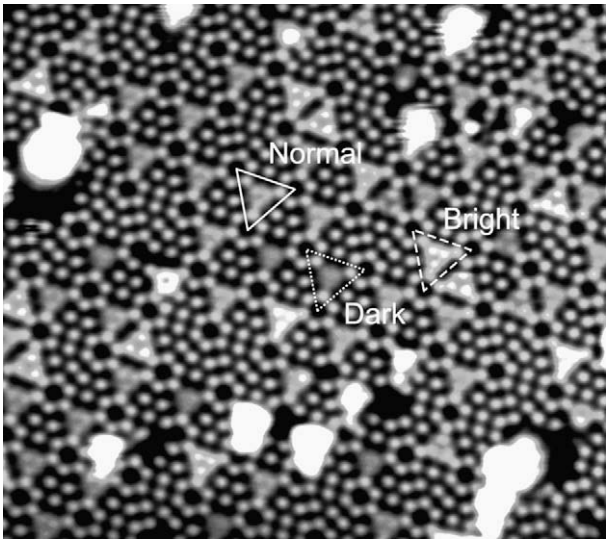

Fig. 4. Empty-state (+2.0 V) 235 × 235 Å^2 STM image of the Cu magic cluster array illustrating the presence of the three types of the magic clusters, labeled "Normal" (in a solid frame), "Bright" (in a dashed frame), and "Dark" (in a dotted frame). The "Normal", "Bright" and "Dark" clusters constitute 76%, 14% and 10% of all clusters, respectively. 86% of the clusters occupy the faulted 7 × 7 half unit cells.

sive determination of the structure of the Cu magic clusters as well as for establishing their correspondence to the counterparts in the experimentally acquired STM images. In particular, the most crucial test of the model validity is associated with reproducing the experimentally observed complicated bias-dependent STM appearance of clusters [4] in the simulated STM images.

4. Conclusion

Using scanning tunneling microscopy observations and density functional theory calculations, composition and structural properties of the Cu magic clusters formed on Si(1 1 1)7 × 7 surface have been studied. Composition of the Cu magic clusters has been evaluated from the quantitative consideration of the Cu and Si mass transport occurring during irreversible transition of magic clusters into the Si(1 1 1)'5.5 × 5.5'-Cu reconstruction upon annealing. Basing on the results of the evaluation, it has been suggested that the Cu magic clusters resemble fragments of the Cu_2Si-silicide monolayer incorporated into the rest-atom layer of the Si(1 1 1)7 × 7 HUCs. Calculations have shown that of nineteen models under consideration the five models have formation energies lower than that of the adsorbate-free Si(1 1 1)7 × 7 surface. In turn, the three of five models, having the lowest formation energies and the compositions which are the closest to that estimated in the experiment, are concluded to be the most plausible configurations. Their counterparts have been found in the experimentally acquired STM images.

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