Ag-induced zero- and one-dimensional nanostructures on vicinal Si(111)

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The formation of a Ag-stabilized regular step lattice on vicinal Si(111) miscut towards $[11\bar{2}]$ is reported. The step bunching characteristic of the clean surface is prevented by single-domain Si(111)-(3×1)-Ag reconstruction. The nanostructured surface is used as a template for growing one-dimensional arrays of 1 nm sized Ag quantum dots with a preferential spacing of 1.5 nm along the rows. © 2002 American Institute of Physics. [DOI: 10.1063/1.1509857]

Self-organization on crystal surfaces is a promising alternative for growing uniform nanostructures and templates of regular size and spacing.¹ In particular vicinal surfaces appear as natural substrates for the self-assembly of linear structures. Arrays of quantum wires and dots can be obtained by step decoration and step-flow growth.^{2,3} Also, one-dimensional templates can be tailored at vicinal surfaces by inducing periodic faceting with adsorbates^{4,5} or simply by stabilizing single domains of atomic row structures at terraces.^{2,6}

Here we investigate how surface reconstruction and morphology of Si(111) vicinals miscut towards $[11\bar{2}]$ are affected by Ag adsorption with special emphasis on the nanostructure and device fabrication. We find that (3×1)-Ag reconstruction prevents the equilibrium step bunching characteristic of the clean surface at 870 K. The system displays a regular array of monatomic steps with terraces that contain three equidistant Ag atomic chains. Further deposition of Ag at room temperature (RT) results in linear arrays of quantum dots that nucleate in trenches between the Ag rows.

The experiments were performed in an ultrahigh vacuum (UHV) system (base pressure below 5×10^{-11} mbar) equipped with a commercial Omicron scanning tunneling microscope (STM) and low-energy electron diffraction (LEED). Samples were cut from *n*-type Si(111) wafers (0.05–0.1 Ω cm) with 4° and 6.1° miscuts towards $[11\bar{2}]$. The clean surface was prepared by direct current heating with the current flowing parallel to the step direction to prevent electromigration effects on the step distribution.^{7,8} The surface temperature was monitored by an infrared pyrometer with the emissivity set to 0.4. The wafers were initially outgassed at 970 K for 1 h, followed by repeated flashing to 1500 K for a few seconds to remove the oxide layer and SiC. To produce ordered arrays of step bunches, we followed a procedure similar to the one given by Lin *et al.*:⁹ flashing to 1500 K (10 s), followed by fast (10 s) cooling to 1140 K (slightly above the (1×1)–(7×7) transition for Si(111) vicinal towards $[11\bar{2}]$)¹⁰ and slow cooling (≤ 1 K/s) to 920 K, where the sample was held for a further postanneal of 30 min to allow step bunches to order. The pressure during the

whole procedure never exceeded 3×10^{-10} mbar. Ag was evaporated from an e-beam source with the deposition being monitored by a fluxmeter calibrated against a crystal balance. Typical evaporation rates were 0.3 monolayer (ML)/min. The pressure during evaporation was in the 10^{-11} mbar range.

Vicinal Si(111) surfaces miscut towards $[11\bar{2}]$ undergo spontaneous step bunching.^{10,11} Figure 1(a) shows a large scale image of the clean surface with an array of bunched steps. The total periodicity of stepped bunches and flat (111) terraces reaches a self-limited size of approximately 70 ± 10 nm, in agreement with previous reports.^{9,12,13}

Deposition of submonolayer coverages of Ag and subsequent annealing to 850–900 K leads to partial erosion of the ordered step arrays, triggered by the formation of (3×1) domains. The (3×1) structure is oriented almost exclusively along the direction of the step, contrary to Ag induced struc-

FIG. 1. (a) STM image of the clean surface. The image is differentiated to enhance the step bunches. The step-down direction is from the lower left to the upper right; the size is 600 nm. (b) (Partially) debunched surface after Ag adsorption and redesorption. Differentiation and step-down direction like in (a), but the size is 350 nm. (c) Regular step array after (3×1) formation. Each line corresponds to a single step edge [cf. Fig. 2(b)]. Occasional multiple steps separate regular stepped regions. The step-down direction is along $[11\bar{2}]$; the size is 200 nm. (d) LEED pattern of the (3×1)-reconstructed surface at 26 eV. Faint residues of other rotational (3×1) domains are indicated in the box. The weak vertical stripes (shown by the arrow) are due to the buckling of step edge atoms [cf. Fig. 2(b)].

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tures on flat Si(111), where all three domains of (3×1) are observed, usually in addition to coexisting $(\sqrt{3}\times\sqrt{3})$ and (7×7) phases.^{14–16}

To optimize the long-range order and to maximize the (3×1) coverage in one domain, we investigated the elementary preparation steps more closely. Figure 1(b) shows the same surface as in Fig. 1(a) after subsequent deposition of 1 ML Ag followed by annealing to 870 K for 30 min. The Ag has desorbed and the surface has transformed into (7×7) reconstructed terraces of varying width, separated by monatomic steps which have partially coalesced into poorly defined bunches. We conclude that Ag promotes debunching of the surface upon annealing, since no debunching is observed directly after Ag deposition at RT. Since annealing above the Ag desorption temperature of 820 K (Ref. 14) is needed for sufficient step mobility, the surface morphology is kinetically determined by the competing factors of Ag promoted debunching and (re-)bunching of the clean terraces after Ag desorption. Thus, in this case good long-range ordering cannot be achieved by mere Ag deposition and annealing.

To facilitate better ordering, Ag was deposited on the clean surface after rapid (≈ 100 K/s) quenching to RT from above the (1×1) – (7×7) transition temperature, thereby minimizing the number and size of preexisting step bunches. STM images of the quenched surface prior to Ag deposition (not shown) reveal a surface morphology similar to the one in Fig. 1(b).

After deposition of approximately 0.3 ML Ag and subsequent annealing to 870 K for 10 s, (3×1) reconstruction is formed. Cycling this desorption/annealing sequence a few times further improves long-range order, overcoming the limitations of mass transport at this temperature. Alternatively, Ag can also be deposited at 870 K, but special care has to be taken in balance the deposition and desorption rates. Figure 1(c) demonstrates the surface quality achieved by this preparation. On the mesoscopic (μm^2) scale the main part ($>90\%$) of the surface is covered by only one (3×1) domain. Only occasionally are other rotational domains found extending over only small areas. Due to the size of the electron beam in our LEED setup (2 mm), faint residues of such rotational domains are usually found in LEED images, as seen in Fig. 1(d). Additionally, near the cathode and anode edges of the sample, we find residual $(\sqrt{3}\times\sqrt{3})$ or (7×7) domains, respectively. We attribute this to electromigration of Ag towards the cathode,¹⁷ since the observed distribution depends on the direction of the current. Heating by electron bombardment should eliminate this migration effect.

The (3×1) spots in the LEED image [Fig. 1(d)] are split due to superlattice diffraction.¹⁸ From the splitting an average step separation of 4.2 ± 0.3 nm is derived,¹⁹ compatible with the dominant terrace width of approximately 3.8 nm observed by STM in Fig. 1(c). Incorporation of wider or narrower terraces, varying in width by multiples of the (3×1) unit cell size, accounts for the misfit of the local slope (4.7° for 3.8 nm terraces separated by single bilayer steps) to the macroscopic miscut. This leads to residual imperfections of the step lattice over large (μm^2) areas, which could eventually be overcome by matching the macroscopic miscut to preferred terrace sizes.

Another weak feature in the LEED image of Fig. 1(d) is

FIG. 2. High-resolution STM images of a few (3×1) reconstructed terraces. Each terrace is shown in a full gray scale for clarity. The step-down direction is from the upper right to the lower left. Three dots in each image indicate the position of Si-related maxima in calculated STM images (Ref. 22). (a) Empty state image ($U_{\text{tip}} = -1$ V, $I = 50$ pA, size = 7.7 nm). A indicates Si adatoms. The bright rows on the terrace correspond to the Ag atom sites. (b) Filled state image ($U_{\text{tip}} = 1.5$ V, $I = 100$ pA, size = 5 nm). The bright step edge row is probably due to Si states. It exhibits slight buckling of 0.05 Å (see the inset, where a single row with better contrast is shown).

faint streaks at the $\times 2$ position along the $[1\bar{1}2]$ azimuth, i.e., parallel to the step edge direction. These can be explained by high-resolution STM images: Figure 2 displays a close-up view of a few (3×1) reconstructed terraces for both filled and empty states. In the empty states image [Fig. 2(a)] ball-like features (marked A) are located at step edges in the step down direction. These are probably due to Si adatoms with two nearest neighbor spacing along the step edge direction ($[\bar{1}10]$). The $\times 2$ spacing is likely the cause of buckling of step edge atoms with the same periodicity, which show up as prominent bright rows in filled state images [Fig. 2(b)]. In the inset a single step edge row with higher contrast is seen. The difference in apparent height of alternating bright and shallow atoms along the row is 0.05 Å. We propose that the bright step edge rows and the adatom features both correspond to Si atoms rather than to Ag, since upon (3×1) formation excess Si atoms from the (7×7) phase have to be incorporated at steps.²¹ The strong bias dependence of the adatoms and the nucleation of Ag on the step edge rows (see below) further support this assignment.

The triangles in both filled and empty states images correspond to maxima due to Si surface states in calculated STM images of the metal induced (3×1) reconstruction in the honeycomb chain-channel (HCC) model proposed by Erwin and Weitering.²² The additional bright row seen in empty states images [Fig. 2(a)] corresponds to the metal atom position and is due to a superposition of states from Si and metal atoms. We note that Erwin and Weitering found distortion of the Si honeycombs for the case of Ag, leading to (6×1) symmetry in agreement with previous^{14,16,21,23} work. In STM images, the nearly equilateral triangle of filled state maxima [cf. the dots in Fig. 2(b)] was found to be distorted by pairing of maxima in neighboring rows. The direction of this pairing alternates in neighboring (3×1) unit cells, leading to the (6×1) periodicity. For the stepped surface, we observe the same distortion occasionally on wider terraces. On an average terrace of approximately 3.8 nm width, we do not observe (6×1) formation. The small terrace size could facilitate strain relief by relaxation near steps, thus eliminating the driving force for (6×1) formation.²²

After fabrication and characterization of the stepped Ag/Si(111)- (3×1) surface, we can use this array as a template

FIG. 3. (a) Array of Ag nanodots grown on a (3×1) -stabilized step lattice [cf. Fig. 1(c)] after RT deposition of approximately 0.5 ML of Ag. The arrows mark terraces narrower than 3.8 nm where no dots nucleate. The distribution of the dot spacings is shown in (b). Pronounced peaks indicate preferred separations along $[110]$, with a clear maximum at $4a_0$ ($a_0=0.384$ nm). A section of four dots, seen in the inset, displays uniform shape of approximately 1 nm in diameter and 0.2 nm in height.

for further Ag growth. As shown recently for flat Si(111), one-dimensional arrays of Ag nanodots nucleate at RT on (3×1) -Ag reconstructed areas with a preferential spacing of $3a_0-5a_0$, when $a_0=0.384$ nm is the lattice spacing along $\langle 110 \rangle$.²⁴ We find very similar behavior on stepped templates (Fig. 3), with uniform Ag nanodots of 1 nm diameter and 0.2 nm height nucleating in the trenches between the Ag rows in the (3×1) structure. The nearest neighbor distance is preferentially $4a_0$, with multiples up to $7a_0$ being observed. The existence of clear peaks in the distribution [Fig. 3(b)] suggests nucleation at well defined lattice sites. Strictly one-dimensional lines of dots are found on 3.8 nm wide terraces, whereas narrower terraces prevent nucleation [shown by arrows in Fig. 3(a)]. On wider terraces (not shown), a second line of Ag dots grows parallel to the first. The structural characteristics can thus be fine tuned by controlling the terrace size, i.e., by different macroscopic miscuts.

In addition to nanodot nucleation on the terraces, we observe nucleation on the bright step edge row of the (3×1) structure [cf. Fig. 2(b)]. The nucleated rows again are strictly one dimensional, but the dots display a less regular shape and are less well ordered along $[110]$. The Ag nucleation at this sites provides further evidence that the step edge rows consist of Si atoms or dangling bonds rather than of Ag-related features, since on the terraces Ag atoms preferentially adsorb on Si-related sites.

In summary, we have shown that Ag adsorption on vicinal Si(111) can be used for fabrication of ordered nanoscale arrays. Ag induced (3×1) reconstruction stabilizes a well ordered step array on vicinal Si(111) miscut towards $[11\bar{2}]$, preventing the equilibrium step bunching characteristic of the clean surface.¹⁰ The main terrace width changes by multiples of the (3×1) unit cell size, 3.8 nm being the preferred

width for 6° miscut samples. By matching the macroscopic miscut to the (3×1) cell size, sample homogeneity on the μm scale can be further improved. The filled and empty state STM images of the detailed terrace structure are in accord with the previously proposed HCC model.²² Using the (3×1) reconstructed step array as a template, one-dimensional chains of Ag nanodots can be grown that display a preferential nearest neighbor separation of four lattice constants along $[11\bar{0}]$. The interaction mechanism responsible for this distance selection remains to be explored by further investigation.

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