The tip role on STM images of Ag/Si(111) $\sqrt{3} \times \sqrt{3}$

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Abstract. By employing scanning tunnelling microscopy (STM), the surface atomic structure of Ag/Si(111) $\sqrt{3} \times \sqrt{3}$ has been studied in detail. Both honeycomb-chain-trimer (HCT) and inequivalent-triangle (IET) structures have been observed at room temperature. Si trimers, which were invisible in earlier STM studies, form a bright hexagonal pattern surrounded by a honeycomb chain from the Ag trimers. We found that the obtained images to a large extent depended on the STM tip state. Our finding indicates the important role of the tip state in the tunnelling process and consequently the interpretation of STM images.

1. Introduction
Scanning tunnelling microscopy is a spectacular method to study surface structures with atomic resolution. Quickly after its invention [1], one realizes that the interpretation of STM images can be extremely challenging. This is because STM images surface electronic states, which indirectly relate to individual surface atoms. Another fundamental problem in the STM measurement is that it only senses the tails of wave functions at the surface that protrude just a few of Å into the vacuum. Surface electronic states that are localized between the first and second layer or very fast decay into the vacuum are invisible by STM. However, this problem can be partially overcome if a tunnelling probability is greatly enhanced by selecting a proper wave function from the STM tip. In this study, we show that the Si trimers of the Ag/Si(111) $\sqrt{3} \times \sqrt{3}$ surface, which were "missing" in earlier STM studies [2, 3, 4, 5], can be directly observed under such a tip condition.

Ag/Si(111) $\sqrt{3} \times \sqrt{3}$ is one of the prototypical surfaces that has been studied by STM during the last decades [2, 3, 4, 5]. Both filled-state and empty-state images showed a honeycomb pattern that has been described by the HCT model in the literature [6, 7]. Theoretical simulations indicated that the bright protrusion of the honeycomb pattern represents the center of Ag trimers rather than individual Ag atoms [6, 7]. Si trimers, on the other hand, were entirely mysterious since they appear as black holes in the centers of the honeycomb pattern. The calculated band structure of Ag/Si(111) $\sqrt{3} \times \sqrt{3}$ from the HCT model could explain the surface electronic structures from an angle-resolved photoemission measurement [7, 8]. Thus the HCT model seems to be well-established and widely accepted until recently. An inequivalent triangle (IET) model has been proposed for the ground state of the Ag/Si(111) $\sqrt{3} \times \sqrt{3}$ surface [9]. The new model was based on an STM observation, i.e. the Ag/Si(111) $\sqrt{3} \times \sqrt{3}$ surface shows a hexagonal pattern at low temperature (LT), which is in contrast to the honeycomb pattern observed at room temperature (RT) [5]. An asymmetric appearance of protrusions in the STM images has been interpreted as an atomic structure change resulting from two types of Ag trimers. A transition from a surface described by the symmetric HCT model at RT to
an asymmetric IET model was proposed to occur at LT. The transition temperature is believed below 150 K based on photoemission and x-ray diffraction measurements [10, 11]. This result is, however, in contrast with earlier photoemission studies, showing that the valence band spectra are essentially the same down to 70 K [12, 13]. It is important to point out another interesting finding, i.e. the presence of additional Ag atoms on the Ag/Si(111)$\sqrt{3} \times \sqrt{3}$ surface. At RT they form a two-dimensional gas phase, which is insensitive to many surface techniques such as low energy electron diffraction (LEED). The extra Ag atoms are condensed at temperature below 62 K [14]. Once they are removed, the Ag/Si(111)$\sqrt{3} \times \sqrt{3}$ surface reveals its intrinsic electronic structure with well-resolved, extremely sharp Si 2p core-level spectra [13].

In this paper we present data from the Ag/Si(111)$\sqrt{3} \times \sqrt{3}$ surface obtained by scanning tunnelling microscopy. Contrary to the earlier studies, high resolution STM images show an inequivalent triangle structure of Ag trimers at room temperature. The inequivalent appearance of the honeycomb protrusions fits well with the recently reported IET model for this surface. We found that the obtained STM images to a large extent depended on what kind of atoms adsorbed on the apex of the STM tip.

2. Experimental procedure
The STM study was performed in a newly installed VT STM system from Omicron NanoTechnology GmbH at Karlstad University, Sweden. The STM tips made from a W wire were manufactured at Omicron. The Si(111) samples cut from a single crystal wafer (Sb doped, 0.01 Ωcm) were pre-oxidized by an etching method and cleaned in-situ by stepwise direct current heating up to 930 °C. This procedure resulted in a well-ordered surface, as evidenced by a sharp 7×7 LEED pattern. Ag was evaporated onto the Si sample from a tungsten filament source calibrated by a quartz crystal monitor. Evaporation of 1 monolayer (ML) of Ag followed by annealing at 530 °C for 2 min resulted in a sharp $\sqrt{3} \times \sqrt{3}$ LEED pattern. The sample was then annealed at ∼600 °C for 1 min to remove extra Ag. The STM images were recorded in a constant current mode at RT and 100 K. All the voltages given in this paper were sample biased.

3. Results and discussions
Fig. 1a shows a filled-state STM image recorded with a bias of 0.3 V and a tunnelling current of 1.0 nA from the Ag/Si(111)$\sqrt{3} \times \sqrt{3}$ surface at RT. The basic structure in this image is six bright protrusions that form a honeycomb pattern. In the HCT model shown in Fig. 1b, one Si trimer is surrounded by six Ag trimers that conjugate each other. Six Ag trimers correspond to six protrusions of the honeycomb hexagons in Fig. 1a. Si trimers that appear as black holes are located at the centers of the honeycomb hexagons. The observation of the honeycomb pattern is consistent with earlier STM studies of the Ag/Si(111)$\sqrt{3} \times \sqrt{3}$ surface [2, 3, 4]. Fig. 1c was obtained with the same bias and tunnelling current as Fig. 1a at the same area, but their appearances are quite different. The protrusions become inequivalent in Fig. 1c: one is the bright and the other is a slightly darker. The bright protrusions form a hexagonal pattern that gives rise to a characteristic image of the IET structure, as reported in a LT STM study [5]. As illustrated in Fig. 1d, the IET model differs from HCT by a slight rotation and displacement of the topmost Ag atoms. The result is that the small Ag trimer becomes brighter while the large Ag trimer becomes slightly darker in STM images. Obviously, Fig. 1c fits well with the IET model instead of the HCT model. An interesting question is why the surface structure looks different if the STM parameters are the same.

Fig. 2a shows a filled-state STM image that was disturbed by a typical tip reconstruction. In such case, the tip first adsorbed surface atoms and moved away from the surface. This resulted in a bright belt of honeycomb protrusions. Then the tip apex was modified and formed a stable tip state. A change from a honeycomb pattern at the bottom to an IET pattern at the
Figure 1. (a) STM image of the Ag/Si(111)√3 × √3 surface recorded at room temperature, $V_s=-0.3$ V and $I=1.0$ nA, 84×84 A. (b) HCT model. (c) STM image obtained at the same area as image (a), $V_s=-0.3$ V and $I=1.0$ nA, 65×65 A. (d) IET model.

Figure 2. (a) STM image at room temperature, $V_s=-0.3$ V and $I=0.5$ nA, 200×200 A. The surface is disturbed by a tip reconstruction. (b) STM image recorded after image (a) with the same conditions. The upper part of the image is a result of the tip reconstruction. Fig. 2b was recorded just after Fig. 2a was finished. A global IET structure is widely observed over the whole surface. The observation of the IET structure at RT is in sharp contrast to the HCT/IET phase transition reported in literature [5, 9, 10, 11]. The surface defects may play a certain role as exemplified by a famous LT phase transition on the Sn/Ge(111)√3 × √3 surface [15]. One thus may suspect that the surface defects could locally pin the IET phase so that it appears above the transition temperature. Several surface defects are very evident in Fig. 2b. However, since these defects just locally cause a small modification of the surface structure, they can not be the main reason that gives a global appearance of the IET structure. To conclude this part, it is quite clear that the Ag/Si(111)√3 × √3 surface shows the IET structure at room temperature.

In Figs. 1a and 1c, the surface must be the same, while the difference we observed in the
surface structure reflects a change of the tip state. From a previous study of the origin of STM resolution, single atoms on the tip apex are required to obtain a lateral atomic resolution [16]. Another factor that may affect STM measurements is a tip-surface interaction. Such a probe effect previously has been reported on the Si(100) surface [17, 18]. We found that the obtained images to a large extent depended on what kind of atoms on the apex of the STM tip. In the tip-sample interface, there are mainly three possible atoms on the W tip that was used in this study, i.e. W, Ag, or Si. In principle, the Ag/Si(111)$\sqrt{3} \times \sqrt{3}$ surface may present three different patterns seen by three kinds of tip states. Indeed, in addition to the HCT and IET structures, by some modification of the tip we found a third pattern of the Ag/Si(111)$\sqrt{3} \times \sqrt{3}$ surface.

Fig. 3 was obtained from the Ag/Si(111)$\sqrt{3} \times \sqrt{3}$ surface at 100 K using a sample bias of -0.3 V and a tunnelling current of 0.1 nA. Unlike the widely observed honeycomb or inequivalent honeycomb structure, the surface displays another complicated pattern in Fig. 3, i.e. large bright spots that form a hexagonal pattern are surrounded by six small dots that form a honeycomb pattern. Comparing to the atomic model in Figs. 1b and 1d, the large bright protrusions in Fig. 3 must be the missing Si trimers from earlier STM studies of the Ag/Si(111)$\sqrt{3} \times \sqrt{3}$ surface [2, 3, 4, 5]. First, these protrusions form a hexagonal pattern in a way that the Si trimers should do. Secondly, they are precisely positioned in the centers of the honeycomb hexagons. If the honeycombs are the Ag trimers, the large spots must be the Si trimers, and vice versa. Since the assignment to the honeycomb protrusions from earlier STM and theoretical studies strongly points to the Ag trimers, the large bright spots find a reasonable explanation in terms of the Si trimers.

The new pattern of Ag/Si(111)$\sqrt{3} \times \sqrt{3}$ was observed after a tip reconstruction in a similar way as Fig. 2a. In the surface atomic models in Figs. 1b and 1d, Si atoms of the Ag/Si(111)$\sqrt{3} \times \sqrt{3}$ reconstruction are sitting slightly below the topmost Ag plane. Unlike Ag trimers that conjugate each other, the Si atoms form a real isolated trimer in both the HCT and IET models. Since the Si trimers are located between the first and second layer, this could partly explain why they couldn’t be detected in the earlier STM studies. Initially each Si has three dangling bond electrons. Two of them bond to the neighboring Si atoms. The remaining one forms a big $\pi$
bond, which may interact with the surrounding Ag atoms. The $\pi$ state with a $p_z$ character could have a good chance to "stick" its wave function out of the topmost Ag plane. Clearly, a special tip state must be also required so that it could "see" this big Si $\pi$ bond. As mentioned above, there are three possible atoms on the W tip. A single Si atom with a $p_z$ state on the apex of the tip would have a good chance since it gives the largest tunnelling probability by overlapping two similar wave functions. On the other hand, a single Ag atom on the tip can easily interact with Ag trimers as evidenced by the LT condensation of additional Ag atoms into the Ag trimer sites of the underlying $\sqrt{3} \times \sqrt{3}$ surface [14]. Thus a single Ag atom may be more sensitive to the Ag trimers and gives rise an IET appearance of the $\sqrt{3} \times \sqrt{3}$ reconstruction. W that has a $d_z$ ($85\%$) state on the tip apex has no special interaction with the topmost Ag trimers. As a consequence of less sensitivity, the surface seen by a single W atom may just appear as a honeycomb pattern shown by previous STM studies.

4. Summary
In conclusion, the surface atomic structure of the Ag/Si(111)$\sqrt{3} \times \sqrt{3}$ surface has been investigated by STM. In contrast to recent studies, our STM images clearly show an inequivalent triangle structure of the Ag trimers at room temperature. This information is important since an IET structure is supposed to be a LT phase in the argument of the surface phase transition. We found that the obtained images to a large extent depended on what kind of atoms on the apex of the STM tip. Si trimers, which were invisible in earlier STM studies, form a bright hexagonal pattern surrounded by a honeycomb chain from the Ag trimers. Our finding indicates the important role of the tip state in the tunnelling process and consequently the interpretation of STM images.

Acknowledgments
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