The atomistic growth of silver clusters on a Si(111)7×7 surface

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Abstract. We report here the growth of silver nanostructures on a Si(111)7×7 surface using scanning tunneling microscopy (STM). It is found that each Ag atom hops each half unit cells of 7×7 structure and forms dimers, trimers, tetramers and pentamers inside the half unit cells. We estimate intercell hopping rates of (1.39±0.16)×10⁻⁴ 1/s for trimers and (1.33±0.14)×10⁻³ 1/s for tetramers. We also observed the intracell motion of trimers.

1. Introduction

It is of importance to understand the processes of adsorption, diffusion and clustering to grow nanostructures. These processes are unique for every kind of substrate and the adsorbate. The case of metal on the reconstructed Si(111)7×7 surface is also characteristic. The Si(111)7×7 consist of relatively large half unit cells (HUCs), i.e., unfaul ted (UHUC) and faulted part (FHUC) [1]. Adsorbed single metal atoms like silver can diffuse on the surface. However the ability to diffuse is limited by the dimer rows, which constitute the boundaries of HUCs. At room temperature (RT) the single adatom demonstrates in STM images as the brighter HUC than empty HUC [2]. The single atom on the reconstructed surface can be described as a unique diffusing object, however trapped in HUC for some time rarely performing intercell jump. Sobotík et al. measured the thermal intercell Ag adatom hopping rates, namely the temperature dependence of hopping rates [3]. The low temperature STM experiment showed a single atom at a stable adsorption site in the HUC [4]. The intracell diffusion of a single atom inside HUC is thermally activated [5]. Moreover STM experiments revealed the formation of Ag adatom structures composed of more than a single atom on the HUCs [6]. Despite the fact that the knowledge on the diffusion of the single adatom on Si(111)7×7 increased still the knowledge on clustering process on this substrate is unsatisfactory. The analysis of the structure (cluster) formation is not trivial due to multitude of the participants (atoms) as well as complicated interactions on the surface. In our previous paper, we observed the intercell diffusion of single atoms and measured the hopping rate to UHUCs. We also measured the intercell movement of dimer in a HUC [7]. In this report, we present the measurements of the diffusion of silver atoms on
Si(111)\textsuperscript{7×7}, formation processes of structures like dimers, trimers, tetramers and pentamers. We also present the intracell motion of trimers in HUCs.

2. Experimental details
Experiments are performed in a UHV system, which consists of an analysis chamber and a sample preparation chamber. The analysis chamber is equipped with a STM (VT-STM, Omicron) and an electron beam evaporator (EFM3, Omicron). The evaporator is set at an oblique incidence position so that we can obtain STM images short after the deposition. The base pressure of the analysis chamber is lower than 1.4×10\textsuperscript{-8} Pa and lower than 2.0×10\textsuperscript{-8} Pa during deposition. Commercial n-type Si(111) wafers (phosphorus-doped, \textasciitilde3 \textmu m) are used as the sample substrate. Clean Si(111)\textsuperscript{7×7} surfaces are prepared by heating the sample substrate up to 1,490 K (20 times for 10 s) while passing through the current directly in the sample preparation chamber. We carefully cool down the sample substrate from 1200 K to room temperature at a rate of 0.5 K/s and obtain well-ordered surface. Ag atoms are deposited at a rate of the 0.0005 monolayer (ML) per second. 1 ML is defined as the density of Si atoms on a Si(111) surface, i.e., 7.8×10\textsuperscript{14} atoms/cm\textsuperscript{2}. The deposition rate is calibrated by counting the number of Ag atoms by STM. We get tunneling contact about 5 minutes after finishing the deposition. The coverage varies from 0.011 ML to 0.088 ML. We obtain STM images in a constant current mode, and the STM drift correction mode enables us to obtain images of the same area. Each frame is obtained in 2 min. The sets of collected images are used to make pseudo movies. The STM is operated at a bias of \textasciitilde2.0 V. A current of 100 pA is used to minimize STM tip effects. W tips are prepared by electrochemical etching. All the measurements are carried out at room temperature.

3. Results and Discussion
Figure 1A shows image of clean Si(111)\textsuperscript{7×7} and figure 1B represents the image of the surface obtained after the deposition of 0.016 ML. Figures 1A and B are observed at the bias voltage of -2.0 V. Both images present area of 33×33 nm\textsuperscript{2}. In figure 1B, we observe the silver structures as bright protrusions in HUCs. All the structures are confined within HUCs. The higher the coverage, there is more Ag structures which consist of more Ag atoms in HUCs. By looking at the STM image, it is possible to determine the number of silver atoms in HUC like single atoms, 2 atoms and 3 atoms.

To obtain better statistics, we observe the images with the size of 70×80 nm\textsuperscript{2} where 1,437 HUCs are traced. After 5 min., a single Ag atom exists in 190 UHUCs and 255 in FHUCs. Two Ag atoms are observed in 31 UHUCs and 50 in FHUCs. More than 3 Ag atoms are imaged in 29 UHUCs and 28 in FHUCs. The Ag atoms diffuse with the time and form clusters. Once clusters are formed, they are not dissolved into small clusters or Ag atoms.

The direct impingement of a single Ag atom or intercell hopping of monomer to the occupied HUC by a single silver adatom leads to the two Ag atom occupation of HUC. Two single Ag atoms are trapped inside HUC. We call the double occupation of HUC the dimer. The dimers in FHUC and in UHUC are shown in figures 2B and D, respectively. Figures 2(A, B) and (C, D) are two sets of

![Figure 1](image_url)
sequential measurements: the image B and D are observed 2 min. after taking images A and C, respectively. There are two monomers in adjacent HUC at the images A and C outlined by parallelogram. The intercell jump leads to formation of the dimers in both cases and it occurs within 2 min. The presence of the monomer structure in adjacent HUC does not change the images of monomer as shown in figure 2.

A HUC holds 3 silver atoms. The triple occupation (3 Ag atoms) of HUC we call the trimer. The trimers in FHUC and UHUC are formed by intercell jump. We observe intercell jump of a single Ag atom to the dimer in adjacent HUC. Figures 3(A, B) and (C, D) are two sets of sequential observation images after 2 min as shown in figure 2. The structures outlined by parallelograms in figures 3B and D are trimers in FHUC and in UHUC respectively. The observation of trimers reveals the movement of Ag atoms inside HUC. By the movement, the bright protrusions seen at STM images and representing trimers change the position inside HUC. The intracell movement of the trimer in FHUC is shown in figure 4. We can clearly observe the change of conformation of the 3 atom silver entity inside FHUC on the 3 presented images.

In the experiment, we observe 45 configurations with monomers adjacent to a dimmer in UHUC as shown in figure 3C. With the time, monomer jumps to the dimer and form a trimer. We count the number of the configuration for 2 hours and 30 min. By the analysis of number of the configuration with the time, we estimate hopping rate as equal to \((1.39\pm0.16)\times10^{-4}\) 1/s using the method of least squares.
Figure 5. The tetramer formation in UHUC. At the image (A) we can see the dimer in UHUC with monomers in 2 adjacent HUCs. After 2 min. the monomer jumps to the dimer and form a trimer as shown at image (B). After 25 min. next monomer jump to the trimer and forms tetramer as shown at image (C).

Four Ag atoms in HUC represent a tetramer. The tetramers can be formed in the process of intercell hopping of monomer to the HUC occupied by the trimer. Figure 5 presents 3 images describing tetramer formation in UHUC. In figure 5A, we show the dimer in UHUC with monomers in 3 adjacent HUCs outlined by trapezoid. After 2 min, the monomer jumps to the dimer and forms a trimer as shown in figure 5B. After 25 min, next monomer jump to the trimer and forms tetramer as shown in figure 5C. When the trimer is present in adjacent HUC, the jump of monomer to the trimer is relatively fast and with 100% probability for trimer in HUC. We observed 15 configurations and obtained the estimated hopping rate of $(1.33\pm0.14)\times10^{-3}$ 1/s. The formation of tetramer in FHUC has also been measured for 15 configurations. The hopping rate of monomer to the trimer in FHUC is faster and within 1 or 2 frames which corresponds to the rate of $(1.88\pm0.14)\times10^{-3}$ 1/s.

Figure 6. STM Images of pentamer formation in UHUC. A: tetramer in UHUC and monomer in adjacent FHUC. B: the same tetramer with monomer after 2.5 h. C: tetramer in UHUC and monomer in adjacent FHUC. D: image taken 2 minutes after C and presents the pentamer in UHUC.

Figure 7. The STM images of the formation of the pentamer in FHUC. A: the dimer in FHUC is surrounded by 3 monomers outlined by triangle. B: after two minutes all monomers jump to dimer and form the pentamer in FHUC.
The observation of the tetramer in UHUC (4 Ag atoms in HUC) reveals the fact that the hopping rate of the jump of monomer to the tetramer is anisotropic. Firstly, it is important to notice that tetramer in UHUC looks always similar, the bright non-moving oval protrusion closer to the one corner holes of HUC (see figure 6A). From this observation we can distinguish each adjacent HUC to the UHUC with tetramer and in this way distinguish 3 different directions. The adjacent HUC and corresponding directions are labeled with arrows and numbers 1, 2, and 3 as shown in figure 6B. We observe the jump of monomer to tetramer from 2 and 3 directions, but in the case of direction 1 we never observe a jump even if the time of observation is as long as 2.5 h. In figure 6D, we measure the pentamer after the jump of the monomer to the tetramer.

The formation of the pentamer in FHUC has also been measured. Figure 7 shows the formation of the pentamer in FHUC. The dimer in FHUC is surrounded by 3 monomers (outlined by triangle) shown in figure 7A. Two minutes later all monomers jump to a dimer and form the pentamer in FHUC as shown in figure 7B.

4. Conclusion
Imaging of the surface by STM allows getting information about dynamic processes such as surface diffusion. Diffusion on the surface at room temperature is usually relatively fast process, hardly measurable by the STM. However in particular circumstances (certain surfaces) STM is capable of measuring diffusion parameters even if imaging is relatively slow, working in the frame by frame mode. Such an example is the intercell diffusion of metal atoms on the Si(111)7×7. The diffusing Ag atoms cluster when they meet other adsorbed structures. There is close relation of the diffusion to the clustering. The diffusion can be influenced by other adsorbed silver atoms. The formation of the structures on Si(111)7×7 surface in HUC during the intercell diffusion and clustering is the step process resulting in the increase of the number of atoms of the structure. In this way it is possible to observe structures in HUCs consisting of particular number of atoms and determine dynamic parameters for the hopping to particular size of the cluster.

References
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