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Peculiarities of Al magic cluster self-assembly on Si(100) surface

V.G. Kotlyar [a], Yu.V. Luniakov [a], A.V. Zotov [a,b,c], A.A. Saranin [a,b,*]

[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

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ABSTRACT

Using scanning tunneling microscopy observations and density functional theory calculations, regularities of the Al magic cluster array self-assembly on Si(100) surface has been elucidated. While a single Al cluster occupies an area of $4a \times 3a$, an ordered Al-cluster array exhibits a 4×5 periodicity, as the clusters in the array are separated by the $4a \times 2a$ "spacers". The plausible structural model for the "spacer" was proposed in which the "spacer" is arranged as an ordinary $4a \times 3a$-Al cluster in which the central atomic row with the topmost Si atom is missing. Appearance of the "spacers" in the Al-cluster array was found to reduce formation energy of the array. Ability to incorporate the rows of Al-"spacers" into the completed 4×3 In-cluster array was demonstrated.

1. Introduction

Recently, supported nanoclusters on surfaces have become an object of the extensive investigations not only because of a pure scientific interest but also because of potential applications for atomic-scale electronic devices and catalysts. For most of these applications, the uniform size distribution and ordered spatial arrangement are highly desired. Promising approach to reach this goal is associated with using self-assembly of the identical-size clusters (surface magic clusters [1]) forming highly ordered two-dimensional lattice on a suitable surface. The most advanced results have been sofar obtained with the surface magic clusters of group-III metals (Al, Ga, and In) [2–6] and some other metals (e.g., Na, Pb, and Cu) [7–10] on crystalline Si surfaces (mainly, on Si(111)7×7 surface). For these cluster arrays, a number of the profound results have recently been obtained, including elucidation of their specific electronic properties [8,11–15] foundation of their pronounced catalytic activity [16], finding the possibilities to modify composition, structure and properties of the clusters [17–19], demonstrating the prospects of the cluster as a prototype of the atomic-scale device [20].

In the present investigation, we have considered the structural properties of the magic cluster arrays formed by Group-III metals (Al and In) on Si(100) surface. Using scanning tunnelling microscopy (STM) observations and density functional theory (DFT) calculations, we have addressed the following main questions.

- Why does Al-cluster array have the 4×5 periodicity [21,22], while a single Al cluster occupies the $4a \times 3a$ area [22–24]? [$a = 3.84$ Å, the lattice constant of the unreconstructed Si(100)1×1 surface.]
- What is the atomic structure of the 4×5 Al-cluster array?
- Is it possible to fabricate a mixed array of Al and In clusters and how is such an array arranged?

2. Experimental and calculation details

Our experiments were performed with Omicron STM operated in an ultrahigh vacuum ($\sim 2.0 \times 10^{-10}$ Torr). Atomically clean Si(100)2×1 surfaces with a minimal number of defects were prepared using the surface preparation procedure described in Ref. [25]. Indium was deposited from a tantalum foil tube at a rate of 0.1 ML/min. Aluminum was deposited from an Al-wrapped tungsten filament at a rate of 0.2 ML/min [1 ML(monolayer) = 6.8×10^{14} cm^{-2}, top Si atom density on the unreconstructed Si(100)1×1 surface]. In and Al clusters are formed by depositing a corresponding metal onto the Si(100)2×1 surface held at about 500 °C. For STM observations, electrochemically etched tungsten tips cleaned by *in situ* heating were employed. All STM images were acquired in a constant-current mode after cooling the sample to room temperature (RT).

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

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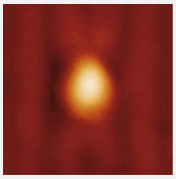
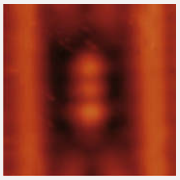
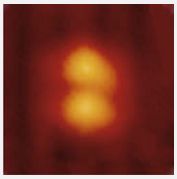
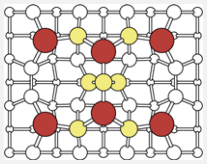
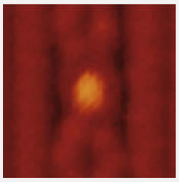
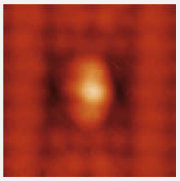
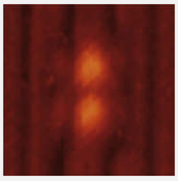
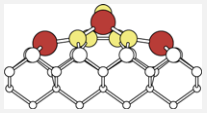
Table 1
STM appearance of single Al and In magic clusters at various bias voltages. STM-image size: 32 × 32 Å^2. Structural model [35] (top and side views) of the cluster is presented at the right panel. Six metal atoms are shown by black (red in the on-line version) circles, seven Si atoms incorporated in the cluster are shown by gray (yellow in the on-line version) circles, Si atoms of the Si(100) substrate are shown by white circles.

Metal	Sample bias voltage			
	−2.0 V	+1.0 V	+2.0 V	
In				
AL				

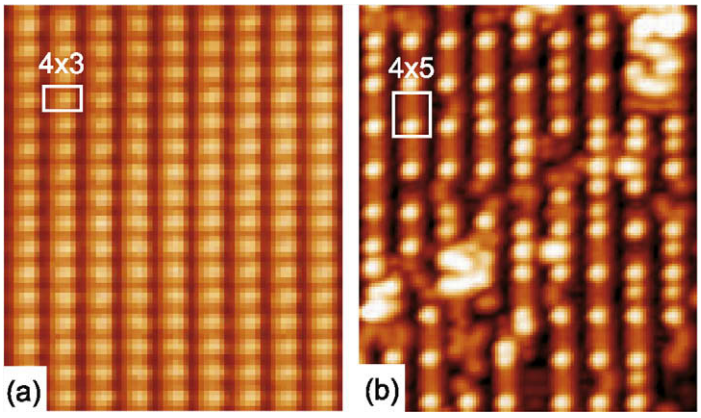


Fig. 1. (a) 140 × 185 Å^2 filled-state (−2.0 V) STM images of the completed (a) 4 × 3-In and (b) 4×5-Al magic cluster arrays on Si(100) surface.

The plane-waves total-energy calculations reported here were performed by using the Vienna Ab Initio Simulation Package (VASP) [26–29] based on density functional theory (DFT) [30] with projector-augmented wave (PAW) pseudopotentials [31]. The local density approximation (LDA) after Ceperley–Alder [32] in the Perdew–Zunger parametrization [33] for the exchange and correlation functional have been employed. Wave functions were represented using a plane-wave basis set with a kinetic energy cutoff of 250 eV. The supercell geometry used in this study was simulated by a repeating slab of eight Si atomic layers and a vacuum region of 10 Å. The 5 × 4 unit cell was used to fulfill the periodic boundary condition in the lateral directions. The adsorbed Al atoms were added on the top reconstructed 5 × 4 surface, and the dangling bonds on the unreconstructed bottom surface were saturated by the hydrogen atoms. The Brillouin zone integration was performed with a 2*k*-point grid originated from *k*-point (0.25, 0.25, 0). In all the calculations, the top atomic layers were fully relaxed, and the bottom two atomic Si layers were kept at the bulk positions. The geometry was optimized until the total energy is converged to 10^{-4} eV and the total force is converged to 10^{-3} eV/Å. The sensitivity of formation energies on kinetic energy cutoff, *k*-points setup, and the total energy/force numerical accuracy has been tested and found to have a negligible effect on the total energy differences.

To compare the structures having different number of silicon and Al atoms in the different proposed models, we have used the surface formation energy defined as [34]:

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

Table 2
Formation energies of the 4 × 5-Al clusters consisting of the 4*a* × 3*a*-Al Bunk's cluster [35] and "spacers" of various types. For the models M1–M22, the occupation of the sites, numbered according to Fig. 2, either by Si or Al atoms are shown. The model M0 represents the case when the "spacer" is essentially a region of the bare dimerised Si(100)2 × 1 reconstruction. The formation energies for the various models are referred to the lowest-energy model M22, shown in Fig. 2.

Model	Atoms (see Fig. 2)						Energy, eV
	1	2	3	4	5	6	
M0	Si	Si	Si	Si	–	–	2.15
M1	Si	Si	Si	Al	Si	Si	2.80
M2	Si	Si	Si	Si	Al	Si	3.31
M3	Si	Si	Al	Al	Si	Si	2.15
M4	Si	Si	Si	Al	Al	Si	2.44
M5	Si	Si	Al	Si	Al	Si	2.51
M6	Si	Si	Si	Si	Al	Al	2.82
M7	Al	Si	Si	Al	Si	Si	2.30
M8	Si	Al	Si	Al	Si	Si	2.16
M9	Si	Si	Al	Al	Al	Si	1.75
M10	Si	Si	Si	Al	Al	Al	2.12
M11	Si	Al	Si	Al	Al	Si	1.83
M12	Al	Si	Si	Al	Al	Si	2.00
M13	Al	Si	Al	Si	Al	Si	1.83
M14	Si	Si	Al	Al	Al	Al	1.38
M15	Si	Al	Al	Al	Al	Si	1.22
M16	Al	Si	Al	Al	Al	Si	1.09
M17	Si	Al	Si	Al	Al	Al	1.57
M18	Si	Al	Al	Si	Al	Al	1.56
M19	Al	Al	Al	Al	Si	Si	0.82
M20	Al	Al	Al	Al	Si	Al	0.42
M21	Al	Al	Al	Si	Al	Al	0.77
M22	Al	Al	Al	Al	Al	Al	0.00