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Layer-by-layer etching of Si(100)-2×1 with Br_2: A scanning-tunneling-microscopy study

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Layer-by-layer etching of Si(100)-2×1 at 900 K with Br_2 has been studied with scanning tunneling microscopy. Preferential etching of S_B (ragged) step edges dominates at low Br_2 exposures but etch pits that are one layer deep (vacancy islands) also appear on the terraces. The elongated shapes of the vacancy islands indicate that etching proceeds at a much faster rate along the dimer row direction than perpendicular to it. Chains and two-dimensional islands due to Si regrowth appear on the terraces. With increased exposure, the vacancy islands form networks on the terraces and become connected to step edges. Studies of Si(100) after extended Br etching reveal global morphologies that are steady state and expose no more than three layers on a given terrace. Hence, the surface roughness is bounded.

Dry etching of semiconductors with reactive gases has been studied extensively using surface science techniques.[1] The goal has been to improve the understanding of the etching process so that these technologically significant processes can be controlled. The etching of Si surfaces with halogens has been particularly well studied, with emphasis on halogen adsorption, surface chemistry, and etching.[1] It has been speculated that layer-by-layer removal (atomic-layer etching) could be important for nanofabrication and three-dimensional circuitry.

The scanning tunneling microscope (STM) can be used to study adsorption and surface etching phenomena with atomic resolution. For example, Feltz, Memmert, and Behm[2] used the STM to study oxygen etching of Si(111)-7×7 at 950 K. They determined that the oxygen etching reaction was dependent on the terrace size and on the density of structural defects that could act as nucleation centers for pit formation. Patrin *et al.*[3] extended semiconductor STM etching studies to GaAs(110). In their study of Br_2 etching at 720 K, they showed that single-layer etching was much faster than double-layer etching. Moreover, single-layer etching in the $[1\bar{1}0]$ direction was at least ~ 4.5 times faster than in the [001] direction, thus producing rectangular etch pits.

Spontaneous etching of Si(100) with Br_2 takes place at temperatures as low as 380 K,[4] yielding different etch products at different temperatures. In temperature-dependent studies of Br adsorption on Si(100), discussed in detail elsewhere,[5] we found interesting changes in the morphology of the surface steps and terraces at 900 K. Hence, in this paper we focus on etching of Si(100)-2×1 at 900 K under conditions of constant Br_2 flux. We show that the early stages of etching are characterized by preferential modification of ragged S_B step edges since they have a large number of kink sites compared to the smooth S_A step edges. (The step edges are named S_A and S_B according to Chadi's notation.[6]) A small number of single-layer-deep etch pits (vacancy islands) are also produced on the terraces at low Br exposures. Chains and two-dimensional islands that develop on the terraces reflect the nucleation of Si atoms released by the etching process. For higher Br_2 fluences, the vacancy islands increase in number, they are elongated along the dimer row direction, and they become connected. Those that extend to the step edges contribute to step-edge roughness. Continued exposure to Br_2 at fixed flux produces a steady-state surface morphology with no more than three layers etched on any given terrace. This assures "layer-by-layer" etching. We show that this boundedness is due to the anisotropic nature of etching and the two-domain character of Si(100).

The experiments were conducted using an ultrahigh vacuum Park Scientific Instruments STM. The operating pressure in the system was $\sim 4\times10^{-11}$ Torr. We used polished *p*-type Si wafers (B-doped, resistance <0.01 Ω cm) that were oriented to within 0.5° of (100). The wafers were cleaned *ex situ* by rinsing in ethanol. They were cleaned *in situ* by degassing overnight at 600 °C, followed by flashing at 1200 °C for 1–2 min. This procedure has been shown to produce well-ordered Si(100)-2×1 surfaces with low defect densities.[7] An electrochemical cell was used to provide molecular Br_2.[8] The dosages, measured as the product of electrical current through the cell and the time of exposure to the source, are given in units of mA sec. The source produces molecular bromine that dissociates on reaching the surface.[4,9] The chamber pressure was kept below 8×10^{-11} Torr during Br_2 dosing. Sample temperatures were measured using an optical pyrometer. Electrochemically etched tungsten tips were cleaned using electron beam bombardment prior to imaging. The tip scanner was calibrated with the lattice constant of the Si(100) surface and the height of monatomic steps. All images were acquired in the constant tunneling current mode. They are presented as gray-scale images where the brightness is proportional to the measured height.

Figures 1(a)–1(d) represent 2000×2000 Å^2 STM images of the occupied states that were acquired after exposing clean Si(100)-2×1 surfaces to Br_2 fluences of (a) 0, (b) 0.4, (c) 1.2, and (d) 2.4 mA sec. The surface steps down from the upper left corner to the lower right corner in all of the images. In all cases, the Br_2 flux was kept constant and only the exposure time was changed. Samples were rapidly cooled to room temperature immediately after shutting off the Br_2 source. The clean surface of Fig. 1(a) shows the familiar S_A and S_B single-height

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steps.[6] For a Si(100) surface with a miscut of 0.5°, the average step spacing would be approximately 160 Å, as confirmed by STM results. The areal ratio of S_A to S_B steps is ~70%. This has been observed consistently for various samples having the same miscut and under similar conditions of clean surface preparation. Therefore, we do not expect factors such as external strain[10] to affect this ratio from one experiment to another. Small-scale images of the clean surface show alternating 2×1 domains on subsequent terraces, exhibiting dimer resolution in occupied-state images.[11]

Several aspects of the Si(100) surface are important for understanding etching and the associated changes in step structures. The dimer rows in the upper terrace are parallel to the step edges for S_A steps and they are orthogonal to the step edges for S_B steps. Neglecting long-range strain effects, the formation energy of S_A steps, E_A, is ~0.01 eV/a where a, the dimension of the surface unit cell, is 3.84 Å.[6] For comparison, the energy of S_B steps, E_B, is ~15 times higher.[6] Both steps are straight at 0 K but kinks form and the steps meander from their equilibrium configuration at higher temperature.[12] Structurally, a kink in a straight line S_A step amounts to an additional dimer unit such that the dimer bond is per-

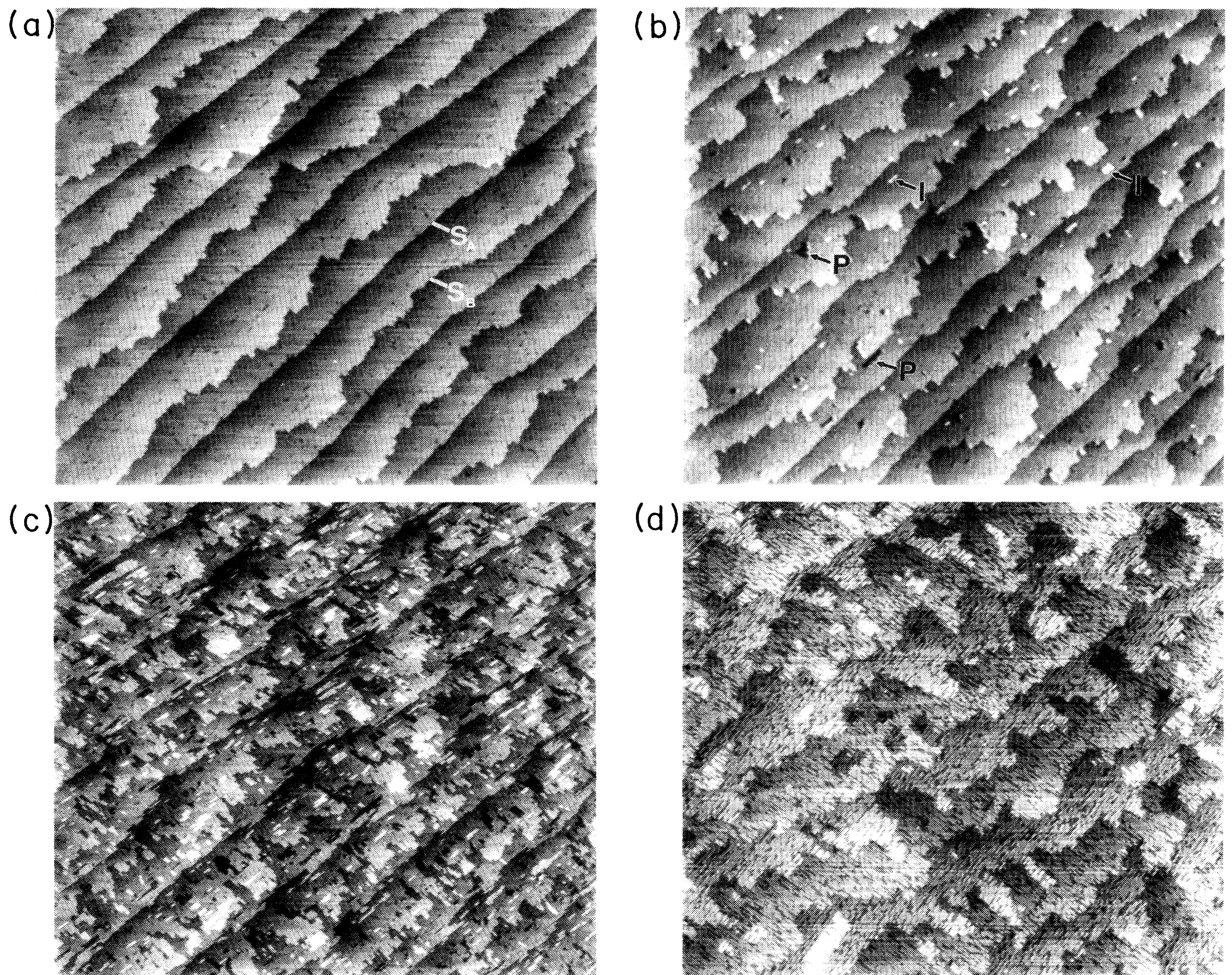

FIG. 1. Occupied-state STM images (2000×2000 Å^2) of (a) Si(100)-2×1 (−1.4 V, 1.5 nA). Typical single height steps are labeled as S_A (smooth) and S_B (ragged). The areal ratio of S_A is ~70%. (b) Si(100)-2×1 after 0.4 mA sec Br_2 fluence at 900 K (−3.1 V, 2 nA). Preferential etching of S_B steps has occurred since the areal ratio of S_A and S_B has increased by 15% compared to the clean surface. This also produces more squareness in the S_B steps. Terrace etching produces one-layer-deep vacancy islands or etch pits, denoted *P*. Most vacancy islands are elongated along the dimer rows with aspect ratios of >10:1. Bright features, marked *I*, represent Si islands nucleated on the terraces. (c) Si(100)-2×1 after 1.2 mA sec Br_2 fluence at 900 K (1.4 V, 1.5 nA). Both S_A and S_B steps show an increasingly mixed character. The number of vacancy islands has increased more than by a factor of 3 relative to (b). Second-layer etch pits have formed inside the first-layer vacancy islands. (d) Si(100)-2×1 after 2.4 mA sec Br_2 fluence at 900 K (1.4 V, 1.6 nA). Both step types exhibit a highly mixed appearance. The vacancy islands have grown and have connected with each other and/or with step edges.

pendicular to the step. A kink in a straight line S_B step produces a dimer unit in a direction parallel to the step. Therefore, kinks in S_A steps are of S_B type and vice versa. Since the energy of S_B steps is higher, kinks are less favored on S_A steps. Hence, S_A steps remain relatively straight even at higher temperatures. The opposite is the case for S_B steps and they exhibit a more ragged appearance.

Figure 1(b) was obtained after a relatively small fluence of 0.4 mA sec Br_2 at 900 K. (A fluence of ~ 1.5 mA sec at 300 K is estimated to be equivalent to 1 monolayer on the surface. However, it is difficult to estimate the effective Br coverage at 900 K based on the 300-K value since the sticking coefficients change with temperature, the surface structure, and composition.) Inspection of Fig. 1(b) and STM images obtained at higher fluence show increased linearity in the S_B step profile, i.e., an increase in the average kink-kink separation. Analysis of Fig. 1(b) shows that the result of such etching is to increase the areal ratio of S_A to S_B terraces by $\sim 85\%$, thus indicating that the S_B steps are etched preferentially.

The preferential etching of the S_B steps over S_A steps can be explained in terms of the formation energies of steps. Again neglecting long-range strain effects, dimer removal from a perfectly straight S_A edge forms a new S_B edge of length $4a$ while dimer removal from a perfectly straight S_B edge creates the equivalent of an S_A edge of length $2a$.[13] Given the different formation energies, dimer removal from the straight S_B step edge would be favored over removal from the straight S_A step edge. Also, dimer removal from the terrace would be the most difficult since that is equivalent to the creation of an S_A edge of length $2a$ and an S_B edge of length $4a$. Inspection of Fig. 1(b) does show minimal terrace etching. Single-atom removal from a dimer such that the other atom becomes unstable and is free to diffuse on the surface is also possible. It can be seen that the relative atom-removal energies will follow the same trend as discussed above for dimer removal.

Similar arguments demonstrate that etching will be easiest at existing kinks because there is no net step creation. Even more favorable etching would involve the removal of atoms from a single dimer row that extends outward beyond the step edge since this effectively reduces the step length. Since the S_B steps of the clean surface possess kinks, the initial stages of etching would occur on these S_B steps, into the step. Etching of S_A steps would start at the few existing kinks and would be parallel to the step. That it is easier to remove atoms from the ends of dimer rows is also supported by studies of high-temperature growth of Si on Si(100) (Ref. 14) and vacancy kinetics on Si(100) under low-energy Xe ion bombardment.[15]

While terrace etching is less likely than edge etching, inspection of Fig. 1(b) shows that a few dark patches or etch pits, marked P, do form on both types of terraces. These pits are a single layer in depth and represent vacancy islands. High-resolution images of this surface show that the dimer rows of the exposed underlying layer are orthogonal to the dimer rows on the main terrace, as expected. In a simplistic picture, a vacancy island is created on the terrace by the removal of a terrace dimer. This missing dimer gives rise to a kink site on the terrace that favors the removal of subsequent terrace dimers. Two possibilities arise for the removal of the second dimer from this newly created kink site, namely, the next dimer that is removed can be along the dimer row direction or it can be along the dimer direction. Energy arguments favor the former by a factor of ~ 15, the ratio E_B/E_A. Note that a chain of missing dimers along the row direction on a terrace forms an S_A step edge while an S_B step edge is created by etching in the dimer direction. Thus, the shape of the islands should reflect this anisotropic nature of etching and they should be elongated in the direction of the dimer rows. Figure 1(b) shows that a majority of the islands have aspect ratios of $> 10{:}1$ with the longer direction being parallel to the dimer rows. However, analogous to homoepitaxial growth of Si on Si(100),[16] it is possible that these shapes do not represent equilibrium island shapes but are merely kinetically limited structures. More experiments are being conducted to explore this possibility.

Bedrossian and Klitsner[15] recently examined vacancy formation and diffusion on Si(001)-2×1 exposed to a low-energy Ar-ion beam at 723 K. They found that vacancies could form stable islands on S_A terraces. On S_B terraces, however, no vacancy islands were formed because the vacancies could reach S_B step edges and be accommodated. In our studies, we have observed that the number of vacancy islands on the two types of terraces is quite comparable, implying a different mechanism of vacancy island formation. As discussed above, we propose that islands are formed upon etching by the removal of a dimer, thereby establishing a kink site, and the subsequent removal of atoms from adjacent dimers.

Figure 1(b) shows a few bright protrusions, labeled I (for islands), on the mildly etched surface. Most represent one-dimensional chains that are oriented perpendicular to the substrate dimer rows on both types of terraces. These features are not characteristic of the clean Si(100) surface.[11] They are 1.4 Å in height, equal to the height of a single step on Si(100). Hence, they are most likely Si islands that have formed from Si atoms freed from stable surface bonds when Si dimers are broken as $SiBr_x$ desorbs during etching. These atoms can diffuse on the surface at 900 K; some will reach steps where they can be accommodated while others can bond to diffusing Si atoms, forming stable nuclei that grow on the terraces. Such growth structures have previously been reported for the case of Si on Si(100).[16,17]

The image of Fig. 1(c) was obtained after a Si(100) surface was exposed to a fluence of 1.2 mA sec, nearly three times as much as for Fig. 1(b). At this stage, both types of step edges exhibit substantially greater roughness but the peninsulas and the vacancy islands retain their straight edges. Etching anisotropy is easily observable at this stage because a large number of vacancy islands are elongated in the dimer row direction. In addition, the removal of Si as a result of etching has produced isolated missing dimer and atom rows. High-resolution images

show that some of the vacancy islands develop smaller vacancy islands inside them as etching proceeds to the second layer. These second layer islands are also elongated in the dimer row direction. The third layer is etched only in a few areas.

Figure 1(d) shows results of etching with a fluence ~2 times that of Fig. 1(c). The original S_A and S_B step structures have almost disappeared as both edges have a highly mixed character and the step structure is that of randomly wandering steps. Most of the vacancy islands have probably connected with each other and with the step edges as a result of increased etching. Consequently, fewer vacancy islands are seen on the terraces. This surface morphology does not change even if the fluence is increased by another factor of 3, indicating that a steady-state condition has been achieved. Under these conditions, no more than three atomic layers are seen on any given terrace. The roughness of the surface for this type of Si(001) etching will always be bounded and will not increase in proportion with the Br_2 fluence.

We believe that the boundedness in the roughness of the surface is due to the "pyramid effect," an effect used to explain the boundedness in the interface width during homoepitaxial growth of Si on Si(100).[18] Here the roughness of the surface is determined by the number of layers that can be etched at a given time. The etch pits or vacancy islands formed on the terraces contribute to roughening while etching of step edges related to the miscut of the surface does not. The vacancy islands are elongated due to anisotropic etching and removal of Si from the second layer is possible when it is exposed on the terrace. Thus, etching of the second layer to expose the third layer requires the formation of a vacancy island "inside" the first vacancy island. The longer dimension of the second island would be parallel to the smaller dimension of the first because of the etching anisotropy and orthogonality of the dimer rows on any two adjacent terraces, constraining the length of the second-layer vacancy island to be less than or equal to the smaller dimension of the first-vacancy island. In the limiting case, any etch pit must be an inverse pyramid such that the depth of the pyramid is governed by the shorter dimension of the rectangular base. Therefore, the anisotropy in etching ensures that the roughness of the surface remains bounded at all times and it etches in almost a layer-by-layer fashion.

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[1]For an excellent review, see H. F. Winters and J. W. Coburn, Surf. Sci. Rep. **14**, 161 (1992).

[2]A. Feltz, U. Memmert, and R. J. Behm, Chem. Phys. Lett. **192**, 271 (1992).

[3]J. C. Patrin, Y. Z. Li, M. Chander, and J. H. Weaver, Appl. Phys. Lett. **62**, 1277 (1993).

[4]R. B. Jackman, R. J. Price, and J. S. Foord, Appl. Surf. Sci. **36**, 296 (1989).

[5]M. Chander, Y. Z. Li, J. C. Patrin, and J. H. Weaver (unpublished).

[6]D. J. Chadi, Phys. Rev. Lett. **59**, 1691 (1987).

[7]B. S. Swartzentruber, Y.-W. Mo, M. B. Webb, and M. G. Lagally, J. Vac. Sci. Technol. A **7**, 2901 (1989).

[8]N. D. Spencer, P. J. Goddard, P. W. Davies, M. Kitson, and R. M. Lambert, J. Vac. Sci. Technol. A **1**, 1554 (1983).

[9]V. Eteläniemi, E. G. Michel, and G. Materlik, Surf. Sci. **251/252**, 483 (1991).

[10]F. K. Men, W. E. Packard, and M. B. Webb, Phys. Rev. Lett. **61**, 2469 (1988).

[11]See, for example, R. J. Hamers, R. M. Tromp, and J. E. Demuth, Phys. Rev. B **34**, 5343 (1986).

[12]O. L. Alerhand, A. N. Berker, J. D. Joannopoulos, D. Vanderbilt, R. J. Hamers, and J. E. Demuth, Phys. Rev. Lett. **64**, 2406 (1990); T. W. Poon, S. Yip, P. S. Ho, and F. F. Abraham, *ibid.* **65**, 2161 (1990); E. Phelke and J. Tersoff, *ibid.* **67**, 465 (1991).

[13]We note that kinks observed on the S_B steps always have an even number of dimers. This is because an odd number of dimers would mean the formation of the high-energy S_B' step that does not have rebonded atoms at the edge [see C. Roland and G. H. Gilmer, Phys. Rev. B **46**, 13 437 (1992); B. S. Swartzentruber, Y.-W. Mo, R. Kariotis, M. G. Lagally, and M. B. Webb, Phys. Rev. Lett. **65**, 1913 (1990); for a detailed structure of the S_B' step, see D. J. Chadi, *ibid.* **59**, 1691 (1987)]. Thus, it can be argued that removal of one dimer from an S_B edge essentially requires an energy of $2a[E_A+(E_B'-E_B)]$. From Ref. 6, $E_B'-E_B=0.16$ eV. This energy is less than $4E_B$. Thus, dimer removal from the ends of dimer rows is still favored.

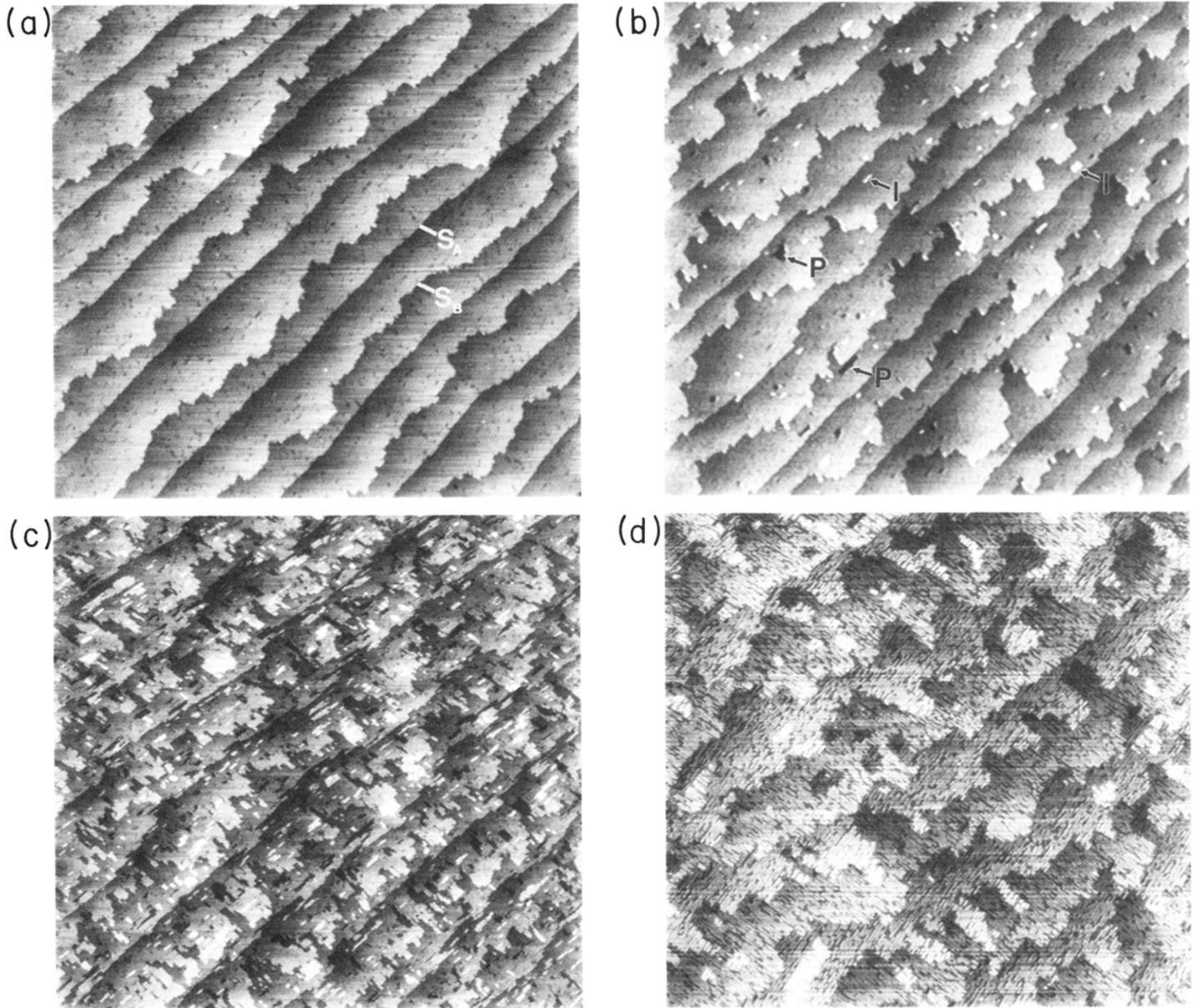
[14]K. Sakamoto, K. Miki, and T. Sakamoto, Thin Solid Films **183**, 229 (1989); A. Hoeven, J. Lenssinck, D. Dijkkamp, E. van Loenen, and J. Dieleman, Phys. Rev. Lett. **63**, 1830 (1989).

[15]P. Bedrossian and T. Klitsner, Phys. Rev. Lett. **68**, 646 (1992).

[16]Y.-W. Mo, R. Kariotis, B. S. Swartzentruber, M. B. Webb, and M. G. Lagally, J. Vac. Sci. Technol. A **8**, 201 (1990).

[17]R. J. Hamers, U. K. Kohler, and J. E. Demuth, J. Vac. Sci. Technol. A **8**, 195 (1990).

[18]Y.-W. Mo, R. Kariotis, D. E. Savage, and M. G. Lagally, Surf. Sci. **219**, L551 (1989).



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