Magic nanoclusters of group III metals on Si(100) surface

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Using scanning tunneling microscopy observations, the ability of group III metals, In, Al, Ga and Tl, to form identical-size magic nanoclusters upon high-temperature adsorption on Si(100) has been examined. Magic clustering has been detected in In/Si(100) and Al/Si(100) systems. In both cases, atomic structure of the nanocluster is plausibly described by the model of Bunk et al. [Appl.Surf.Sci. 123/124, 104 (1998)], in which six metal atoms and seven Si atoms form a stable pyramid-like cluster. In the case of In/Si(100) system, the perfectly-ordered 4×3 superlattice built of magic nanoclusters can be formed. The Al/Si(100) nanoclusters has been found to form local arrays with a 4×5 periodicity. In Ga/Si(100) and Tl/Si(100) systems, no indication of magic clustering has been detected. The criteria for magic cluster formation are discussed.

Keywords: Scanning Tunneling Microscopy; Al; Ga; In; Tl; Si(100);

I. INTRODUCTION

Magic nanoclusters, i.e., the clusters with enhanced stability at selected sizes, have recently become a fascinating object of a modern physics research. The first direct observation of the magic cluster growth supported by a substrate has been reported by Lai and Wang [1] for Ga submonolayers deposited onto the \(\sqrt{3}\times\sqrt{3}\) reconstructed Ga/Si(111) surface. In that case, the spatial distribution of magic clusters has been found to be random. Very recently the possibility to form perfectly ordered arrays of identical-size magic clusters (which are essentially 2D artificial cluster crystals) has been demonstrated. The goal has been achieved with group-III metals, Al [2–4], In [4, 5] and Ga [4, 6], deposited onto a Si(111)7×7 surface. In these cases, the substrate acts as a template for the surface-mediated magic clustering. The forming clusters are built of exactly six metal atoms linked by three Si atoms and reside at the centers of both the faulted and unaffected halves of 7×7 unit cells. As a result, the cluster superlattice displays the same periodicity as a substrate, namely, 7×7. A similar, albeit not identical behavior has been observed for thallium (Tl), the heaviest element of the group III metals. Upon deposition onto a Si(111)7×7 surface, Tl has been found to form a superlattice of almost identical nanoclusters consisting of about nine adatoms each [7, 8]. The main results on magic clustering of group III metals on a Si(111)7×7 surface are summarized in a number of review papers [4, 9, 10].

It is remarkable, that the growth of group III metals on Si(100) surface presents also vivid examples of magic clustering. In the present paper, we review our recent results and reported data on the adsorption of group III metals, In, Al, Ga, Tl, on Si(100)2×1 surface with the emphasis on the magic cluster formation.

II. EXPERIMENTAL

Experiments were performed with Omicron STM operated in an ultrahigh vacuum (∼1×10⁻¹⁰ Torr). Atomically clean Si(100)2×1 surfaces with a minimal number of defects were prepared using the surface preparation procedure described in Ref. [11]. In, Ga and Tl was deposited from a Ta foil tubes, Al from a heated Al-covered W wire. The samples were heated by radiation from the tungsten heater located at the sample back or by passing DC current through them. For STM observations, electrochemically etched tungsten tips cleaned by in situ heating were employed. The STM images were acquired in a constant-current mode after cooling the sample to room temperature.

III. RESULTS AND DISCUSSION

A. Low-temperature growth

In the low-temperature range (from room temperature (RT) to about 350 °C), group III metals (Al, In and Ga) on Si(100) demonstrate a very similar behavior. Upon metal adsorption, Si substrate dimers are preserved, while metal adatoms form symmetric dimers which are located in the troughs between Si dimer rows and are oriented parallel to Si dimers. Metal dimers are arranged into the rows which are running perpendicular to Si dimer rows. Stacking of metal dimer rows results in the 3×2, 5×2 and 2×2 superstructures at local metal coverages of 0.33, 0.4 and 0.5 ML, respectively [12]. Thus, under these conditions (i.e., at reduced temperatures and adsorbate coverages below ~0.5 ML), no adsorbate clusters other than dimers are formed. Therefore, our prime interest concerns the growth at elevated temperatures of about 500–600 °C.

B. In/Si(100)

Formation of the submonolayer In/Si(100) interface at temperature of ~500°C furnishes the most vivid example...
FIG. 1: 500 × 500 Å² filled state (+1.8 V) STM images of the In/Si(100) interface formed upon adsorption of (a) 0.15 ML and (b) 0.5 ML of In at 500 °C. In magic clusters (seen as bright dots) are distributed almost randomly at low coverage but become aligned into the well-ordered 4×3 superlattice at saturating coverage.

FIG. 2: Atomic structure of the magic cluster formed by group III metals, In and Al, on Si(100) as proposed by Bunk et al [18]. The most of the recent experimental and theoretical studies support this structural model, in which six metal atoms (shown by shaded circles) and seven Si atoms (shown by large open circles) form a pyramid-like cluster occupying 4a × 3a area.

TABLE I: 40×40 Å² STM images of Al and In nanoclusters acquired at various bias voltages.

| Metal | Tip bias voltage |
|-------|-----------------|
|       | +2.0 V | −2.0 V | −1.0 V |
| In    | ![Image]     | ![Image] | ![Image] |
| Al    | ![Image]     | ![Image] | ![Image] |

Results on the formation of perfectly ordered nanocluster arrays pose interesting questions on the mechanisms involved in this process. First, one can see that in contrast to the case of metal clusters on the Si(111)7×7 surface, formation of the cluster superlattice at the In/Si(100) interface is not primarily based on the template effect of the substrate. The cluster superlattice has a periodicity different from that of the original substrate surface, i.e., 4×3 versus 2×1. Thus, the self-alignment of nanoclusters should involve a kind of inter-cluster interaction. The question is what the physical nature of this interaction is. Second, ordering of the nanoclusters, which are ini-
FIG. 3: (a) Original almost defect-free Si(100) substrate surface. (b) The same surface after deposition of 0.11 ML of Al followed by annealing to 500 °C. The scale of the images is 400 × 300 Å² and they have been acquired at $V_t = +1.2$ V and $V_t = +2$ V, respectively. When the high-temperature Al submonolayer growth is conducted at the Si(100) substrate with a low density of the missing-dimer defects, the most of Al atoms become incorporated into the Al-Si clusters. The Si islands are due to agglomeration of Si atoms released during Al-Si nanocluster formation.

Possibly, the cluster motion is a seeming effect, while in fact there is a continuous process, in which some cluster disintegrate and new ones appear when the sample is heated to a sufficient temperature. Our observations have shown that the magic cluster formation takes place up to In desorption temperature of ∼600 °C.

Atomic structure of the In/Si(100) cluster has been a subject of furious debates of the last years. Recently, two models of its atomic arrangement have been treated as the most plausible candidates. The first model was proposed by Zotov et al. [15] and was modified later by Saranin et al. [14]. The model was based mainly on the STM observations and took into account the preservation of the 4×1 reconstruction on the Si(100) substrate after removal of In atoms upon H exposure [16, 17]. The other model was proposed by Bunk et al. [18], predominantly based on X-ray diffraction (XRD) data. The results of the most subsequent experimental and theoretical studies using various techniques, including XRD [19], photoelectron diffraction [20], photoelectron holography [21], first
FIG. 4: (a) Original Si(100) substrate surface with the enhanced density of the missing-dimer defects. (b) The same surface after deposition of 0.10 ML of Al followed by annealing to 500 °C. The scale of the images is 400 × 300 Å² and they have been acquired at $V_t = +1.5$ V and $V_t = +1.9$ V, respectively. When the high-temperature Al submonolayer growth is conducted at the Si(100) substrate with a high density of the missing-dimer defects, the most of Al atoms become incorporated into the top Si layer (seen as dark regions), while formation of the Al-Si clusters is suppressed. The Si islands are due to agglomeration of Si atoms released at Si substitution for Al.

principles total energy calculations [22–24] and STM image simulations [23, 25], favour the model of Bunk et al. [18], in which six In atoms and seven Si atoms form a stable pyramid-like Si$_7$In$_6$ cluster (see Fig.2).

C. Al/Si(100)

Submonolayer Al/Si(100) system at temperatures of around 500 °C also demonstrates a tendency towards magic cluster formation. The bias-dependent STM appearance of the Al/Si(100) nanoclusters appears to be similar to that of In/Si(100) nanoclusters, as one can see in Table I. Both clusters show up as a single round protrusion in the filled state images, as a pair of oval protrusions in the empty state images at about −2 eV bias and as three oval protrusions in empty state images at about −1 eV bias. In the very recent theoretical studies using first principles total energy calculations [24, 26, 27] and STM image simulations [26], it has been suggested that the magic clusters formed by Al on Si(100) are identical to those formed by In, i.e. they also have the structure described by the Bunk’s model (see Fig.2).

However, the tendency for magic clustering in the case of Al/Si(100) system is not as unambiguous as in the case of In/Si(100) system. It has been found [28] that cluster formation is not a unique possible way for Al interaction with a heated Si(100)2×1 surface. In fact, there are
two competitive mechanisms. First mechanism prevails at Si(100) surface with a low density of missing-dimer defects and resides in the formation of the Al-Si clusters (see Fig. 3). The second mechanism is stimulated by the presence of missing-dimer defects and resides in substitutional incorporation of Al atoms in the top Si(100) substrate layer (see Fig. 4). Both mechanisms result in the liberation of the surface Si atoms which agglomerate into the flat islands.

Though each Al/Si(100) cluster occupies the 4a×3a area, just like the In/Si(100) cluster, they do not form the ordered 4×3 arrays. Instead, the alignment of Al/Si(100) nanoclusters results in the formation of arrays with a 4×5 periodicity (see Fig. 5). Taking into account Al coverage (∼0.5–0.6 ML) when 4×5-Al develops and its bias-dependent STM appearance, we have suggested the atomic arrangement of the 4×5-Al as shown in Fig. 6. As one can see, the structure is built of ordinary Al/Si(100)4×3 clusters interconnected through “reduced” 4×2 clusters, i.e., the 4×3 clusters in which the central atomic row is missing. In the filled states, the “reduced” cluster is seen dark, except for the case when its central dimer is a mixed Al-Si dimer. In the latter case, it shows up as a bright protrusion in between two neighbouring 4×3 clusters. Due to asymmetry of the mixed dimer, this protrusion is shifted from the central point towards one of the 4×3 clusters.

D. Ga/Si(100)

As at low temperatures Ga on Si(100) exhibits a behavior similar to that of In and Al, one could also expect the similarity in their behavior at higher temperatures. In other words, by analogy with the In/Si(100) and Al/Si(100) systems one could expect the magic clustering in the Ga/Si(100) submonolayer system. Moreover, the first principles total energy calculations [24] prove the stability of the Bunk’s cluster built of Ga atoms. However, observation of Ga/Si(100) magic clusters has not been reported so far.

To test this possibility, we have applied to the Ga/Si(100) system the growth procedures similar to those used for In/Si(100) and Al/Si(100) magic cluster formation, namely, RT deposition of 0.1–0.5 ML of Ga followed by annealing to ∼600 °C or direct Ga deposition onto the Si(100) heated to the same temperatures. In the experiments, no indication on the Ga/Si(100) magic cluster formation has been found. Instead, Ga atoms displace Si atoms and form array built of Ga dimers embedded in the top Si(100) substrate layer. This process is illustrated in Fig. 7. One can see in Fig. 7a that within the same terrace there are two types of features. The more bright features are known to correspond to Ga ad-dimers. The less bright features are plausibly Ga dimers embedded in the top Si(100) layer. Indeed, one can ensure that Ga dimers embedded in the upper terrace (low left half of Fig. 7a) have an STM appearance (i.e., apparent height and shape) identical to the Ga ad-dimers at the terrace which is one atomic layer lower (up right half of Fig. 7a). Figure 7b shows the Si islands which are developed due to Si liberation during formation of embedded Ga dimers. Atomic arrangement of the array of Ga dimers embedded in the top Si(100) substrate layer is illustrated in the sketch in Fig. 8. One can see that in agreement with the STM observations a single embedded Ga dimer occupies an area of 2a×3a. This holds also for Ga dimers forming a row aligned perpendicular to the top Si dimer rows. When embedded Ga dimers form a row along the top Si dimer rows, each Ga dimer occupies an area of 2a×2a. In the latter case, the stress introduced into the second Si layer is apparently less than for cases when substitutional Ga dimer occupies 2a×3a area. Hence, the most of embedded Ga dimer rows are aligned along the top Si dimer rows (see Fig. 7).

E. Tl/Si(100)

We have also tested Tl, the heaviest element of the group III metals, as a possible candidate for magic clustering on Si(100). The results of our STM observations
FIG. 7: (a) 500×470 Å² empty state (−2.1 V) STM image illustrating formation of Ga substitutional dimers upon annealing of ∼0.2 ML of Ga to 620 °C. Within one terrace, substitutional Ga dimers are seen as less bright compared to Ga ad-dimers. (b) 820×600 Å² empty state (−1.8 V) STM image showing Si islands developed due to agglomeration of Si atoms liberated at embedded Ga dimer formation.

[29] have shown that Tl on Si(100) exhibits behavior quite different from that of other group III metals. Upon adsorption in the temperature range from RT to about 250 °C Tl has been found to form arrays with a 2×3 and 2×2 periodicity (see Fig. 9). In contrast to the cases of Al, In and Ga, these surface structures are built not of dimers but of Tl adatoms occupying the valley-bridge sites on the intact Si(100)2×1 surface (see Fig. 10). Thallium atoms appear to be weakly bonded to the Si(100) substrate: they are highly mobile and desorb from the surface at temperatures above 270 °C. No indication on magic clustering in Tl/Si(100) system has been found.

IV. CONCLUSIVE REMARKS

We have tested group III metals adsorbed on Si(100) surface as candidates for the formation of identical-size magic clusters. The results of examination are summarized in Table II. It has been found that the tendency for magic clustering competes with the tendency for substitutional metal adsorption, i.e., displacement of Si atoms and formation of metal dimers embedded in the top Si(100) substrate layer. Dominance of each tendency is believed to be associated with the covalent radius of the adsorbate. For greater covalent radius, the magic clustering prevails, for lower radius the substitutional adsorption dominates. Indeed, among Al, In and Ga, the indium has
FIG. 8: Schematic model showing the array built of Ga dimers embedded in the top Si(100) substrate layer. Ga atoms are shown by dark gray circles, Si atoms of the dimerised top Si(100)2×1 layer by light gray circles, Si atoms of the deeper layers by white circles with sizes decreasing with depth.

The research on magic clusters on semiconductor surfaces is at a very early stage of development. The number of systems for which magic clustering have been identified experimentally is very limited. The main regularities of magic clustering of group III metals on Si(100) surface established in the present study are believed to be useful in a search for the new candidates. The shown possibility to grow magic clusters in In/Si(100) and Al/Si(100) systems, including ability to form a perfectly ordered magic cluster arrays, provides fascinating objects for further investigations to ensure fundamental understanding of the mechanisms involved in their self-assisted growth as well as to explore their quantum properties.

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FIG. 10: Schematic model of the Tl/Si(100) interface. Tl atoms occupy valley-bridge sites on the intact Si(100)2×1 surface and form atomic rows running perpendicular to the Si-dimer rows. Stacking of Tl atomic rows produces the regions with the 2×2 or 2×3 periodicity.

TABLE II: Ability of group III metals to form magic clusters on Si(100) as a function of metal covalent radius.

| Metal | Covalent radius, Å | Magic clusters | Substitutional dimers |
|-------|--------------------|----------------|----------------------|
| Ga    | 1.22               | NO             | YES                  |
| Al    | 1.43               | YES            | YES                  |
| In    | 1.63               | YES            | NO                   |
| Tl    | 1.70               | NO             | NO                   |
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