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Surface Science 516 (2002) 203–206

SURFACE SCIENCE

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# First principles study of Al–Si nanosized clusters on Si(100)-2 × 1

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Received 12 April 2002; accepted for publication 1 July 2002

## Abstract

Ab initio local density approximation calculations were performed to investigate the energetics and atomic structures of Al–Si nanosized clusters on Si(100)-2 × 1. The transition from the Al-2 × 2 surface phase to Al–Si nanosized clusters has been found energetically favorable. Three different cluster models were considered. The first one was proposed by Kotlyar et al. The second model was proposed by Bunk et al. for the Si(100)-In system and was adopted by Cocolletzi and Takeuchi for Si(100)-Al(3 × 4) reconstruction. Third model is the mixture of the first and second. It has a pyramidal form like the Bunk–Cocolletzi cluster, but eight Al atoms like Kotlyar's cluster. The Bunk–Cocolletzi model has been found the most favorable.

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**Keywords:** Silicon; Aluminum; Surface structure, morphology, roughness, and topography; Clusters; Ab initio quantum chemical methods and calculations

## 1. Introduction

It is well known [1] that in the low-temperature range (from room temperature to about 350 °C) aluminum forms dimers that are located in the troughs between Si dimer rows and are oriented parallel to Si dimers. Recent scanning tunneling microscopy and surface forced microscopy studies [2–6] reveal that the deposition of Al onto the Si(100) surface at temperatures above 450 °C

leads to the formation of nanosized Al–Si clusters. The atomic structure and composition of the Al–Si clusters still remain unclear.

Kotlyar et al. [6], using Auger electron spectroscopy (AES), low energy electron diffraction and STM, have proposed a structural model of the Al–Si nanocluster. According to this model, each cluster moves six Si atoms from the Si(100)-2 × 1 structure and contains eight Al atoms, four of which substitute four Si atoms in silicon dimers forming Al–Si dimers. Other four Al atoms form two Al–Al dimers on the top of the cluster (see Fig. 1). This model has eight Al atoms and has no dangling bonds.

However, the orientation of Al–Al dimers on the top of the cluster is not determined correctly.

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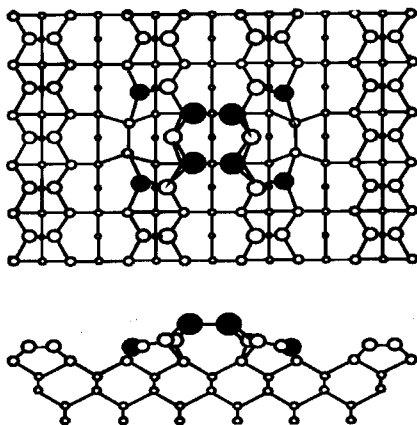


Fig. 1. Atomic scheme of Kotlyar's Al-Si nanocluster: Al-Al dimers are *parallel* to Si-Si dimers of substrate. Black circles are Al atoms, white circles are Si atoms.

Kotlyar et al. oriented them parallel to Si-Si dimers of substrate, but in their work [6] there is no direct experimental information about such orientation. Authors observed two bright oval protrusions in the center of the cluster and four dim protrusions around them. They interpreted bright protrusions as Al-Al addimers and dim protrusions as Al atoms in the mixed Al-Si dimers. However, their oval protrusions stretched along Si dimers rows. Therefore, an alternative orientation of Al-Al addimers may be proposed: namely, orthogonal to Si dimers of substrate (Fig. 2).

The model of Kotlyar et al. is compared with a model proposed for the Si(100)-(3 × 4)-In surface

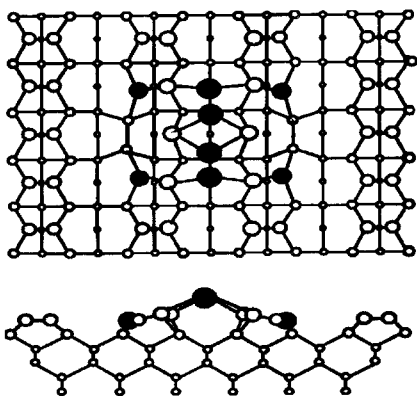


Fig. 2. Atomic scheme of Kotlyar's Al-Si nanocluster: Al-Al dimers are *orthogonal* to Si-Si dimers of substrate.

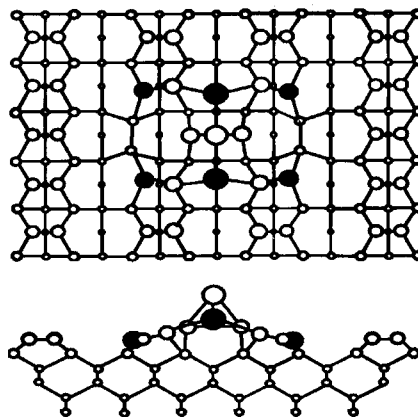


Fig. 3. Atomic scheme of the Bunk-Cocolezzi Al-Si pyramid-like nanocluster.

phase by Bunk et al. [7,8], but used by Cocolezzi and Takeuchi [9] as a subunit for the explanation of the Si(100)-(3 × 4)-Al reconstruction (see Fig. 3). Then we will call this model as the Bunk-Cocolezzi model. This model also has no dangling bond but it has only six Al atoms. A character feature of the pyramid-like the Bunk-Cocolezzi model is a trimer on top. This trimer is formed by a Si atom occupying the highest vertical position and bonded to two Al atoms at lower vertical positions.

The aim of this work is to show the energy advantage for the transition from the Al-2 × 2 structure to the Al-Si nanosized cluster system and to compare different models of Al-Si nanoclusters.

## 2. Method and details of calculations

The calculations were performed using the FHI96MD code [10] with the next characteristics: the Car-Parinello type of electronic structure calculations [11] in the frame of the local density approximation after Ceperly and Alder [12] in the parameterization of Perdew and Zunger [13] with nonlocal norm-conserving pseudopotentials [14] in the Kleinman-Bylander form [15]. The silicon surface Si(100)-2 × 1 was simulated by a periodic slab geometry. The unit 5 × 4 supercell contained

six atomic layers and four vacuum layers. We used a plane-wave basis set with an energy cutoff of 10 and 14 Ry. The lattice parameter used for Si substrate was equal 5.36 Å, which corresponds to the theoretical equilibrium lattice. To avoid the artificial electrostatic field, which arises from the periodic boundary conditions, we used a planar dipole layer as proposed by Neugebauer and Scheffler [16], and to saturate the bottom slab layer we used a layer of hydrogen atoms. The Al and Si atoms of the top five layers were relaxed. The only one k-point (0.5; 0.5; 0.0) was used. Pseudopotentials were constructed using the FHI98PP code [17].

### 3. Results and discussions

To test our techniques we simulated the Al-2 × 2 surface dimer structure and have found that the energy of the Al addimers oriented parallel to Si dimers is lower than the orthogonal case by 0.42 eV per dimer. It is close to the value of 0.33 eV obtained by Northrup et al. [18].

Then, we calculated equilibrium geometries for Kotlyar's model for two different orientations of Al–Al dimers (Figs. 1 and 2). We have found that orthogonal orientation is more preferable than parallel. The energy difference is 0.45 eV for  $E_{\text{cut}} = 10$  Ry and 0.48 eV for  $E_{\text{cut}} = 14$  Ry, or approximately 0.24 eV per Al–Al dimer.

To calculate the energy profit for the transition from the Al-2 × 2 structure to the Al–Si cluster we need to find the chemical potentials of Al in the both cases and to compare them. The chemical potential of Al in the Al-2 × 2 structure ( $E_{\text{Al}(2 \times 2)}$ ) can be easily obtained from the comparison of the energies of the Al-2 × 2–Si(100) phase ( $E_{\text{AlSi}(2 \times 2)}$ ) and the pure Si(100)-2 × 1 surface ( $E_{\text{Si}(2 \times 1)}$ ):

$$E_{\text{Al}(2 \times 2)} = [E_{\text{AlSi}(2 \times 2)} - E_{\text{Si}(2 \times 1)}] / N_{\text{Al}}$$

where  $N_{\text{Al}}$  is the number of Al atoms in the used cell.

Determination of the Al chemical potential in the cluster is a more complicated task because a part of the Si atoms ( $N_{\text{Si}}$ ) of the silicon substrate is absent. Therefore, we need at first to find the chemical potential of Si ( $E_{\text{Si}}$ ) and then to calcu-

late the chemical potential of Al in the cluster ( $E_{\text{Al}(cl)}$ ):

$$E_{\text{Al}(cl)} = [E_{\text{cl}} - E_{\text{sub}} - N_{\text{Si}}E_{\text{Si}}] / N_{\text{Al}}$$

where  $E_{\text{cl}}$  is the energy of the Al–Si cluster (together with silicon substrate),  $E_{\text{sub}}$  is the energy of the Si(100)-2 × 1 substrate.

This approach allows us to compensate the different numbers of atoms in different cluster models and to take into account the influence of the H saturated surface on the total energy of the system. The Al chemical potential obtained by this way contains the energy changes of the silicon surrounding and describes the ability of Al to incorporate into one or another Al–Si structure.

The chemical potentials of Al in the Al-2 × 2 phase and in orthogonal Kotlyar's model have been found of –58.02 and –59.02 eV, respectively. Thus, the transition from the Al-2 × 2 phase to the Al–Si nanosized clusters of Kotlyar's type is energetically favorable, and the gain of this transition is 1.0 eV per Al atom. However, our calculations show that the model of Bunk–Cocolezzi is more favorable than Kotlyar's model. The chemical potential of Al for this model has been found to be –59.44 eV, e.g. by 0.42 eV larger (at the absolute value) than for Kotlyar's model. In this case the energy gain for the transition from the Al-2 × 2 phase to the Al–Si nanocluster is about 1.4 eV per Al atom.

The Bunk–Cocolezzi model seems very stressed. Besides it has only six Al atoms, while the AES analysis [6] gives the number of Al atoms in the Al–Si nanocluster about eight. Therefore, we studied additionally a mixed model: namely, we replaced two Si atoms of the Bunk–Cocolezzi model by Al atoms (see Fig. 4) to make the number of Al atoms equal to eight. These Si atoms formed in the Bunk–Cocolezzi model a dimer under the Al–Si–Al trimer. In the mixed model the corresponding Al atoms do not form a dimer. Each of them is bonded to three Si atoms including the top atom, and there are no dangling bonds in this model. Calculations show that the chemical potential of Al atom in the mixed model is –59.16 eV. Therefore, the mixed model is more preferable than Kotlyar's model, but less preferable than the model of Bunk–Cocolezzi.

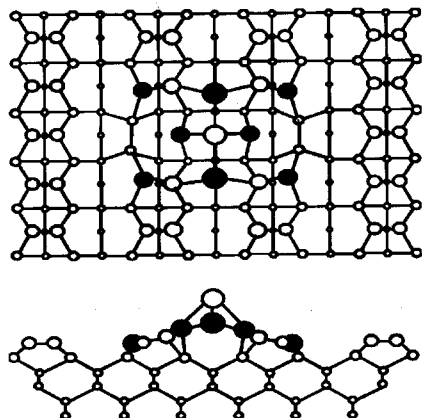


Fig. 4. Atomic scheme of the mixed Al-Si nanocluster. It has a pyramidal form, like the Bunk-Cocolezzi cluster, but eight Al atoms, like Kotlyar's cluster.

#### 4. Summary

The *ab initio* simulation of Al-Si nanoclusters on Si(100) surface shows that such clusters are more stable energetically than the Al- $2 \times 2$  surface structure. The three structural cluster models were tested: Kotlyar et al. [6], Bunk-Cocolezzi [7–9] and a mixed model. The Bunk-Cocolezzi pyramid-like model has been found the most favorable. The energy profit for the transition from the Al- $2 \times 2$  phase to the Bunk-Cocolezzi Al-Si nanocluster is about 1.4 eV per Al atom.

#### Acknowledgements

Author is grateful to Prof. V.G. Lifshits and Dr. V.G. Kotlyar for helpful discussions. This work was supported by the FCP Program "Inte-

gratsia" and the Russian Research Program "Physics of Solid State Nanostructures".

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