



# Dynamics of Sn and Zn atoms on a Si(1 1 1)-7 × 7 surface

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## Abstract

The adsorption of Sn and Zn on a Si(1 1 1)-7 × 7 surface was studied by a scanning tunneling microscopy (STM). Single Sn atom is adsorbed in the faulted and unfaulted half unit cells at low coverage. When the half unit cells comprising an adsorbed single Sn atom are separated each other, no diffusion of the Sn atom to the neighboring half unit cell takes place at room temperature although the Sn atom undergoes rapid migration over the three center Si-adatoms in the half unit cell. When an adjacent half unit cell adsorbs a Sn atom, however, the two single Sn atoms in the two adjacent half unit cells are rapidly agglomerated to a Sn<sub>2</sub>-dimer, that is, the diffusion barrier is lowered at the border. In addition, the single Sn atoms in the adjacent two half unit cells undergo replacement with a center Si-adatom, and a Si<sub>4</sub>-cluster is formed. On the other hand, adsorbed Zn atoms on a Si(1 1 1)-7 × 7 surface prefer to form one Zn<sub>3</sub>-dot in each half unit cell. As a result, a honeycomb layer composed of Zn<sub>3</sub>-cluster is established as increasing the coverage. These results suggest that the adsorbate–adsorbate interaction plays important role in the formation of the precursor state, which is responsible for the feature of the surface reaction and catalysis.

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**Keywords:** Adsorption of Sn, Zn; Si(1 1 1)-7 × 7 surface; STM; Surface restructuring; Clusters of Sn<sub>2</sub>, Zn<sub>3</sub>, and Si<sub>4</sub>; Replacement of surface atoms; Supra-honeycomb layer of Zn<sub>3</sub>; Precursor state

## 1. Introduction

It is known that some impurities influence the surface reaction, and co-catalyst of minor elements might be a similar phenomenon but their role is mysterious. The reaction of silicon with methyl chloride known as the Rochow reaction,  $\text{Si} + 2\text{CH}_3\text{Cl} \rightarrow (\text{CH}_3)_2\text{SiCl}_2$ , is catalyzed by Cu in the presence of small amount of Zn and/or Sn as the co-catalyst. The role of these met-

als in catalysis, however, is not clear, although clean surfaces of silicon are precisely studied in the atomic level.

Sn and Si belong to the same group in the periodic table, and Sn takes two forms; semi-conductive  $\alpha$ -Sn of the sp<sup>3</sup>-hybridization and metallic  $\beta$ -Sn. Therefore, the adsorption of Sn on Si surfaces has been extensively studied, but the most studies have been focused on the surface structures at high coverage of Sn. That is, a limited number of studies have been reported on the dynamics of Sn atoms on the surface at low coverage. The adsorption of Zn on the silicon surfaces in the UHV system, in contrast, has been studied very few because high vapor pressure of Zn has kept at a distance. In this paper, dynamic properties of Sn and Zn atoms were studied on the Si(1 1 1)-7 × 7 surfaces

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by means of scanning tunneling microscopy (STM). By careful studies of the adsorbed Sn and Zn atoms, it was found that the electronic structure is influenced by the weak interaction of adsorbed metal atoms on the specific sites, so that the specific structures are stabilized by the weak interaction.

## 2. Experimental

A rectangular Si(1 1 1) wafer of 1 mm  $\times$  7 mm  $\times$  0.3 mm (n-type, ca. 0.1  $\Omega$  cm) was degassed in a UHV–STM system (JSPM-4500S, JEOL) at 450  $^{\circ}$ C for 12 h, and a clean surface was obtained by flashing the degassed sample at about 1250  $^{\circ}$ C by direct current. The sample was flashed not to exceed  $1 \times 10^{-7}$  Pa of the chamber pressure by controlling the flashing time until a clean and well ordered Si(1 1 1)-(7  $\times$  7) surface was obtained. When the thermal drift becomes sufficiently small, Sn or Zn was deposited on it in the treatment chamber by heating a tungsten filament winding Sn or Zn wire. After the deposition of Sn or Zn, the sample was transferred to the STM chamber of the pressure of ca.  $2 \times 10^{-8}$  Pa and was subjected to STM experiment. Deposition rate of Sn was about 0.2–0.4 ML  $\text{min}^{-1}$  and that of Zn was estimated to be about 0.4–0.8 ML  $\text{min}^{-1}$  by counting the number of

Sn or Zn atoms on the silicon surface. The STM image was obtained at constant current mode by using an electrochemically prepared tungsten tip.

## 3. Results and discussion

### 3.1. Sn on Si(1 1 1)-7 $\times$ 7

When Sn is adsorbed on a Si(1 1 1)-(7  $\times$  7) surface, an ordered structure of either ( $\sqrt{3} \times \sqrt{3}$ )R30 or ( $2\sqrt{3} \times 2\sqrt{3}$ )R30 is stabilized depending on the coverage of Sn [1]. The ( $2\sqrt{3} \times 2\sqrt{3}$ )R30 surface was inferred as a two-layer structure by scanning tunneling microscopy [2]. The electronic structure of ( $\sqrt{3} \times \sqrt{3}$ )R30 and ( $2\sqrt{3} \times 2\sqrt{3}$ )R30 Si(1 1 1)–Sn surfaces was also studied by the spectroscopic methods [3,4], and the phase change by charge density wave was reported on the ( $\sqrt{3} \times \sqrt{3}$ )R30 Si(1 1 1)–Sn surface by Ottaviano et al. [5]. However, the mechanism for the formation of the ordered surfaces has been little studied. As shown in this paper, the dynamic behavior of a Sn atom on the Si(1 1 1)-7  $\times$  7 surface and its array at low coverage are entirely different from the ordered surface established at high coverage [6].

Fig. 1a shows a typical feature of Sn atoms adsorbed on a Si(1 1 1)-7  $\times$  7 surface at 0.02 ML coverage. Bright

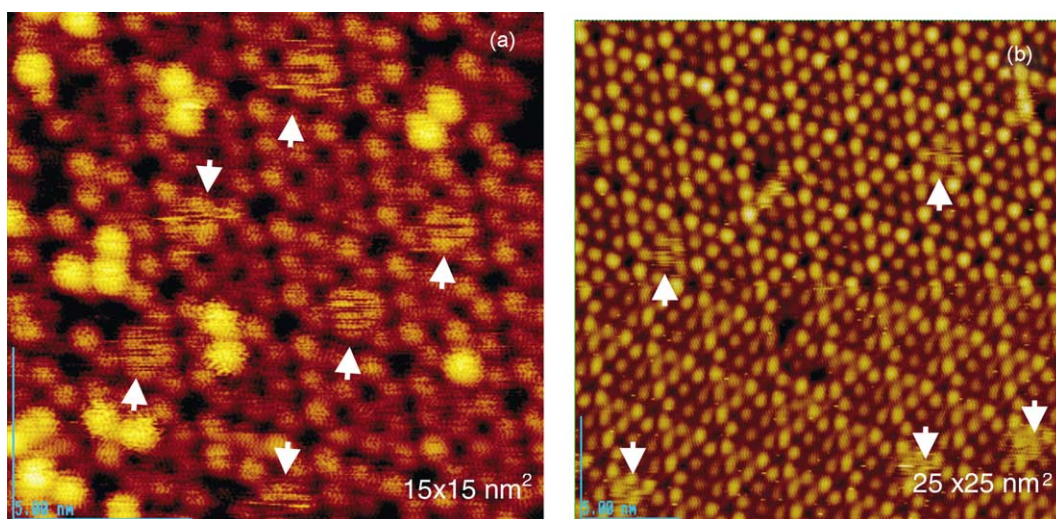


Fig. 1. Filled state image of the Sn adsorbed Si(1 1 1)-7  $\times$  7 surface. (a) Sn<sub>2</sub>-dimer and single Sn are predominant. Noisy feature indicated by the arrow reflects a moving isolated single Sn atom inside the half unit cell;  $V_b = -2.0$  V and  $I_t = 0.08$  nA. (b) Only isolated single Sn atoms are seen at low coverage as the noisy feature on the surface;  $V_b = -2.0$  V and  $I_t = 0.20$  nA.

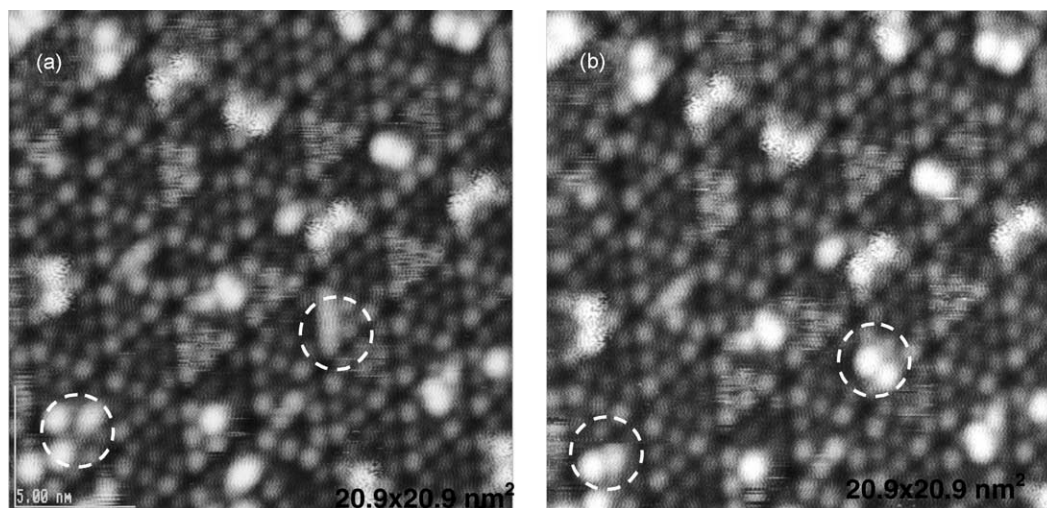


Fig. 2. Rapid motion of isolate single Sn giving noisy half unit cell and slow motion of Sn<sub>2</sub> in the half unit cell at room temperature. (a) and (b) were obtained with an interval time of 45 s;  $V_b = -2.0$  and  $I_t = 0.129$  nA.

pairs are recognized in a lot of half unit cells, where most of them are on the center adatoms. Fig. 2a and b was the image obtained at the same area with an interval time of 85 s. It is well known that the bright pair moves seldom in the half unit cell at room temperature, that is, only the bright dots within the two circles have been changed the adsorption sites in the 85 s.

In addition, we can recognize several half unit cells having noisy feature at the central part of half unit cells as shown in Fig. 1a. We deduced that the noisy feature reflects a single Sn atom moving over the three center adatoms in a half unit cell. It should be pointed that the single Sn atom moving over the center adatoms in the half unit cell does not diffuse to neighboring half unit cells at room temperature. As a result, a lot of noisy halves were observed on the surface at nominal exposure of Sn but bright Sn<sub>2</sub> pairs were recognized very few as shown a surface with 0.003 ML in Fig. 1b. These phenomena suggest that a single Sn atom is surrounded by a high diffusion barrier when a single Sn atom is isolated on the surface. If this is the case, why so many bright Sn<sub>2</sub> pairs can be formed at a coverage of 0.02 ML in Fig. 1a. We inferred that a specific process for the formation of Sn<sub>2</sub> pairs may take place on the Si(1 1 1)-(7 × 7) surface.

In order to shed light on the formation process of the Sn<sub>2</sub>-dimer, we repeated a rapid rescanning in

126 s just after the deposition of Sn (Fig. 3a and b). We found noisy rhombic unit cells in Fig. 3a at the point shown with the arrows, where adjacent faulted and unfaulted half unit cells have a single Sn atom, respectively. Interestingly, these noisy rhombic features disappeared about 2 min after, and the formation of new Sn<sub>2</sub>-dimer was necessarily recognized in the corresponding half unit cell as pointed by the arrows in Fig. 3b. This might be the specific process for the preferential formation of Sn<sub>2</sub>-dimer on the Si(1 1 1)-7 × 7 surface at low coverage of Sn. That is, rather high diffusion barrier surrounding each half unit cell retards surface diffusion of an isolated single Sn atom, but the barrier is suddenly lowered when another single Sn atom comes in an adjacent half unit cell. If this is the case, it may realize the existence of precursor state. The idea of precursor state has been accepted to explain some adsorption and surface reactions although the precursor itself has never been detected. We could say that the noisy rhombic unit cell observed in Fig. 3a may be a precursor state for the formation of Sn<sub>2</sub>-dimer. When the coverage of Sn is increased a little, the probability for the formation of the precursor state will be markedly increased so that Sn<sub>2</sub>-dimers are preferentially formed on the Si(1 1 1)-7 × 7 surface as observed in Fig. 1a.



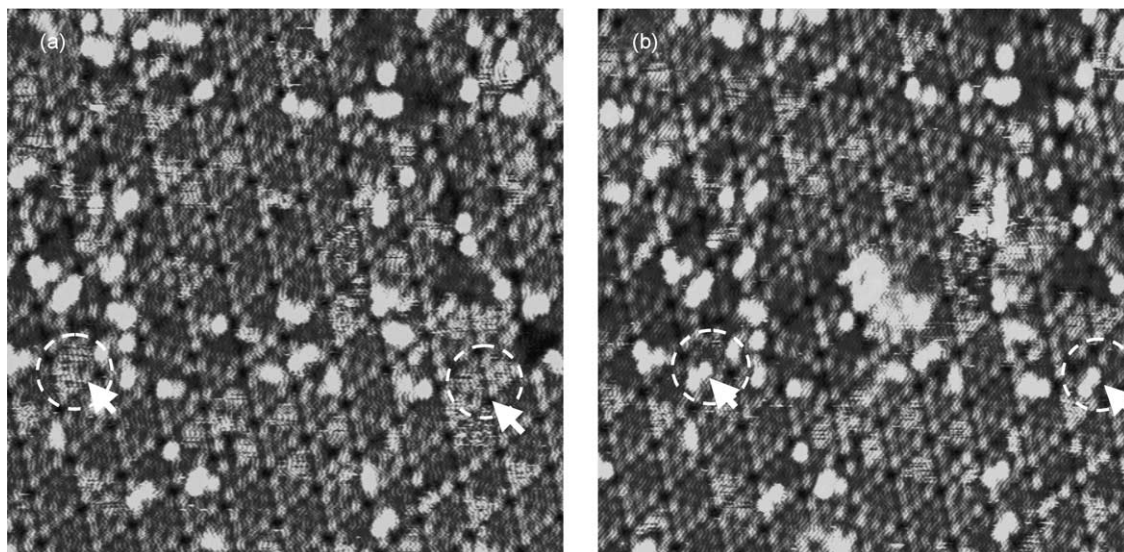


Fig. 3. Dynamic behavior of single Sn atoms on Si(111)-7 × 7;  $V_b = -2.0$  V and  $I_t = 0.03$  nA. (a) STM image obtained 40 s after the deposition of Sn. (b) Single Sn atoms adsorbed in adjacent half unit cells (indicated by arrows) undergo rapid change. The Sn atoms observed in (a) were changed to Sn<sub>2</sub>-dimer within 126 s at room temperature.

Another interesting phenomenon is that the formation of noisy rhombic unit cells provide not only the Sn<sub>2</sub>-dimer but Si<sub>4</sub>-tetramer as shown in Fig. 4. This fact suggests that the noisy rhombic unit cells

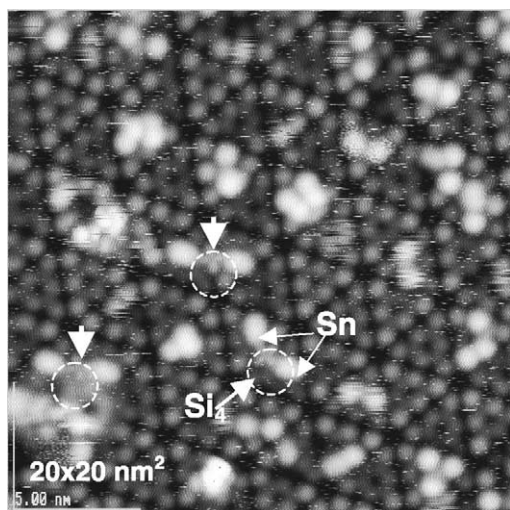


Fig. 4. Single Sn atoms adsorbed in adjacent half unit cells undergo replacement with Si-adatoms. The released Si atoms form Si<sub>4</sub> at the border of the adjacent half unit cells;  $V_b = -2.0$  V and  $I_t = 0.113$  nA.

are the precursor state not only for the formation of Sn<sub>2</sub>-dimer but may be a precursor state for the replacement reaction of a Sn atom with a Si center adatom in the adjacent half unit cells. The two Si atoms released in each half unit cell form a Si<sub>4</sub>-tetramer by bonding with the other two center Si-adatoms at the border of the two half unit cells. The Si<sub>4</sub>-tetramer formed by such a replacement reaction is similar to the Si<sub>4</sub>-cluster formed on a Si(111)-(7 × 7) surface by depositing Si atoms [7–9]. These results are schematically depicted in Fig. 5a.

So far the chemical reaction has been explained by assuming an appropriate activation complex reflecting the potential energy surface. We can explain the reaction rate by the idea of potential barrier but “the characteristics of chemical reaction cannot be predicted by it”. The formation of Sn<sub>2</sub>-dimer and Si<sub>4</sub>-cluster on the Si(111)-7 × 7 surface is a typical case, that is, if an elementary reaction involves a precursor state, the feature of chemical reaction is difficult to explain without the precursor state. For example, so far the selectivity in catalysis has been explained by the relative reaction rate, but it merely expresses the phenomena by other words. The characteristics of the catalyst for a reaction may be reflected by such a destined

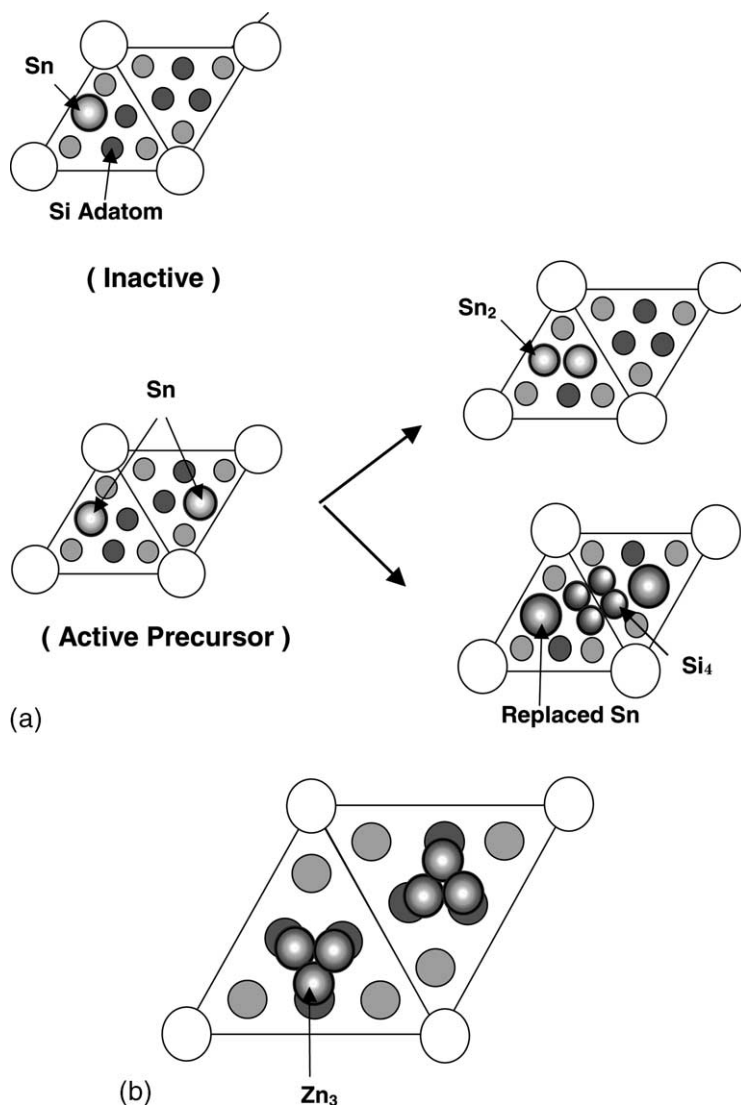


Fig. 5. (a) An isolated single Sn in the half unit cell is inactive, but the two single Sn atoms in the adjacent half unit cells are active to agglomerate or to replace with Si-atom. (b) A model for  $Zn_3$ -cluster.

state as the precursor state [10]. In case of Sn atoms on the  $Si(111)\text{-}7 \times 7$  surface, local electronic state may change with the dynamic motion of the single Sn atoms in the adjacent half unit cells, by which the fluctuation of the potential barrier may be induced and the  $Sn_2$ -dimer and the  $Si_4$ -cluster are preferentially formed. We could say that the feature of prominent catalysis and/or co-catalyst is difficult to explain without consider such a prerequisite state for the reaction [13].

### 3.2. Zn on $Si(111)\text{-}7 \times 7$

As it has been discussed earlier, the dynamic feature of Sn atoms on the  $Si(111)\text{-}7 \times 7$  surface is sensitively influenced by the local circumstances caused by adsorbed Sn atoms on the  $Si(111)\text{-}7 \times 7$  surface, and two single Sn atoms in adjacent half unit cells induce dramatic change of the potential barriers, which is responsible for the formation of precursor states. Taking these facts into account, we studied the adsorption of

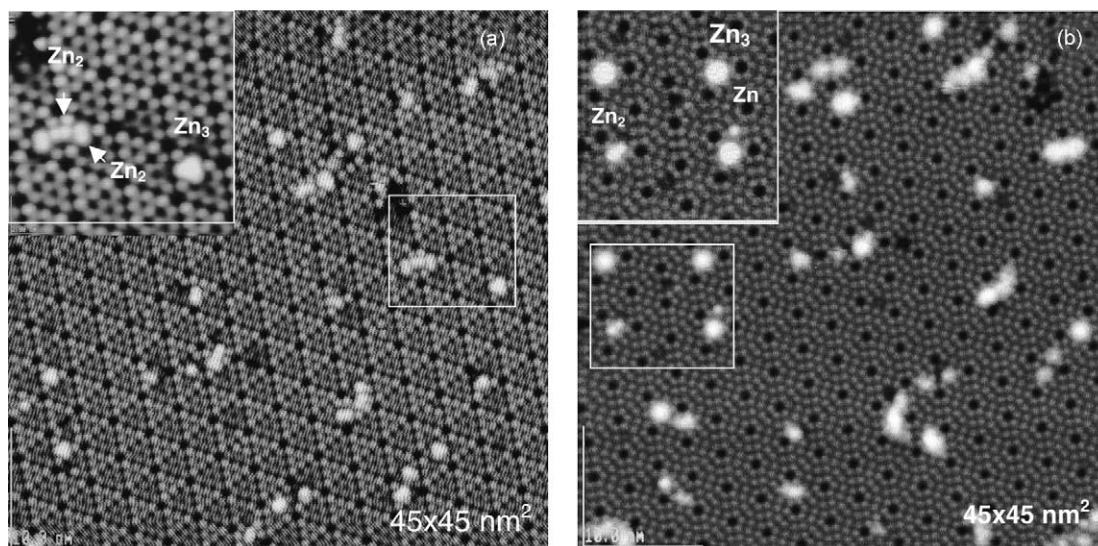


Fig. 6. STM features of Zn atoms adsorbed on Si(111)-7 × 7. (a) Occupied state image of Zn<sub>3</sub> on Si(111)-7 × 7;  $V_b = -2.2$  V and  $I_t = 0.05$  nA. An inserted zoom-in image ( $12 \times 12$  nm<sup>2</sup>) shows Zn<sub>2</sub> and Zn<sub>3</sub>;  $V_b = -2.0$  V and  $I_t = 0.15$  nA. (b) Distinctive Zn, Zn<sub>2</sub>, and Zn<sub>3</sub> species recognized in an empty state image;  $V_b = 2.0$  V and  $I_t = 0.05$  nA.

Zn on a Si(111)-7 × 7 surface from very low coverage to monolayer by focusing on the mutual interaction of adsorbed Zn atoms.

Fig. 6a and b shows a feature of adsorbed Zn atoms on a Si(111)-(7 × 7) surface at about 0.04 ML, where Fig. 6a shows an occupied state feature obtained at a negative bias potential of -2.2 V and Fig. 6b corresponds to an empty state feature of the surface obtained at a positive bias potential of 2.2 V. It is known that the bright dots of Zn have a triangular shape of uniform size at the negative bias potential (occupied state) while they take a round shape image at the positive potential (empty state) as shown in Fig. 6. Zoom-in image inserted in Fig. 6a shows three coalesced Zn<sub>2</sub>-dimers in the adjacent halves, which may be the transit state to the triangular shape Zn<sub>3</sub>-clusters. It is known that the adsorption of such ordinary metals as Pb, Sn, Ag, Pd, Tl, and K preferentially takes place on the faulted half of the Si(111)-7 × 7 surface, but it is clear that the Zn<sub>3</sub>-dots almost equally occupy the faulted and unfaulted halves. As a result, the corner hole of the 7 × 7 structure is surrounded by six bright Zn<sub>3</sub>-dots as shown in Fig. 7a, so that the Si(111)-7 × 7 surface is finally covered with a honeycomb layer composed of Zn<sub>3</sub>-dots as shown in Fig. 7b. It should be pointed out that the 7 × 7 struc-

ture was recovered when the Zn<sub>3</sub>-dots were removed by evacuation at ca. 520 K. That is, the reconstructed 7 × 7 structure of the Si(111) surface is not lifted up by adsorption of Zn atoms. Taking account of the fact that Zn<sub>3</sub>-dots are predominant and very few single Zn atoms exist on the Si(111)-7 × 7 surface, we can deduce that the migration of adsorbed single Zn atoms are rapid on the surface so that they undergo stabilization by forming Zn<sub>3</sub> in the half unit cell. This is quite contrast to the behavior of an isolated single Sn atom on the Si(111)-7 × 7 surface, where the single Sn atoms are trapped in the isolated half unit cells.

As the intensity of the STM image is reflected by both the real corrugation and the local density of states, the STM image of the Zn adsorbed Si(111)-7 × 7 surface changes with bias potential. As Hamers et al. [11] showed, the tunneling conductance for the different Si-sites changes less sensitively with the potential when the bias potential is higher than 1.5 V. In contrast, when the bias potential is negative, the conductance changes differently at the different Si-sites. It was confirmed that the potential dependence of the STM image of the Zn-Si(111)-7 × 7 surface was similar to that reported for the Si(111)-7 × 7 surface. A zoom-in image of Fig. 6a shows that the



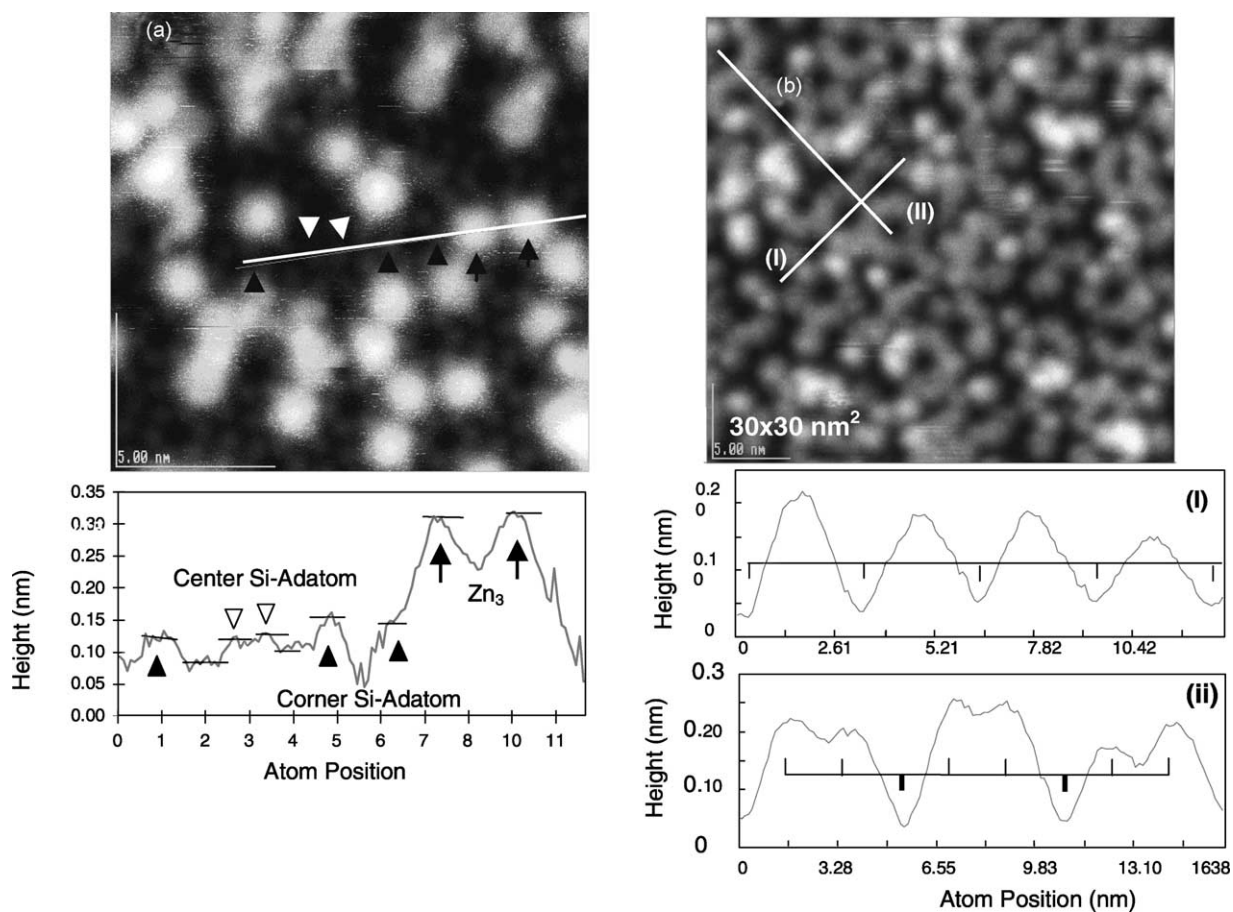


Fig. 7. Corrugation of Zn<sub>3</sub>-dot and a honeycomb monolayer formed on Si(111)-7 × 7. (a) STM image of an empty state of Si(111)-7 × 7 having Zn<sub>3</sub>-dots and the corrugation of it; V<sub>b</sub> = 3.0 V and I<sub>t</sub> = 0.05 nA. Honeycomb monolayer composed of Zn<sub>3</sub>-cluster.

Si-adatoms aside of the Zn<sub>3</sub>-dots in the neighboring half unit cells are necessarily dim at a negative bias potential of −2.2 V. In contrast, every Si-adatoms have almost equal intensity when the bias potential is 2.0 V as shown in Fig. 6b. Taking these facts into account, the heights of Si-adatoms and Zn<sub>3</sub>-dots were deduced at the bias potential of 3.0 V along the line

drawn in Fig. 7a. The evaluated values are summarized in Table 1, where the values are the height from the center Si-adatom of the unfaulted half unit cell (U).

It should be pointed out that the height of the Si-adatoms in Fig. 7a fits surprisingly well with that of the Si(111)-7 × 7 surface obtained by the AFM [12].

Table 1  
Corrugation (nm) of atoms along the line in Fig. 7a

Si-rest atom	Center Si-adatom	Corner Si-adatom	Bright (Zn) <sub>3</sub> -dot	Reference
−0.04 (U), −0.03 (F)	0.01 (F), 0 (U)	0.03 (F), 0.02 (U)	0.18–0.19	This work
–	0.019 (F), 0 (U)	0.034 (F), 0.015 (U)	–	[12]

F and U are the atoms on either faulted or unfaulted half, respectively.

The height of Zn<sub>3</sub>-dot in Fig. 7a is evaluated to be 0.18–0.19 nm from the center adatom (0.21–0.23 nm from the rest atom), which is undoubtedly smaller than the diameter of Zn atom (ca. 0.27 nm). If three Zn atoms of the Zn<sub>3</sub>-cluster locate on the top of the three center Si-adatoms, Zn–Zn distance should be close to the Si–Si-adatom distance of 0.76 nm, which is undoubtedly too long to make an ordinary Zn–Zn bond. Taking account of the fact that Zn<sub>3</sub>-cluster is stabilized on the Si(111)-7 × 7 surface, the Zn–Zn distance may be shortened by gathering the three Zn atoms to the center of the half unit cell. As a result, Zn<sub>3</sub>-dot is a little down from the center adatom level as depicted a model in Fig. 5b.

An interesting fact is that the depth of the honeycomb holes on the monolayer accomplished surface (Fig. 7b) is almost equal to the height of Zn<sub>3</sub>-dot from the corner Si-adatom level (0.16–0.17 nm) measured in Fig. 7a. This fact means that the honeycomb layer is accomplished by the array of Zn<sub>3</sub>-clusters one in each faulted and unfaulted halves.

Zn and Sn are indispensable co-catalyst for selective formation of (CH<sub>3</sub>)<sub>2</sub>SiCl<sub>2</sub> in the Rochow reaction, Si + 2CH<sub>3</sub>Cl → (CH<sub>3</sub>)<sub>2</sub>SiCl<sub>2</sub>. It is known that H<sub>2</sub>O, NH<sub>3</sub> and CH<sub>3</sub>OH undergo dissociation on a pair site of Si-adatom and Si-rest atom, where the dangling bond on the Si-adatom is almost empty while that on the Si-rest atom is almost filled. Taking these facts into account, a feasible dissociation of CH<sub>3</sub>Cl in the Rochow reaction might be accelerated on a specific pair site of Cu–Si by forming Cu–Cl and Si–CH<sub>3</sub>. If this speculation would be correct, Zn and Sn may change the electronic state of the Cu–Si pair sites on which the dissociation of CH<sub>3</sub>Cl and

the following reaction of Si–CH<sub>3</sub> with CH<sub>3</sub>Cl are promoted.

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