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# Lattice accommodation of low-index planes: Ag(111) on Si(001)

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Deposition of nonreacting metals on semiconductors usually results in three-dimensional islands that often exhibit a different crystal orientation than the substrate. Using the kinetic pathway of low-temperature growth, a continuous and smooth Ag film with a (111) orientation is formed on Si(001). The interface planes fit nearly exactly within a (3×4) unit cell of the Si(001) surface. The remaining small mismatch is adjusted by periodic arrays of interfacial defects. The orientation of the Ag(111)-film is strictly determined by the orientation of the Si bonds: From step to step of the Si(001) substrate the Ag(111) crystallites rotate by 90°.

Heteroepitaxial growth of metals on semiconductors is governed by a variety of problems which arise from the difference in lattice constant, surface and interface free energies, and the kinetics of growth. Due to the high mobility of metal atoms (even at room temperature) they usually form islands of three-dimensional (3D) clusters.[1,2] Continuous metal films could be grown at lower temperatures,[3] which, however, show a high density of threading defects as observed for growth of Ag on Si(111).[4] As an additional complication metal surfaces usually tend to roughen during growth due to a barrier for interlayer diffusion (Schwoebel barrier) at the step edges.[5–7]

In general the systems are also lattice mismatched which again increases the tendency towards islanding. This and the difference in the type of lattice (diamond versus fcc or bcc) are also the reasons for the occurrence of 3D clusters with a different crystal orientation than the substrate, as observed for room-temperature formation of Ag(111) 3D clusters on Si(001).[8,9] Obviously a system with a Ag(111)/Si(001) interface is energetically more favorable than that with a Ag(001)/Si(001) interface. The question arises: How do these two completely different lattices fit together?

In this paper we demonstrate that the use of the kinetic pathway (growth at temperatures lower than 130 K) results in a layer growth of continuous Ag(111) films on Si(001) substrates. If the Ag films are thicker than 15 ML, annealing at 300 K results in a flat surface morphology without islanding of the Ag film. Although the Ag/Si system exhibits a high lattice mismatch [$a_{\mathrm{Si}}: 5.431$ Å (diamond), $a_{\mathrm{Ag}}: 4.086$ Å (face centered)] the ratio of Si to Ag lattice constants is almost exactly equal to 4:3. Therefore the two different interface lattices with (001) and (111) orientation can be adjusted with a very small remaining mismatch of 2.2% which is compensated by parallel arrays of interfacial dislocations.

Furthermore, the azimuthal orientation of the Ag(111) film is strictly determined by the dimer orientation on the terraces of the Si(001) substrate[10] and rotates by 90° from one atomic step to the neighboring step on the Si surface. The Ag film is composed of (111) crystallites with alternating azimuthal orientation [the dense packed rows of the Ag film either in the [011] or [01$\bar{1}$] directions of the Si(001) substrate] and a size which depends on the misorientation of the Si(001) substrate.

Experimental results were obtained by *in situ* examination with spot profile analyzing low-energy electron diffraction (SPA-LEED) (Refs. 11 and 12) and with *low temperature* scanning tunneling microscopy (STM).[4] The samples were prepared under ultrahigh vacuum conditions with Ag evaporation from a tantalum crucible. Clean Si(001) samples (Wacker Chemitronic, n-type, oriented within 0.1° in the {100} plane) were prepared by degasing followed by a short flash to 1150 °C to remove the native oxide. Deposition took place at 130 K (SPA-LEED experiment) or 90 K (STM experiment), respectively. After deposition the Ag film was annealed at room temperature. The LEED data have been recorded at room temperature, the STM data at 90 K.

Instead of formation of 3D clusters (as observed for growth at room temperature[9]), deposition at 130 K results in an epitaxial layer growth mode. This is proved with monolayer intensity oscillations of the (00) spot *during Ag deposition.*[13] This is in contrast to the random growth mode of Ag on Ag(111) which is usually observed.[6,14] The random growth mode could be changed by introducing a surfactant, which causes a 2D-layer growth mode by increasing the density of 2D islands of monatomic height.[14,15] Here a similiar reason may apply: In the very early stage of growth the Ag nucleates on a semiconductor surface with completely different orientation and lattice constant. This may result in an increased 2D-island density, as observed for growth of Ag on Si(111).[4]

Annealing of a 20 ML Ag film to 300 K results in the peculiar LEED pattern (electron energy 109 eV) shown in Fig. 1 (the LEED pattern at 130 K shows very broadened spots due to surface roughness). The (00) spot at the origin of the figure is surrounded by 12 first-order spots and many higher integer order spots. This pattern is easily explained as superposition of two LEED patterns of Ag(111) surfaces which are rotated by 90° with respect to each other. For all electron energies all the first-order spots have identical intensity reflecting the equal occurrence of twinned domains in the (111) Ag film.[16] At a closer look, however, there remains, instead of a sixfold or twelvefold symmetry, only a twofold symmetry of the

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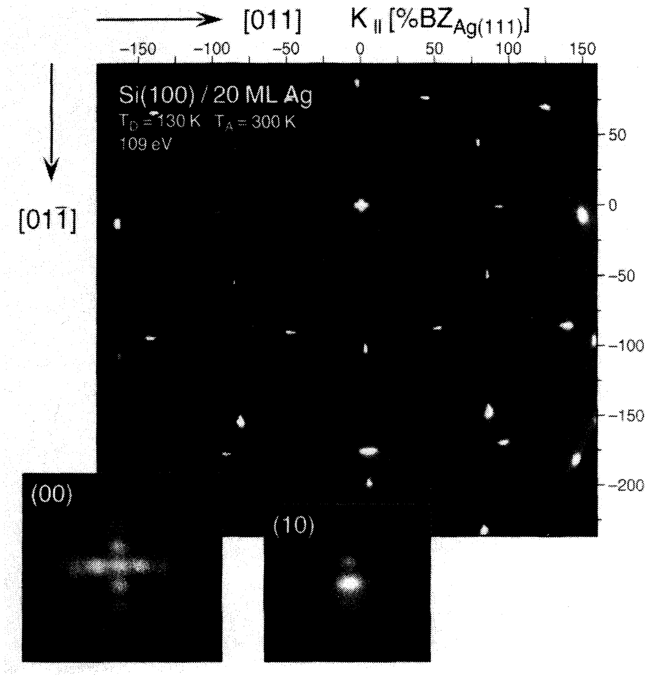

FIG. 1. LEED pattern of 20 ML Ag on Si(001) after annealing to 300 K. The (00) spot at the origin is surrounded by 12 first-order spots and many higher integer order spots. The spots are elongated in either the [011] or [01$\bar{1}$] directions. The pattern is a superposition of two hexagonal patterns rotated by 90°. The insets show the splitting of the (00) spot and one first-order spot into satellites.

LEED pattern: The (00) spot has the shape of a plus sign and the integer order spots are elongated in either the [011] or [01$\bar{1}$] directions. The spots of each of the two rotated (by 90°) hexagonal LEED patterns are elongated only in one direction.

Using higher magnification, the nature of the elongated spots becomes apparent: Each of the integer order spots is split into short chains of satellite spots with a separation of 1.4% of the Brillouin zone (100% BZ is the distance between the integer order spots), i.e., a periodicity length $L \simeq 180$ Å. This is shown for the (00) spot (measured at 436 eV), with higher magnification in the inset of Fig. 1.

These chains of satellite spots are caused by a weak and periodic height undulation of the surface, which has the form of plane waves for each of the two (111)-crystal orientations. The undulation originates from a periodic arrangement of lattice matching dislocations at the interface. The associated strain fields (surrounding each dislocation) elastically distort the lattice up to the surface of the Ag film.[17] During diffraction the electrons undergo an additional small phase shift due to the surface height modulation. The result is the same as expected for a phase grid for electrons.[18–20] As usual in optics, this leads to a splitting of all spots. The relative intensity of the satellites depends on the resulting phase difference during diffraction, i.e., on the electron wavelength or the electron energy. Therefore the amplitude of the height undulation could be estimated from this dependence of the satellite intensities on the scattering condition. The normalized intensities for the central spot and the first three nonequivalent satellites are plotted in Fig. 2 as a function of the scattering phase $S$ (perpendicular scattering vector $k_\perp$ and the $\mathrm{Ag}_{(111)}$ layer distance of $d = 2.36$ Å)

$$S = \frac{k_\perp d}{2\pi},$$

i.e., proportional to the square root of the electron energy. At very low electron energies the satellites are weak because the electrons have a long wavelength and are therefore insensitive to the undulation. The surface height modulation is described by a Fourier series with $D_j$ as coefficients of the height undulation:

$$h(x) = \sum_{j=0}^{N-1} D_j \cos\left(2\pi \frac{x}{L} j\right), \quad N = \frac{L}{a_{\mathrm{Ag}}}.$$

Using a simple approximation for small values of $S$,[20] the satellite intensity is expected to increase with the square of the scattering phase $S$ as

$$I_j = 4\pi^2 S^2 D_j^2.$$

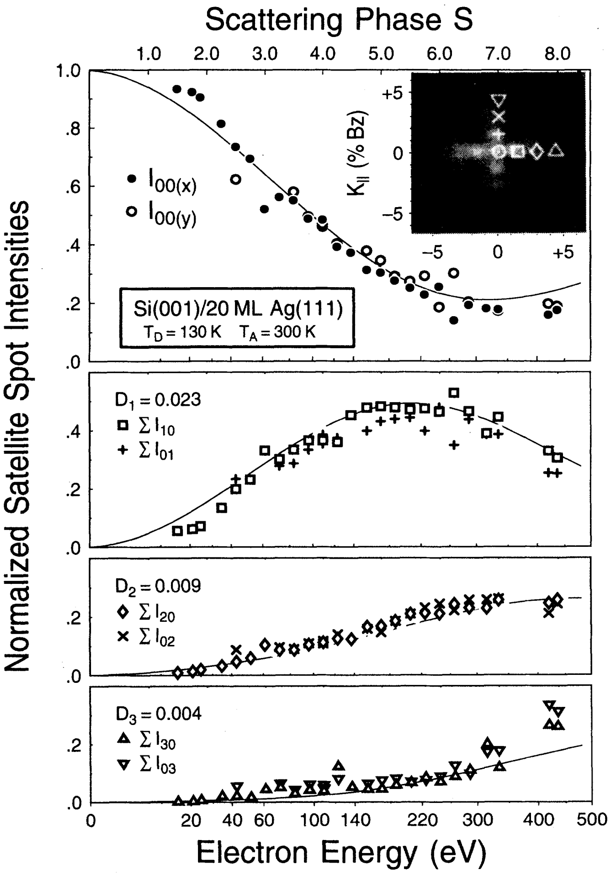

FIG. 2. Normalized satellite intensity as a function of the vertical scattering phase $S$, i.e., proportional to the square root of the electron energy. From the slope of the curves the amplitude of the height undulation is estimated to 0.26 Å. The solid lines represent the calculated intensities for the model described in the text.

From the slope of the parabolas the Fourier coefficients and thus the amplitude of the undulation is estimated to $\Delta h = 0.26\,\text{Å} \pm 0.03\,\text{Å}$. The solid lines in Fig. 2 represent the calculated intensities with the Fourier coefficients of the height function $h(x)$ of $D_1$ ($= D_{N-1}$) $= 0.023$, $D_2 = 0.009$, and $D_3 = 0.004$ in units of the $\text{Ag}_{(111)}$ layer distance of $d = 2.36\,\text{Å}$. The resulting shape of the height undulation is equal to a periodic arrangement of Lorentzian functions.[13,20]

STM has been used to determine the size, orientation, and morphology of the Ag(111) crystallites of the film. Figure 3 shows a 40-ML-thick Ag film on a Si(001) substrate which has been deposited at 90 K and annealed at 300 K. The steps of the underlying Si(001) substrate are still visible at the Ag surface. The azimuthal orientation of the Ag(111) film rotates from Si step to Si step by 90°. This is observed in the alternating orientation of the edges (indicated by perpendicular arrows) of the monatomic high Ag 2D islands on larger terraces. This behavior reflects the strict determination of the azimuthal orientation of the Ag(111) film by the direction of the Si bonds on the Si(001) surface. The Ag grows only in one orientation on each of the alternating Si steps [we assume the dense packed Ag rows aligned parallel to the dimer rows on the Si(001) terraces[21]]. However, twinning with Ag(111) crystallites rotated by 180° is equally observed because there is no preference for the orientation perpendicular to the dimer rows. The twin grain boundaries, however, are hard to identify in Fig. 3. The grain boundaries between the 90° rotated (111) crystallites are not yet identified; there is, however, no simple type of grain boundary in order to match the two lattices.[22]

The weak surface height undulation is observable also with STM for this 40-ML-thick Ag film. The plane-wave-like height undulation could be clearly seen in Fig. 4 after image processing of Fig. 3 by statistical differentiation. The orientation of the plane waves is parallel to the dense packed rows of the Ag, i.e., the step edges of the monatomic high Ag 2D islands on larger terraces. This clearly shows that the orientation of the undulation also rotates [together with the orientation of the Ag(111) crystallites] by 90° for neighboring Si steps. The arrangement of the plane waves exhibits imperfections like varying distances or orientational disorder, which are responsible for the broadening of the LEED satellites.[23]

The amplitude and periodicity of the height undulation is estimated in the small inset of Fig. 5 where the image contrast has simply been enhanced (without filter) so that the plane wave height undulation becomes clearly visible. The plot of a line-cut profile through this terrace has an amplitude of 0.18 Å and a periodicity length of 185 Å which agrees perfectly with the LEED results. This and the LEED intensity dependence of the satellite intensities exclude the occurrence of charge density waves. The amplitude of the undulation is a bit smaller, because the Ag film is twice as thick as that in the LEED experiment.

The reason for this nearly perfect growth (only a few threading defects have been observed with STM) is the almost exact 4:3 ratio of the extremely mismatched lattice constants of Ag (4.09 Å) and Si (5.43 Å). In Fig. 6 the surface lattices for the Si(001) substrate and the Ag(111) face have been drawn. We have assumed the dimer rows parallel to the dense packed rows of the Ag(111).[21] In the $[\bar{1}10]$ direction the distance between three Si atoms (11.52 Å) matches nearly exactly the distance between

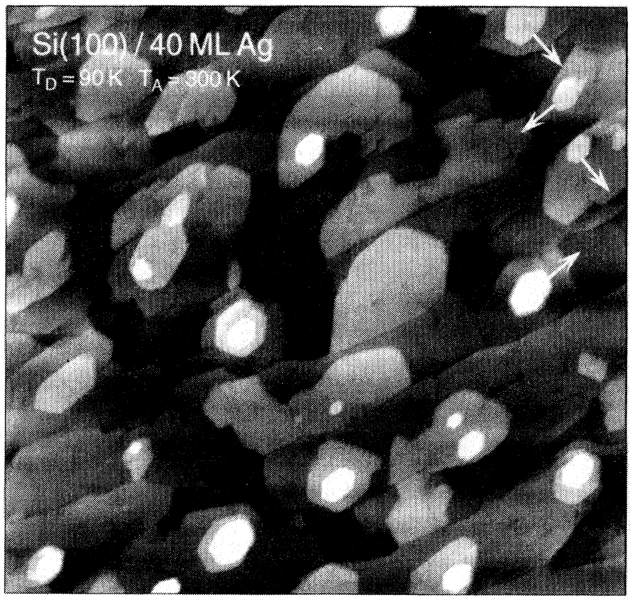

FIG. 3. STM image ($5000 \times 5000\,\text{Å}^2$ wide) of 40 ML of Ag deposited at 90 K and annealed at 300 K. The alternating orientation of the monatomic high 2D islands (indicated by arrows perpendicular to any one of the step edges) reflects the azimuthal rotation by 90° of the Ag(111) crystallites for neighboring steps of the underlying Si substrate.

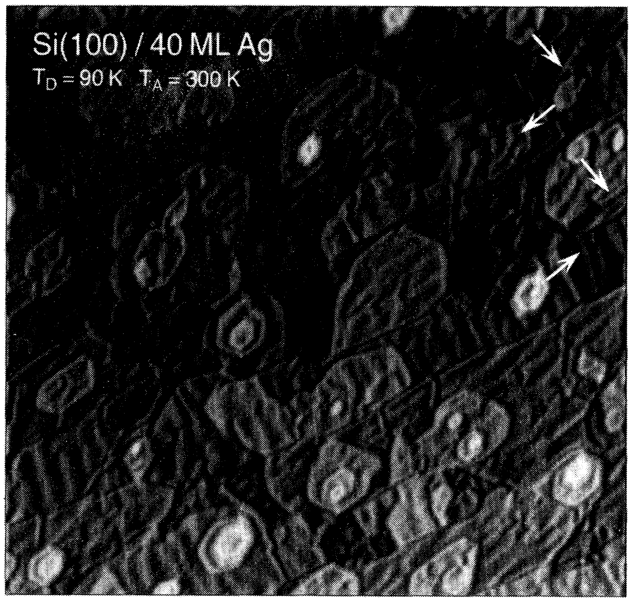

FIG. 4. The STM image of Fig. 3 has been image processed to enhance the contrast on the flat areas. The plane wave height undulation due to the lattice matching interfacial dislocations is now clearly seen. The orientation of the plane waves rotates together with the orientation of the (111) crystallites by 90° for neighbored Si steps.

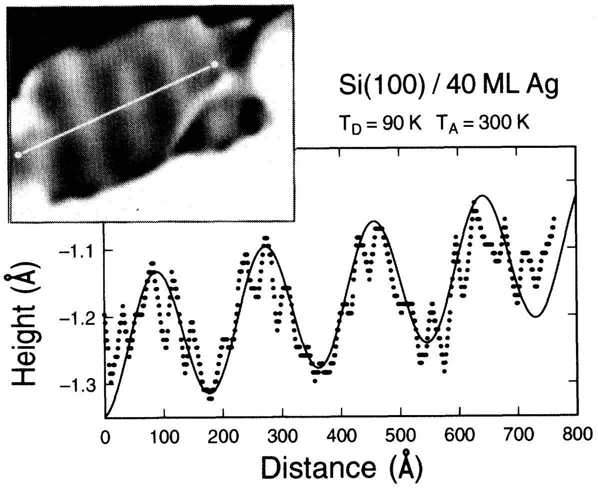

FIG. 5. Increasing the image contrast, the plane wave height undulation due to the interfacial dislocation array becomes visible. Image is $1000 \times 800$ Å$^2$ wide. From the linear cut an amplitude of 0.18 Å and a periodicity length of 185 Å is estimated. The additional high-frequency modulation is an artifact of data acquisition.

four Ag atoms (11.56 Å). The remaining lattice mismatch is only 0.36% (compressive strain). The mismatch in the [110] direction is larger: the separation of the dimer rows of 7.68 Å has to fit with the distance of three dense packed rows of 7.51 Å. The interface, however, has a periodicity of two Si dimer row distances or six dense packed Ag rows. In this direction a mismatch of 2.2% (tensile strain) would remain.

This anisotropic misfit is relieved by arrays of parallel dislocations in the interface plane. We therefore would expect a distance of the dislocations of $\simeq$ 112 Å, i.e., a separation of the satellites by 2.2% $BZ_{Ag(111)}$. In contrast to this we observe an average distance of 180 Å (a satellite separation of 1.4% $BZ_{Ag(111)}$). The reason for part of the residual strain may be the compensation of compressive stress in the $[\bar{1}10]$ direction via tetragonal distortion.

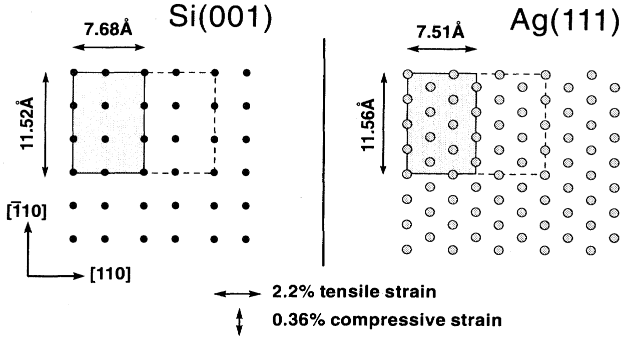

FIG. 6. The lattices of the Si(001)-(2×1) surface and the Ag(111) match almost exactly in the $[\bar{1}10]$ direction. In the [110] direction the Ag lattice has to be expanded by 2.2% in order to match the Si dimer distance.

We have demonstrated the growth of continuous Ag(111) films on Si(001). The reason for the occurrence of the metal (111) orientation on the twofold (001) surface is its lower surface free energy and the almost exact lattice accommodation within a ratio of small integer numbers. Any remaining lattice mismatch is adjusted by an array of parallel dislocations at the interface. Due to the covalent character of the semiconductor surface the azimuthal orientation of the Ag(111) crystallites is strictly determined by the Si dimer orientation: From step to step of the underlying Si substrate the metal crystallites rotate by 90°. We expect the observed phenomena of lattice accommodation and strain relief to be representative for the wide field of metal growth on semiconductor (001) surfaces, with Ag(111) on Si(001) serving as a model system.

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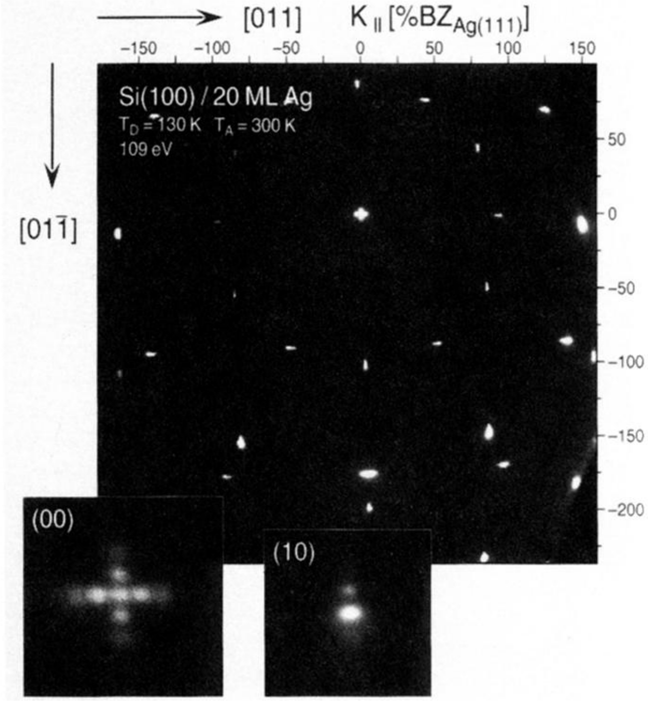

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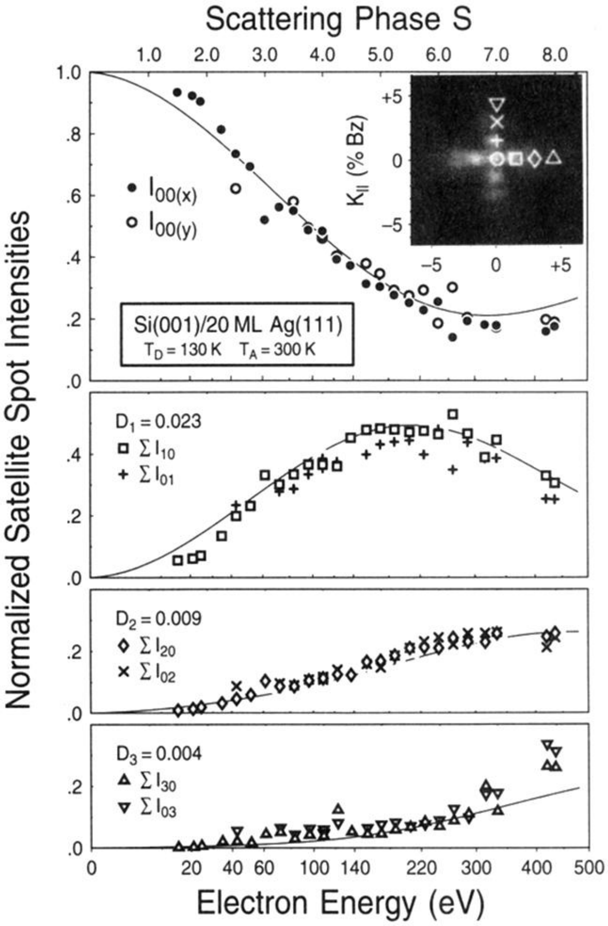

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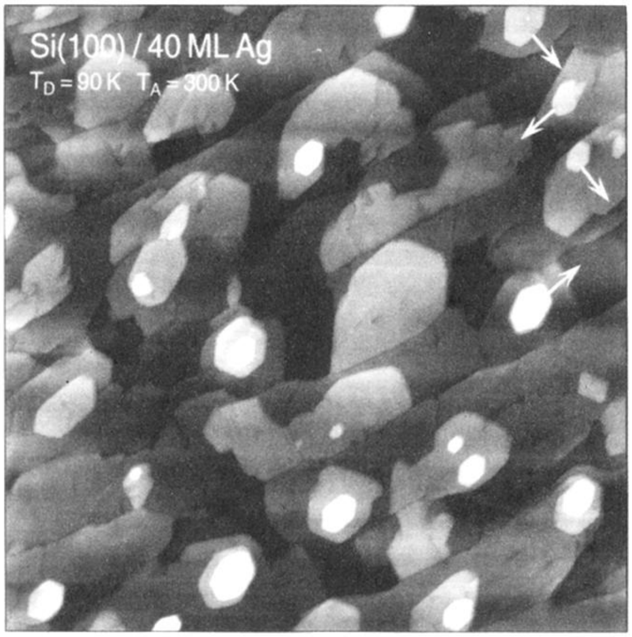
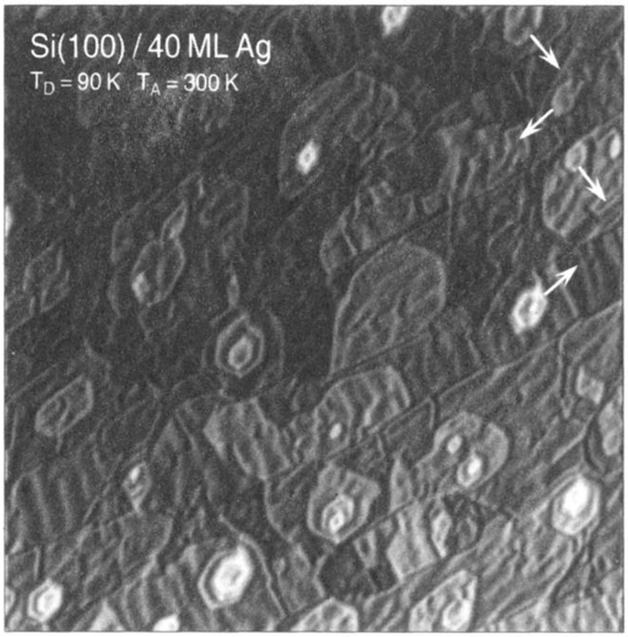


FIG. 3. STM image ($5000 \times 5000$ Å$^2$ wide) of 40 ML of Ag deposited at 90 K and annealed at 300 K. The alternating orientation of the monatomic high 2D islands (indicated by arrows perpendicular to any one of the step edges) reflects the azimuthal rotation by 90° of the Ag(111) crystallites for neighboring steps of the underlying Si substrate.



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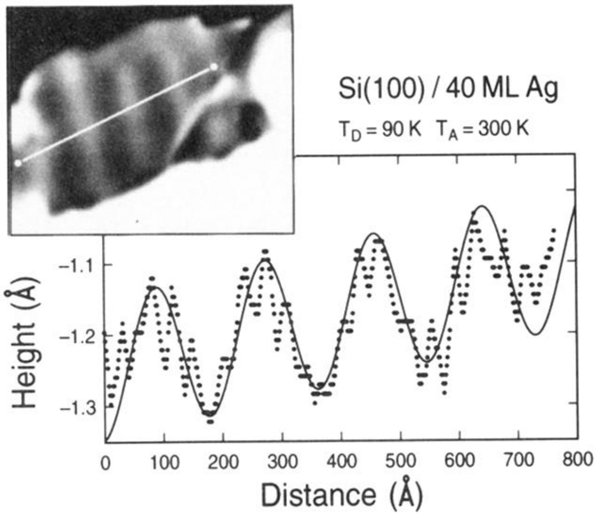

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