

One-Dimensional Surface Reconstruction as an Atomic-Scale Template for the Growth of Periodically Striped Ag Films

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The role of the Si(111)-(4 × 1)-In surface as an atomic-scale geometrical template for the growth of Ag thin films is clarified by scanning tunneling microscopy and low energy electron diffraction. Low-temperature grown Ag films are found to have stripe structures with a transverse periodicity equal to that of indium chains of the Si(111)-(4 × 1)-In. The stripes exhibit a structural transformation at the thickness of 6 monolayers (ML); this relaxation allows the stripes to persist up to a thickness as large as 30 ML ($\cong 7$ nm) while maintaining their mean periodicity. We attribute this stability to a coincidental matching of the periodicity and the corrugation amplitude between the Ag film and the substrate, which is realized by periodic insertion of stacking faults into a Ag fcc crystal.

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Fabrication of artificial nanostructures with tailored morphology and electronic property is a prerequisite for the development of the current nanotechnology. In particular, the self-assembling technique combined with a surface geometrical template to regulate the size, shape, and position of the desired structures has attracted intense interest. This includes magnetic multilayers grown on substrates with V-shaped grooves [1], semiconductor quantum wires [2], and one-dimensional (1D) metallic chains [3–5] on stepped surfaces, and site-specific adsorption of organic supramolecules on a metal surface reconstruction [6]. These well-controlled nanostructures exhibit fascinating properties such as enhanced giant magnetoresistance, [1] modulation of photoluminescence spectra due to the quantum confinement [2], ferromagnetism induced in atomic chains [4], and a highly anisotropic metal-insulator transition at low temperature [5]. However, the control of the *atomic structures* of rather thick films [$>$ a few monolayers (ML)] has rarely been explored, in contrast to the extensively studied *morphological* changes in terms of shape and size. Tailoring *atomic structures* using a template would lead to the creation of a new class of nanomaterials which may show exotic properties.

In this Letter, we demonstrate that an atomic-scale geometrical template can indeed induce a new crystal periodicity into a metal film. We adopt as a template a surface reconstruction with strong 1D characteristics: the Si(111)-(4 × 1)-In [referred to as In(4 × 1)]. This surface, composed of periodic indium atomic chain arrays on silicon, is considered a representative model for 1D reconstructions [7,8]. Ag films are grown on In(4 × 1) surfaces through low-temperature deposition; here, the selection of Ag facilitates comparison to growth behaviors on other substrates, which have been extensively studied in the past decades [9–12]. Scanning tunneling microscope (STM) and low energy electron diffraction (LEED) measurements

clarify that Ag films have stripe structures with a transverse periodicity equal to that of the In(4 × 1) reconstruction. After a structural transformation in an early stage of growth, the stripes persist up to the film thickness as large as 30 ML. We propose an atomic structural model consisting of a Ag fcc crystal with periodic insertion of stacking faults, which is consistent with the experimental findings.

All experiments are performed under ultrahigh vacuum conditions. First, we prepare a well-developed In(4 × 1) surface according to the procedure described earlier [13]. Ag is deposited from a Knudsen cell onto the substrate that is cooled down to about 100 K. If necessary, a shadow mask is placed in front of the sample in order to evaporate a wedge structure. This facilitates the observation of growth evolution using a single sample. Finally, the sample is warmed up to RT. This process is crucial, because a mild annealing induces formation of a flat film through recrystallization of an as-deposited granular film [10,14]. In contrast, a Ag film growth on the In(4 × 1) surface through RT deposition results in formation of 3D-like islands with only faint 1D structures [14]. All STM and LEED measurements are performed at RT.

In the following, topographic features of thin Ag films are described. Figure 1(a) shows an STM image of a Ag film with a nominal thickness of 2.2 ML. The film consists of flat Ag layers 2 to 4 ML in thickness with strong anisotropic shapes [15]. The elongated islands with straight edges (marked with a triangle) are aligned in the direction of the indium chains of the In(4 × 1) substrate. It strongly indicates that the indium chains play the role of a guide for Ag atom diffusion. Note that these islands are grown on the underlying extended Ag film (marked with a cross). This suggests that not only the substrate but also the surface of the Ag film are composed of 1D atomic structures. An STM image of a 3–4 ML thick island with a higher resolution confirms this expectation [Fig. 1(b)]. Note that

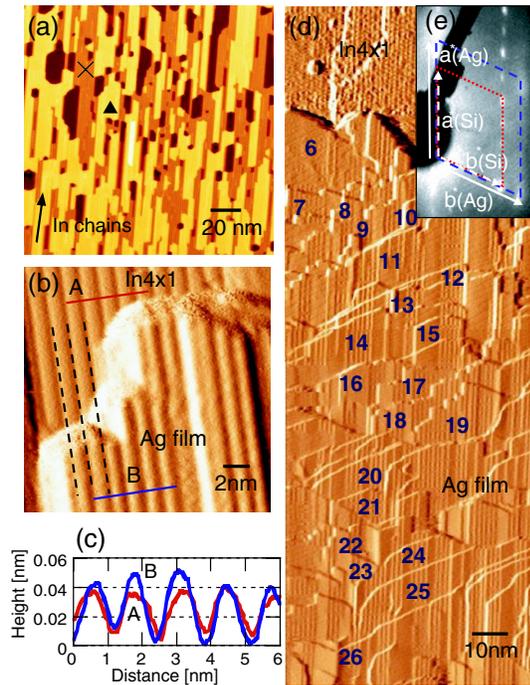


FIG. 1 (color online). (a) An STM image of a Ag film with a nominal thickness of 2.2 ML grown on an $\text{In}(4 \times 1)$ substrate. (b) A derivative STM image of a Ag film 3–4 ML in thickness grown on an $\text{In}(4 \times 1)$ substrate ($V_{\text{tip}} = +1.5$ V). (c) Height profiles measured along line A ($\text{In}(4 \times 1)$) and line B (Ag stripes) in Fig. 1(b). (d) A derivative STM image of a wedge-shaped Ag film fabricated using a shadow mask. The numbers show the local thickness of the film in the unit of ML. (e) A LEED pattern taken from both a Ag film 8 nm in thickness and the $\text{In}(4 \times 1)$ substrate. The solid and dotted arrows indicate the unit vectors of the reciprocal lattice for Ag(111) and Si(111), respectively.

the lateral derivative of the topographic height is displayed in the image, in order to elucidate the small structural features of the surface. The image demonstrates the following facts: (i) the surface of the Ag island consists of equally spaced stripes running in the direction of the indium chains of the substrate, (ii) the periodicity of the stripe is exactly equal to that of the indium chains of the substrate, and (iii) the protruded lines of the Ag stripes and those of the indium chains are aligned in phase. Furthermore, Fig. 1(c) shows that the height profile of the indium chains (line A) and that of the Ag stripes (line B) are nearly identical, both being symmetric with respect to their centers. These facts indicate that the growing Ag layers strictly follow the corrugation of the indium chains without substantial disturbance to them.

The stripes described above constitute a Ag film that is significantly deformed from the intrinsic bulk crystal. Naturally, they are expected to decay rapidly with increasing film thickness (typically within 9 ML) as the bulk properties dominate the substrate effect [16]. However, this is contrary to our observation. Figure 1(d) shows a derivative STM image of a wedge-shaped Ag film, which is

fabricated using a shadow mask. The $\text{In}(4 \times 1)$ substrate is visible in the upper area, and the Ag film increases in thickness in the downward direction. The numbers show the local thickness of the film in the unit of ML. Notably, the stripes on the Ag film persist up to 26 ML in this image. Extensive STM observations confirm the presence of the stripes at least up to the thickness of 30 ML ($\cong 7$ nm). Although stripes are progressively replaced by flat regions as the film thickness crosses this value, the local structure of the stripes remains intact. Further increase in film thickness results in the formation of a Ag(111) surface. This is confirmed by a LEED measurement of a Ag film 8 nm in thickness [Fig. 1(e)]; the figure shows Ag(111) diffraction spots with the corresponding unit vectors of the reciprocal lattice (solid arrows). Note that diffraction spots from the $\text{In}(4 \times 1)$ substrate are also visible, because the LEED measurement is taken in the boundary region of the Ag wedge and the substrate.

The stability of the stripe structure suggests that the energy increase due to its formation is actually minute. This indicates an occurrence of a structural relaxation in the course of film growth, because the film is highly deformed in the early stage. Figure 2(a) shows a derivative STM image of a Ag film with a height of 6 ML. Flat regions accompanying defects (marked with dotted circles) are visible, which are barely observed in thinner films. These defects are assigned to screw dislocations as discussed below. We find that this structural change suddenly

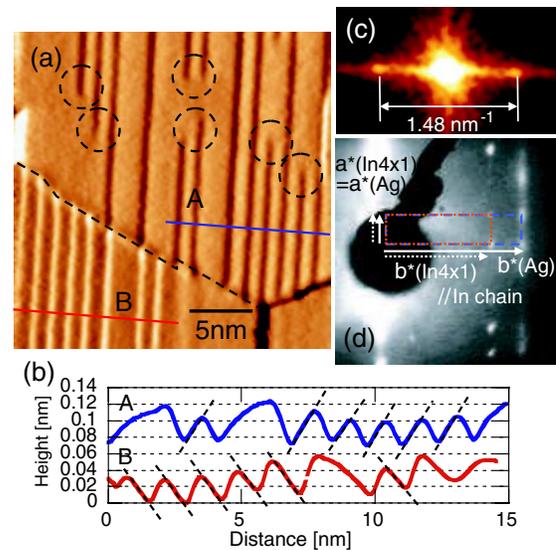


FIG. 2 (color online). (a) A derivative STM image of a Ag film with a height of 6 ML grown on an $\text{In}(4 \times 1)$ substrate ($V_{\text{tip}} = -1.5$ V). (b) Height profiles measured along line A and line B in Fig. 2(a). (c) A power spectrum of the Fourier transformation of an extended STM image of a 6 ML thick Ag film grown on the $\text{In}(4 \times 1)$. (d) A LEED pattern taken from both a Ag film 6 ML in thickness and the $\text{In}(4 \times 1)$ substrate. The solid and dotted arrows indicate the unit vectors of the reciprocal lattice for the Ag stripes and the $\text{In}(4 \times 1)$, respectively.

occurs at 6 ML. A more striking feature is the asymmetric shapes of the cross sections of the stripes. The corrugation across stripes is now stepwise rather than sinusoidal, indicating a transformation from symmetric stripes to an array of tilted nanoplanes. This asymmetric shape is unambiguously confirmed by the presence of two domains where the tilt angles of the stripe planes are opposite to each other. In the image, the domain boundary (dotted line) separates the stripes into the upper-right and lower-left domains. The height profiles taken from the two domains [Fig. 2(b)] give an estimated tilt angle of $3^\circ \pm 0.5^\circ$ for the asymmetric stripe planes. Note that the “flat” regions are also tilted, although their angles are less than those for the stripes. This structural change at 6 ML should release the accumulated deformation energy in the film, thus leading to the observed stability of Ag stripes [17].

After the relaxation, the averaged separation of the stripes still maintains the transverse periodicity of the $\text{In}(4 \times 1)$. Figure 2(c) shows the power spectrum of the Fourier transformation of an extended STM image of a 6 ML thick Ag film. The two bright spots separated by $1.48 \pm 0.09 \text{ nm}^{-1}$ means that the transverse periodicity (a_\perp) of the stripe is $1.35 \pm 0.08 \text{ nm}$, which is in good agreement with that of the $\text{In}(4 \times 1)$ ($a_\perp = 1.33 \text{ nm}$). This is corroborated by a LEED pattern taken from a Ag film 6 ML in thickness [Fig. 2(d)]. The $\text{In}(4 \times 1)$ LEED pattern is simultaneously taken as a reference, as described earlier. The diffraction spots from the Ag film are visible next to those from the $\text{In}(4 \times 1)$. The solid and dotted arrows represent the unit vectors of the reciprocal lattice for the Ag stripes and the $\text{In}(4 \times 1)$, respectively. The ratio of their lengths is 4:3 in the direction parallel to the indium chains, while they are identical in the perpendicular direction. Thus, the Ag film surface is determined to be a $4 \times 3/4$ superstructure commensurate with $\text{Si}(111)$. Figure 3(a) illustrates the atomic structural model of the $\text{In}(4 \times 1)$ [7]. The figure also shows the unit cell of the Ag film (rectangle A) determined from the LEED measurement and that of the $\text{In}(4 \times 1)$ (rectangle B). The former is reduced in size by a factor of $3/4$ from the latter along the indium chain direction. Note that the interatomic distances of the $\text{Ag}(111)$ and $\text{Si}(111)$ planes are 0.289 nm and 0.384 nm, respectively, the ratio of which is almost 3:4. This means that Ag atoms are aligned without changing the interatomic distance of $\text{Ag}(111)$ in the chain direction. In contrast, their alignment is locked to the periodicity of the $\text{In}(4 \times 1)$ in the transverse direction.

The fact that the Ag film is finally transformed into a $\text{Ag}(111)$ surface with increasing thickness suggests that the atomic structure of the striped film resembles the (111) planes of Ag fcc lattice. Indeed, an atomic structural model composed of the fcc crystal with periodic insertion of stacking faults successfully explains our experimental findings. Figure 3(b) shows a schematic illustration of the model. The close-packed Ag atoms of one of the $\langle 111 \rangle$

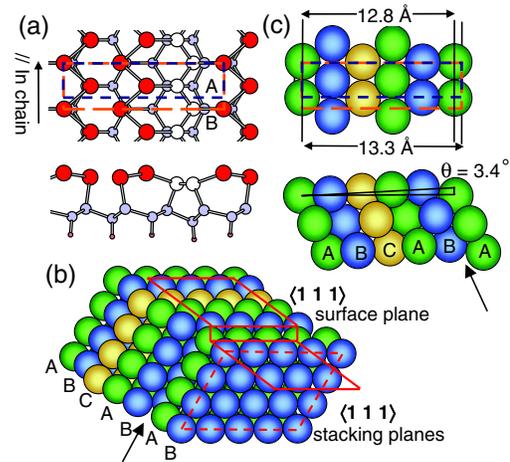


FIG. 3 (color online). (a) The atomic structural model of the $\text{In}(4 \times 1)$ reconstruction (upper panel: top view, lower panel: side view). The red (gray) and white circles represent In and Si atoms on the surface, respectively. The dotted rectangles show the unit cells of the Ag stripes (A) and the $\text{In}(4 \times 1)$ (B). (b) A schematic illustration of the atomic structural model of the Ag stripes. The spheres represent Ag atoms. (c) An atomic structural model of the Ag stripes viewed from different directions (upper panel: top view, lower panel: side view).

planes are stacked through repetition of a sequence unit of $ABCAB$. This introduces a stacking fault per unit in an otherwise perfect fcc lattice (marked with an arrow). The stacking-fault results in periodic steps 0.078 nm in height on another $\langle 111 \rangle$ plane. The Ag atoms of this fractionally stepped surface are found to fit to the $\text{In}(4 \times 1)$ substrate [Fig. 3(c)]. The lattice mismatch between the stacking-fault inserted layers ($a_\perp = 1.28 \text{ nm}$) and the $\text{In}(4 \times 1)$ ($a_\perp = 1.33 \text{ nm}$) is -3.8% , which is small to allow an epitaxial growth generally. The remaining strain due to the mismatch could be released by flat regions adjacent to the stripes. The step height of 0.078 nm on the surface is close to the corrugation amplitude of 0.07 nm for the $\text{In}(4 \times 1)$, [7] which will also leave a small strain energy. The tilt angle of the surface is calculated to be 3.4° from the step height and the lateral periodicity. This agrees well with the experimentally determined value of $3^\circ \pm 0.5^\circ$ for the asymmetric stripes. Furthermore, this model can naturally assign the defects described earlier [Fig. 2(a), dotted circles] to screw dislocations. Note that insertion of a stacking fault is equivalent to the minimum slip of one half of a crystal against the other half. If a slip plane is confined to a finite region, a screw dislocation is generated along the boundary of the slip plane and the pristine crystal.

Ag has an exceptionally small stacking-fault energy among fcc metals. Theoretical and experimental studies have determined the stacking-fault energy per area to be 18 to 38 mJ/m^2 for Ag [18]. This is smaller by a factor of 2 to 3 than those for Au and Cu, and by an order of magnitude than those for other transition fcc metals [19]. This small

energy difference leads to frequent observations of stacking faults in Ag films [20]. Ag films even sometimes take the forms of the hcp structure and related hexagonal lattices as a result of high-density stacking faults [21]. We can, therefore, safely conclude that our atomic structural model is energetically reasonable.

Similar stripe structures could be generally formed if the energy cost due to the presence of stacking faults and the strain in the film is sufficiently lower than the energy gain at the interface. Other noble metals, Au and Cu, have relatively small stacking-fault energies [19]. Furthermore, intrinsic or step-induced anisotropy of Si surfaces leads to a variety of metal-covered 1D reconstructions, e.g., Si(111)-(3 × 1)-Ag and Si(111)-(5 × 2)-Au [22]. The adequate choice of a substrate and a growing film may allow stripe formation by the same mechanism. The strong structural anisotropy of the striped Ag film described here leads to 1D-like electronic states [23], which may provide a new venue for studying the exotic 1D electron physics [22]. This is possible because the electron motion in the normal direction is already frozen due to the quantum confinement or the presence of the Shockley surface state [10]. The striped surface of the Ag film could also be utilized for uniaxial alignment of deposited species, such as magnetic atoms [4], silicon nanowires [24], and organic molecules [6]. The use of silicon substrates facilitates integration into the established semiconductor technology, while Ag should work as a lubricant to enhance the lateral diffusion of growing materials.

In conclusion, Ag stripe structures with a periodicity equal to that of indium chains of the substrate have been grown up to the film thickness as large as 30 ML. We have proposed an atomic structural model consisting of a Ag fcc crystal with periodic insertion of stacking faults. The stability of the stripes is attributed to a coincidental matching of the periodicity and the corrugation amplitude between the striped Ag film and the substrate.

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