PHYSICAL REVIEW B VOLUME 45, NUMBER 7 15 FEBRUARY 1992-I

# Orientational ordering and domain-wall formation in Sb overlayers on GaAs(110)

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(Received 28 October 1991)

Real-space scanning tunneling microscope images of Sb thin films on GaAs(110) show disordered surface structures at 300 K, but an ordered overlayer occurs when annealed. The annealed incommensurate Sb thin film show grains with distinct superstructure orientations. Within each Sb grain, the superstructure exhibits 25-Å periodicity and alignment either 40° or 140° with respect to [1$\bar{1}$0] of the GaAs substrate. Striped domain walls with a mean separation of 110 ± 7 Å are formed in each grain. The superstructure can be explained in terms of a Moiré effect in which the Sb overlayer is rotated by ±7° with respect to the substrate [1$\bar{1}$0] direction.

The periodic variation in the potential energy of a surface will influence the structure, lattice parameter, and orientation of overlayers grown on it.[1] The overlayer can grow pseudomorphically when substrate-adsorbate interactions dominate over adsorbate-adsorbate interactions. In this case, the lattice constant and crystal structure coherently match the substrate. For example, a single layer of Sb is pseudomorphic with GaAs(110), and the lattice strain is relieved by the unrelaxation of the GaAs(110) surface.[2] The stability of the pseudomorphic layer is then determined by competition between misfit dislocations and the coherently strained structure. For example, the first layer of Bi is pseudomorphic with GaAs(110), but misfit dislocations are present every ~25 Å in the [1$\bar{1}$0] direction, presumably because of the increased lateral size of the Bi atoms compared to Sb.[3]

Interesting overlayer structures can occur when substrate-adsorbate interactions are weak. In this case the overlayer can be incommensurate with periodic strains caused by the substrate field. A two-dimensional (2D) system that is incommensurate in only one direction can form a striped domain phase where periodically spaced domain walls relieve strain.[4] In the striped domain phase, the walls will be approximately parallel to one another. A domain wall can be constructed by compressing the commensurate layer along a preferred direction and then adding particles on the substrate that is exposed by the displacement. Considerable experimental and theoretical work on domain walls has focused on rare-gas monolayers adsorbed on hexagonal surfaces.[4] For many of these systems, domain-wall formation occurs when atoms are added to the commensurate phase to create a higher-density incommensurate phase with periodic domain walls.

In this paper we show that the thin Sb films on GaAs(110) form disordered surface structures at 300 K, but an ordered overlayer occurs when annealed. The annealed overlayer consists of grains, each with distinct superstructures oriented either 40° or 140° with respect to the substrate [1$\bar{1}$0] direction. This superstructure can be explained in terms of a Moiré effect in which the Sb overlayer is rotated by ±7° with respect to the substrate [1$\bar{1}$0] direction. The grains contain striped domain walls and the domain walls are spaced periodically with an average distance of 110 ± 7 Å. These scanning tunnel microscope (STM) images provide a rare opportunity to observe the formation of an orientationally ordered thin film containing grains with two distinctly oriented surface-mediated superstructures and periodically spaced striped domain walls.

The measurements were conducted in a ultrahigh vacuum chamber containing a commercial scanning tunneling microscope[5] and reverse-view optics for low-energy electron diffraction (LEED). GaAs(110) surfaces were produced by cleaving sample posts that were Zn doped at $1\times10^{19}$ cm$^{-3}$. The resulting surface exhibited micrometer-size, step-free regions. Electrochemically etched tungsten tips were cleaned *in situ* by electron bombardment. Sb was deposited from a resistively heated Ta boat, and the thickness of the condensed layer was determined by a quartz-crystal microbalance. One monolayer of Sb corresponds to 2.7 Å of Sb [1 ML = $8.85\times10^{14}$ Sb atoms per cm$^2$, i.e., the GaAs(110) surface density]. Sb deposition was done at 300 K. The samples were subsequently annealed for typically ~1 h, including a 15 min warm up. The length scales in the STM images were calibrated in the lateral direction with the substrate lattice and in the $z$ direction with GaAs monatomic steps. The images were acquired in the constant current mode with tunneling currents between 0.1 and 1.0 nA and bias voltages of ±(0.2–3.0) V. Here, the STM images are displayed with the surface [1$\bar{1}$0] direction oriented 135° from the $x$ axis, except where noted.

The 400×400 Å$^2$ image of Fig. 1(a) is typical for 4 ML of Sb deposited at 300 K. To produce it, a single monolayer was deposited and then annealed to 600 K to form a uniform layer on which 3 ML of Sb was deposited at 300 K with no further annealing. The image shows an Sb island (marked $A$) that is ~6 Å higher than the Sb layer below. The disordered appearance of the surface is attributed to the formation of small clusters and stray atoms on this essentially ordered Sb multilayer.[6] Shih, Feenstra, and Mårtensson[6] have reported that Sb films grown at 300 K exhibit a definite layered structure with an average terrace height of ~6 Å. The layered growth mode of Fig. 1(a) is in agreement with their observations and the model proposed by Strümpler and Lüth[7] in which simultaneous multilayer growth occurs. In this case, the lateral diffusion of Sb is small so that the $n$th layer can form be-

 

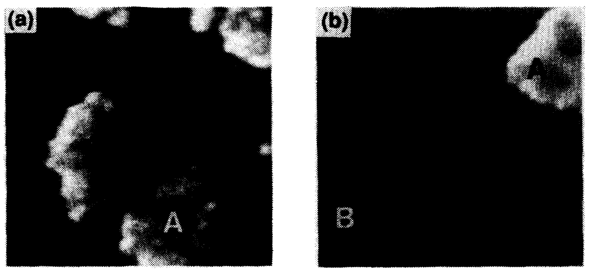


FIG. 1. (a) 400×400 Å$^2$ image for 4 ML Sb on GaAs(110) deposited at 300 K. The irregular island labeled *A* is ~6 Å higher than the area around it. (b) A 400×400 Å$^2$ image following annealing to 375 K. The *A*-type islands exhibit order and a high density of 2-Å high islands labeled *B* have formed. The [1$\bar{1}$0] direction is oriented at 135° from the *x* axis in all figures unless noted otherwise.

fore the $(n-1)$th layer is completed. We note the absence of preferential geometrical shapes or alignment for the Sb islands.

Ordering can be induced on the Sb surface and the clusterlike features on the islands can be eliminated by annealing to 375 K, as shown in Fig. 1(b). In addition to the disappearance of the small Sb clusters on the "*A*" islands, the dominant structural change involved the development of ~2-Å high islands, labeled *B*. The *B*-type islands probably result when atoms and small clusters on the multilayers form ordered arrays during annealing. These *B*-type islands are irregularly shaped and they do not exhibit preferential ordering along any direction for any annealing temperatures.

Figures 2(a) and 2(b) show larger area images of the Sb surface annealed at 475 and 500 K, respectively, that make it possible to follow the evolution of the *A* and *B* islands. Under these conditions the island edges are considerably smoother than those of Fig. 1(b). Annealing at 500 K also promoted lateral growth of *B* islands near the edge of *A* islands, as shown in Fig. 2(b). This indicates that Sb diffused from the higher *A*-type islands to fill in the space between the *B* islands. This is contrary to structures annealed at 375 and 475 K where the *B* islands were present near the edge of *A* islands, as shown in Fig. 2(a). In addition to the *A* and *B* structures, we also found Sb crystallites that did not contain *B* structures and were atomically flat. These crystallites were never found on top of a single 6-Å high *A*-type surface. Occasionally these crystallites exhibited hexagonal symmetry, as indicated with an arrow in the upper left corner of Fig. 2(b). Cross sections showed that the hexagonal Sb crystallites were ~6 Å in height, corresponding to three layers in the [111] direction for the rhombohedral structure.[8]

Figure 2(b) shows a ~500-Å wide region around the *A* island that has formed a nearly complete network of *B*-type islands. A representative 600×600 Å$^2$ portion of this region is shown in Fig. 2(c). These *B*-type regions are derived from two differently oriented superstructures that are oriented at 40° and 140° (±2°) relative to the substrate [1$\bar{1}$0] direction. (Small area superstructures of these type have also been observed for lower annealing temperatures, but we focus on the large areas here.) The distance between the corrugation maxima, evident from the gray scale variations, is 25±2 Å and the modulation height is 0.4 Å. In addition, the superstructure has a phase shift of 180° when it passes through a domain wall (DW), as illustrated in the lower left of Fig. 2(c). The grains derived from the differently oriented superstructures are separated by lines that are decorated with defects, labeled *D* in Fig. 2(c). The defects are less than ~20 Å in diameter, but their size shows a tip voltage dependence. The onset of domain-wall formation began in large *B*-type regions. The domain walls generally begin at one side of a grain and terminate at the other, and they show no preferential orientation with respect to the crystal direction. Nevertheless, adjacent walls tend to run parallel to one another and they do not collide. The formation of striped domain walls generally occurs when an overlayer compresses in a preferred direction and the domain walls provide a low-energy mechanism to relieve uniaxial misfit.[4,9] The corrugation of the domain walls was voltage dependent, ranging from a maximum of ~2 Å at a sample voltage of 0.2 V to a minimum of ~0.2 Å at a sample voltage of 2.5 V, thus indicating that the domain-wall topography represents an electronic effect. Nogami, Baski, and Quate[10] have observed similar effects for Au on

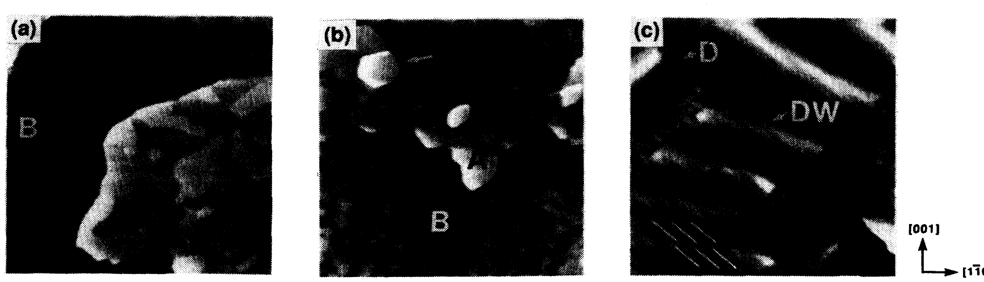


FIG. 2. (a) 1000×1000 Å$^2$ image obtained after annealing to 475 K showing that edges of the *B*-type islands are smoother than in Fig. 1 and that *B*-type islands have formed on the *A*-type region. (b) A 2300×2300 Å$^2$ image obtained after annealing at 500 K. The regions near the *A*-type islands show more *B* character, indicating that Sb diffused from the higher to lower islands. The arrow identifies an island with hexagonal symmetry, indicating the onset of bulklike Sb growth exposing a (111) surface. (c) 600×600 Å$^2$ image obtained after annealing to 500 K showing the two differently oriented superstructures in *B*-type regions at 40° or 140° relative to [1$\bar{1}$0]. Defects (*D*) define the boundaries between individual grains. Striped domain walls (DW) are periodically spaced. The dark region in the lower right is a monolayer Sb step.

Si(111).

Figure 3 shows 2500×2400 Å$^2$ STM image that was obtained after the sample was annealed to 525 K. Under these conditions the Sb overlayer became flatter and large $B$-type regions had formed. Clearly evident are periodically spaced striped domain walls and defects that form the perimeter of a given grain. When defects exist within a grain they terminate a single domain wall. The arrow in Fig. 3 draws attention to a region that did not contain the periodic superstructure. Such regions are not surrounded by defects and domain walls are absent. Other STM images showed that grains, defects, and domain walls were continuous through monatomic substrate steps, multilayer $A$-type islands, and single-layer $B$-type islands. Finally, annealing to 550 K led to Sb desorption and the development of large 2D terraces with heights up to ~18 Å that contained grains with domain walls, defects, and superstructures. This is particularly intriguing because it suggests that the effects of the GaAs(110) surface was still important at the Sb surface 18 Å away.

LEED studies done in parallel with the STM investigations showed patterns that were consistent with those of Hu *et al.*[11] In particular, 4-ML Sb overlayers formed at 300 K did not show any distinct patterns, but annealing to 375 K produced a clear 1×1 pattern along with faint fractional-ordered spots adjacent to integer order spots inside the (10) and ($\bar{1}$0) beam. After annealing to 475 K, fractional-ordered spots appeared in the (01) direction in addition to the (10) spots. The gradual appearance of fractional-ordered spots is consistent with the STM images where the 25-Å superstructure covered a larger portion of the surface. We did not observe any pattern with hexagonal symmetry for the 4-ML Sb thick film, but hexagonal crystallites signal the onset of bulklike Sb growth, as in Fig. 2(b).[11]

Images obtained at lower coverage made it possible to determine the atom registry of the Sb structures with the GaAs substrate. Figure 4(a) is a high-resolution image of a ~200-Å island. The registry of the island and the substrate could be determined because rows on the Sb island

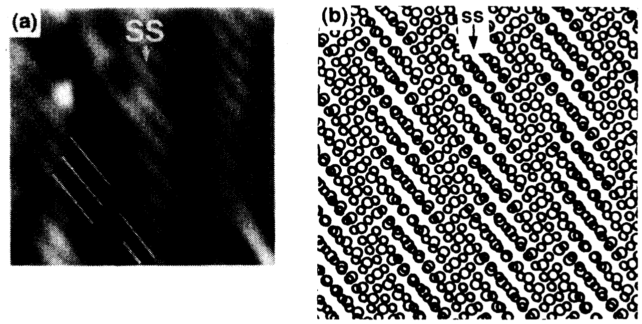


FIG. 4. (a) 85×85 Å$^2$ image of a ~200-Å island after annealing to 400 K showing periodically spaced rows and a superstructure (SS) labeled with an arrow. (b) Moiré pattern generated for the rectangular substrate lattice and the (110) plane of Sb showing the periodically spaced superstructures (SS) oriented 140° from the substrate [1$\bar{1}$0] direction. The Sb lattice is rotated −7° with respect to the substrate [1$\bar{1}$0] direction.

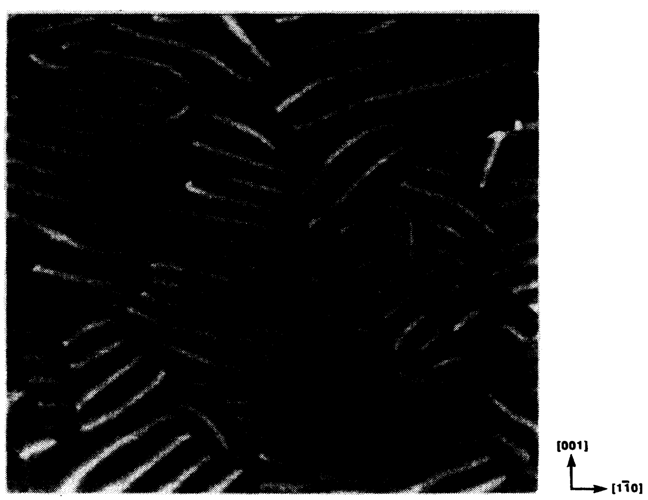


FIG. 3. 2500×2400 Å$^2$ image obtained after annealing to 525 K that shows grains with the superstructure orientations, defects between grains, and periodically spaced domain walls. These structures have been observed in multilayers with thicknesses of ≈6, 12, and 18 Å. The arrow indicates a region that contains neither the superstructures nor the domain walls. The total $z$ amplitude is 2 Å with variation from 0 (black) to 2 Å (white). The small dark region in the upper right is a monolayer Sb step.

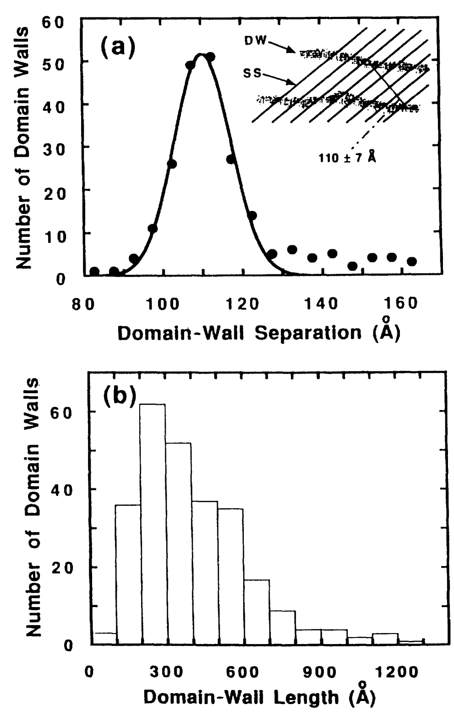


FIG. 5. (a) A distribution of the separation between domain walls for samples annealed at 525 K. The mean separation was 110 ± 7 Å. The inset shows how the domain-wall (DW) separation was defined with respect to the superstructure (SS). (b) A histogram of domain-wall lengths. The average domain-wall length was 250 ± 30 Å for samples annealed to 525 K. This gives an estimate of the mean grain size.

and the first Sb monolayer were both imaged (the 1×1 Sb layer is not seen in this figure). Analysis revealed that the rows on the Sb island were nearly parallel to the substrate rows and the spacing between the rows was close to the lattice constant of GaAs in the [001] direction. Close inspection of Fig. 4(a) shows that the rows shift by $\frac{1}{2}$ the spacing as they pass through the superstructure (labeled SS) as indicated by the lines. We believe that this "apparent" preferential alignment of the overlayer rows with the substrate rows is caused by a Moiré effect. Figure 4(b) shows a Moiré pattern generated for the rectangular substrate lattice (1 atom/unit cell) and the pseudocubic (110) Sb plane [the pseudocubic (110) plane was chosen because atomic resolution images have been obtained for Bi on GaAs(110), also exhibiting two distinctly oriented superstructures, show the (110) plane is parallel to the substrate].[12] The pattern clearly reproduces the periodic superstructure if the overlayer is rotated by $\sim \pm 7°$ from the substrate $[1\bar{1}0]$. The angle was determined from the six pairs of hexagonal spots rotated from GaAs(110) substrate pattern observed in previous LEED studies.[11] The hexagonal spots were used because a hexagonal phase begins to grow on top and locks in with the phase containing the superstructures. In addition, when the Sb rows were directly over the substrate rows in the Moiré pattern, the Sb atoms appeared to be aligned with the substrate rows, as observed experimentally. A simple calculation using the lattice constants of Sb in the $[1\bar{1}0]$ (Ref. 13) and GaAs in the [001] direction, reveals that the spacing between Moiré structures oriented 40° or 140° from $[1\bar{1}0]$ would be ~24 Å for an overlayer rotation of $\pm 7°$, in close agreement to the measured value.[14] To our knowledge these are the first real-space images of an orientationally ordered thin film containing grains with a surface-mediated superstructure.

Quantitative analysis of the domain-wall structure can be done by measuring the separation between adjacent domain walls and the length of the domain walls. The average spacing between domain walls was determined by measuring the distance perpendicular to the periodic superstructure, as shown in the inset of Fig. 5(a). The measurements were taken 200 Å from the grain boundaries at 200-Å intervals to avoid any possible interactions between domain wall and grain boundaries. Figure 5 summarizes the results, and a Gaussian fit indicated that the mean separation between domain walls was $110 \pm 7$ Å (one standard deviation), corresponding to a domain-wall density of $9.1 \times 10^{-3}$ Å$^{-1}$. Notice that the peak is centered about the maximum and this indicates that the domain walls are quite repulsive at 300 K. The tail that extends to the right of the peak resulted from domain walls that were parallel to the Sb superstructure. The onset of domain-wall formation in large *B*-type regions and the periodic separation between domain walls indicates that they are needed to relieve strain in the overlayer.[15,16] Figure 5(b) shows the distribution of domain-wall lengths. From it an estimate of the mean grain size for annealing temperatures of 525 K could be obtained. Under these conditions, the mean domain-wall length was $\sim 250 \pm 30$ Å.

In summary, we have shown that thin Sb films form a disordered overlayer at 300 K, but an ordered overlayer containing grains with two distinctly oriented 25-Å periodic superstructures occurs when annealed. The superstructure can be explained in terms of a Moiré effect in which the Sb(110) pseudocubic plane is rotated by $\pm 7°$ with respect to the substrate $[1\bar{1}0]$. The grains contain striped domain walls spaced $110 \pm 7$ Å apart with a mean length of $250 \pm 30$ Å for samples annealed at 525 K. The appearance of domain walls reflects strain in the overlayer and is attributed to the coalescence of adjacent islands.

This work was supported by National Science Foundation Grant No. DMR-8610837. Discussions with Y.-J. Hu are gratefully acknowledged.

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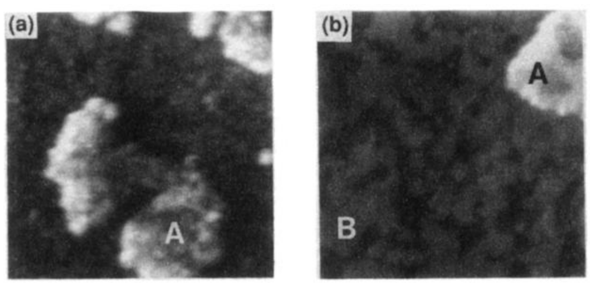



FIG. 1. (a) $400\times400$ Å$^2$ image for 4 ML Sb on GaAs(110) deposited at 300 K. The irregular island labeled *A* is ~6 Å higher than the area around it. (b) A $400\times400$ Å$^2$ image following annealing to 375 K. The *A*-type islands exhibit order and a high density of 2-Å high islands labeled *B* have formed. The $[1\bar{1}0]$ direction is oriented at 135° from the *x* axis in all figures unless noted otherwise.

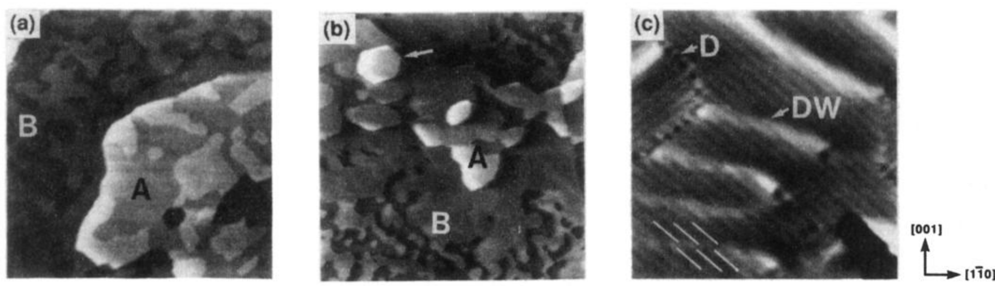
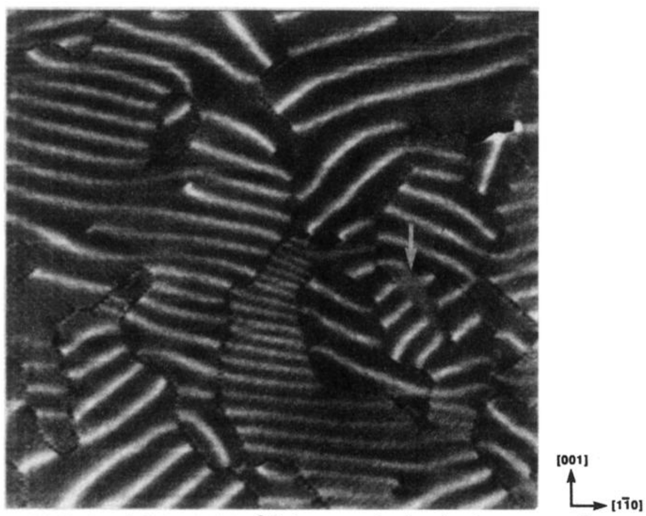



FIG. 2. (a) $1000\times1000$ Å$^2$ image obtained after annealing to 475 K showing that edges of the *B*-type islands are smoother than in Fig. 1 and that *B*-type islands have formed on the *A*-type region. (b) A $2300\times2300$ Å$^2$ image obtained after annealing at 500 K. The regions near the *A*-type islands show more *B* character, indicating that Sb diffused from the higher to lower islands. The arrow identifies an island with hexagonal symmetry, indicating the onset of bulklike Sb growth exposing a (111) surface. (c) $600\times600$ Å$^2$ image obtained after annealing to 500 K showing the two differently oriented superstructures in *B*-type regions at 40° or 140° relative to [1$\bar{1}$0]. Defects (*D*) define the boundaries between individual grains. Striped domain walls (DW) are periodically spaced. The dark region in the lower right is a monolayer Sb step.

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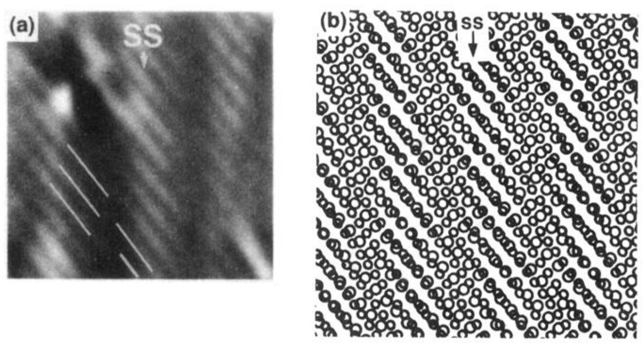


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