

Anisotropic growth of twinned cubic crystals

R. Jagannathan, R. V. Mehta, J. A. Timmons, and D. L. Black
Eastman Kodak Company, Rochester, New York 14652-3208
 (Received 16 March 1993)

The anisotropic growth of twinned platelets having a cubic crystal structure is examined by a ball-model simulation of the growth process. The simulation has suggested that the long-accepted growth mechanism, which relies on the self-regenerating {111} faceted-side-face structure, may need revision. Such a side-face structure is likely to transform into a different structure where the twin bands are bound by {100} planes. Experimental evidence is presented to support this structure for the silver halide system.

Twinned platelets of crystals with cubic lattices have been long studied and used in technological applications. Melt-grown twinned germanium platelets received considerable attention in the mid 1950s for producing sheets or ribbons of the proper thickness for fabricating electronic devices.¹ Twinned platelets of silver halide, which were grown in ionic solution, were also studied as they were useful in photographic products.^{2,3} Recent studies of diamond films suggest that the growth of twinned diamond platelets plays a significant role in the texturing of films that are grown by chemical vapor deposition.^{4,5} The widely accepted explanation for the largely two-dimensional growth of these twinned platelets was originally proposed by Hamilton and Seidensticker (HS).⁶ According to their proposal, germanium platelets contain two or more twin boundaries parallel to their major {111} faces. This leads to the formation of {111} faceted reentrant grooves on the sides of the platelets (Fig. 1). The grooves provide preferential sites for the nucleation of new layers and are regenerated as the layer growth is completed. The enhanced lateral growth of the crystals is thus attributed to the self-regenerating side-face geometry. The details of the growth process of silver halide³ and diamond⁴ platelets are believed to be analogous. A similar mechanism is also believed to operate in the sintering of supported platinum catalysts⁷ and in the transformation of silicon from amorphous to crystalline form.^{8,9} One of the striking features of the HS theory is that it allows a growth layer to spread over the 218.9° ridge [Fig. 1(A)]. At the atomic level, it represents surface diffusion across an edge that exists between two planes in a twinned contact. Surface diffusion can occur across an edge but usually it is a slower process than the layer spreading. In fact, direct observation by field ion microscopy has revealed that at low temperatures atoms do not roll over a plane boundary—instead they are reflected.¹⁰ The extent to which this reflection persists at higher temperatures is not known. How these considerations may differ for atomic crystals versus ionic crystals is also unclear. The edge may represent an energy trap for ionic lattices¹¹ and an energy barrier for atomic lattices.¹² In view of the accepted validity of the HS theory for a broad range of systems, a more detailed examination of the atomic configurations of growth surfaces and the growth process is done with a space-filling ball model of a

twinned silver halide platelet. It suggests that the regeneration of {111} faceted sides of the platelets may be energetically a less likely process. An alternative growth mechanism is suggested where the self-regeneration of side faces is driven by {100} planes in twinned contact with {111} planes. Experimental evidence is presented to support the alternative mechanism for the silver halide system.

The ball model is made by physically stacking a number of identical hard spheres in a sodium-chloride-type face-centered cubic structure with two parallel {111} twin planes. Each sphere represents a pair of silver and bromide ions. The side faces of the resultant model are {111} planes. The dynamics of the growth process is simulated by growing one layer at a time. A layer

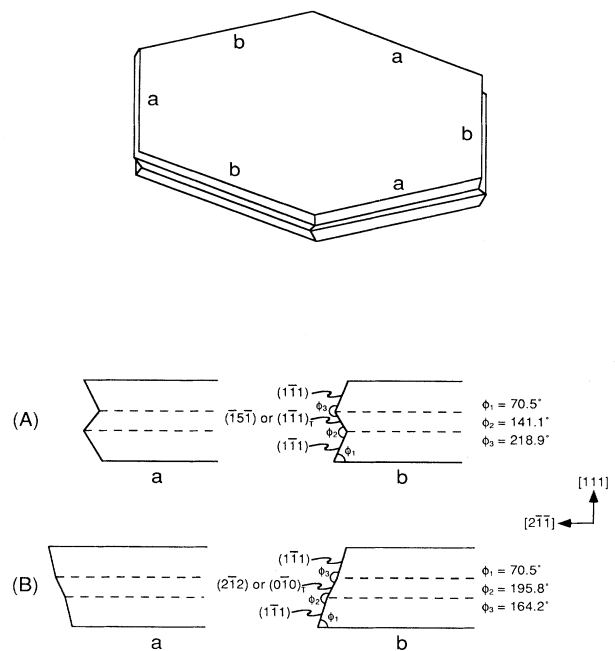


FIG. 1. A hexagonal silver halide platelet containing two parallel twin planes and its side-face structures as seen in a <110> section: (A) ridge-trough structure; (B) rough-smooth structure.

spreads by incorporation of adatoms at the half-crystal positions. The latter are approximated as sites with five or more nearest neighbors. If there are no half-crystal positions on the growth surface, a nucleation event is deemed necessary. The nucleation event is essentially the deposition of a stable two-dimensional cluster on the surface that provides new half-crystal positions.

For a given supersaturation, crystal growth occurs by adsorption and desorption of atoms on crystal surface, with frequencies that are determined by the number of nearest neighbors. An isolated adatom at a surface site on a $\{111\}$ plane of a silver bromide crystal has three nearest neighbors. From statistical thermodynamics, the probability of incorporation at a kink site, therefore, would be $\exp\{(j-3)\mu/kT\}$ times higher than that at a surface site; j is the number of nearest neighbors, μ is the potential energy of one interatomic bond, k is the Boltzmann constant, and T is the absolute temperature. The reentrant corner provides four nearest neighbors to an adatom. Assuming $\mu/kT=4$, the probability of adatom incorporation at the reentrant corner would be 54 times higher than that at a surface site. Therefore, the reentrant grooves are the preferred sites for the nucleation of the new growth layers.

A growth layer is initiated by depositing a two-dimensional stable cluster at the reentrant groove [Fig. 2(a)]. Half-crystal positions are then available for the growth layer to extend in two opposite directions—toward the 70.5° acute lip where a $\{111\}$ side face has a boundary with the major $\{111\}$ face, and also toward the 218.9° ridge, where two $\{111\}$ side faces are in twinned contact with each other. According to the HS theory, the growth layer would form a 109.5° ledge at the ridge. The theory further assumes that nucleation at that ledge is more likely than at the 141.1° reentrant corner. The spreading of the growth layer across the ridge is thus considered energetically favorable. From an energetic viewpoint, it implies that as the growth layer advances towards the ridge, there is no loss of coordination number. The growth layer then continues to spread to the 109.5° obtuse lip, thereby reconstructing the entire side-face structure. The subsequent attempts to extend³ and amend the HS theory for the growth of silver halide platelets, also assume the validity of the rapid spreading of the growth layer across the 218.9° ridge despite invoking a more important role for the non- $\{111\}$ crystallographic planes.^{13,14}

The simulation of the growth process, however, shows that as the growth layer approaches the ridge, half-crystal positions disappear and a vicinal $\{100\}$ face emerges [Fig. 2(b)]. The $\{100\}$ face provides a coordination number of only 4. Thus, there is an unexpected loss of coordination number on the growth surface as the growth layer approaches the ridge. Consequently, the energetics of addition of the next adatom at the boundary of the layer is expected to be less favorable than assumed in the HS theory.

The $\{100\}$ face forms a 164.2° ledge at the ridge [Fig. 2(b)], which is significantly shallower than the 109.5° ledge assumed in the HS theory. Similarly, as the growth layer approaches the 70.5° acute lip, a $\{100\}$ face appears

there as well. There are now three locations on the side-face geometry, each providing four nearest neighbors: a $\{100\}$ face at the 70.5° acute lip, another $\{100\}$ face that has formed the 164.2° ledge at the ridge, and the 141.1° reentrant corner. Since adatom interactions with second nearest neighbors are considered to be important at curved interfaces, it is hypothesized that the propensity for nucleation is highest at the $\{100\}$ face at the acute lip (highest curvature) and lowest at the 164.2° ledge at the ridge (lowest curvature). Under the limiting conditions, the ledge-forming $\{100\}$ face would extend away from the ridge. Eventually, a new side-face configuration emerges where the central side face is a $\{100\}$ face, flanked on either side by $\{111\}$ faces [Fig. 1(B)].

Thus, depending on the energetics of the diffusion across a plane boundary and the intrinsic growth kinetics

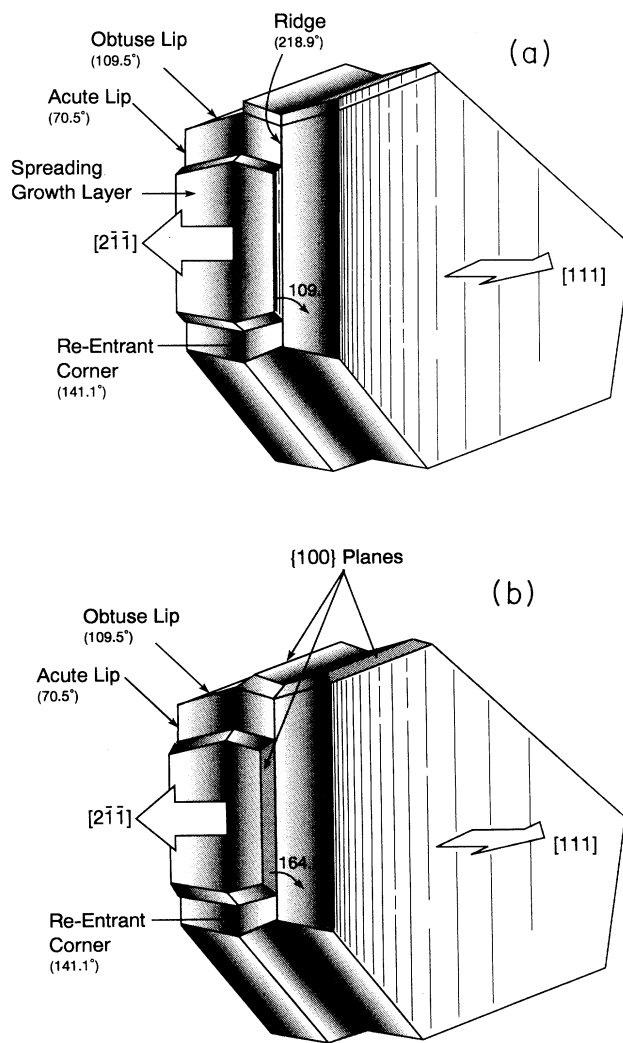


FIG. 2. The transformation of $\{111\}$ faceted-side-face geometry: (a) a platelet with two parallel twin planes showing the 109.5° ledge at the ridge as proposed by the HS theory; (b) a platelet with two parallel twin planes showing the vicinal $\{100\}$ planes as suggested by the ball-model simulation.

of $\{100\}$ and $\{111\}$ planes, the $\{111\}$ bound side-face structure may be transformed as shown in Fig. 2(b). The new side-face structure is identical to the one recently proposed by Ming and Sunagawa.¹⁵ A growth layer can be initiated with a nucleation event on the $\{100\}$ face. Since there is no loss of coordination number as the layer approaches the 195.8° ridge, its spreading across the ridge is likely to be energetically favored, resulting eventually in the regeneration of the side-face geometry. Thus self-regeneration derives from the presence of the $\{100\}$ plane and not on the reentrant corner. Furthermore, under the high excess halide growth environment of silver halide platelets, the $\{100\}$ planes are expected to be atomically rougher than the $\{111\}$ faces. Kink sites on such atomically rougher $\{100\}$ faces would always provide half-crystal positions. A growth layer can be initiated from those sites without necessitating a nucleation event. The additional role of atomic level surface topography of the new structure is recognized by naming it as the "rough-smooth" side-face structure. The preferred lateral growth is then seen as a result of crystal geometry working in concert with the growth environment. The self-regeneration of the "rough-smooth" side-face structure is different from the cooperative growth mechanism proposed by Ming and Sunagawa.¹⁵ The latter invokes lateral growth that is governed alternately by the reentrant groove and the rough surface but does not consider self-regeneration of side-face structures.

The HS theory has been believed to be valid for a silver halide system over the years because of its utility in explaining various parallel as well as nonparallel twinned crystals found in the population of a typical silver halide precipitation. The direct experimental proof of the side-face structure, however, has not been available because of the small thickness of the platelets and other intrinsic difficulties in the sample preparation, including the radiation sensitivity. Some of these obstacles have been overcome in recent years with the application of cryoultramicrotomy to silver halide platelets. The technique involves coating a photographic emulsion on a film base, sectioning an ultrathin ($< 0.06 \mu\text{m}$) slice of that film at liquid nitrogen temperature with a special jig, and observing its transmission electron micrograph (TEM) image.¹⁶ Since the major faces of the platelets usually become parallel to the film base during coating, the sections essentially provide slices of individual platelets that are cut almost perpendicular to the major faces. The TEM image reveals the internal twin plane structure along with the side-face geometry. However, as the slices are cut at random angles to the edges of the platelet, and edge rounding can occur during the sample preparation, unambiguous measurements of angles between side faces are difficult. Yet, qualitative geometric features can be observed with this technique for a large number of crystals. The side-face geometries of a platelet as predicted by different models can thus be verified by this technique.

The alternating side-face geometry of a platelet with three parallel twin planes, consisting only of $\{111\}$ planes, is shown in Figs. 3(a) and 3(b). As suggested in the preceding analysis, the $\{111\}$ faceted reentrant groove in Fig. 3(b) would transform to a $\{100\}$ faceted

250.6° ridge at the central twin plane as shown in Fig. 3(c). Thus, the alternate sides of triply twinned platelets may be either like Figs. 3(a) and 3(b) or like Figs. 3(a) and 3(c). Cryoultramicrotomed sections of such platelets, depending on how the cuts are made, should reveal these features.

Low aspect ratio $\text{AgBr}_{0.992}\text{I}_{0.008}$ platelets were precipitated in a high excess bromide solution growth environment ($p\text{Br} < 1.32$). The mean equivalent circular diameter and thickness of the platelets were $1.40 \mu\text{m}$ and $0.36 \mu\text{m}$, respectively. The TEM of a carbon replica of a representative sample of the crystal population is shown Fig. 4(a). The number density of the particles in the solution was estimated to be 10^{20} – 10^{21} particles/ m^3 . A sample of this solution was coated on the film base and sliced by cryoultramicrotomy. From a total of 90 TEM images of sliced platelets that were examined, about 25% contained three parallel twin planes. Again, only a third of those triply twinned crystals showed the side-face geometry clearly. The slice shown in Fig. 4(b) is typical of those slices with three twin planes and a well-defined side-face structure. The ridges at the two ends of the slice can be seen very clearly. This is a strong evidence supporting the existence of the rough-smooth side-face structure [Fig. 3(c)]. It is interesting that none of the other possible combinations of the side-face structures were found. Perhaps this was influenced by the shape of the platelets. If the sliced platelets were truncated triangles then it is possible that the sections would more likely cut across the large sides of the triangles and reveal the same side-face geometry at both ends of the platelets. Similar evidence for the existence of the $\{111\}$ -bound side-face structure was not found. While this does not prove that it does not exist, in light of the experimental data and the analysis presented in this paper, it is suggested that it is less likely to exist and the ideas about the anisotropic growth of twinned platelets need to be revised.

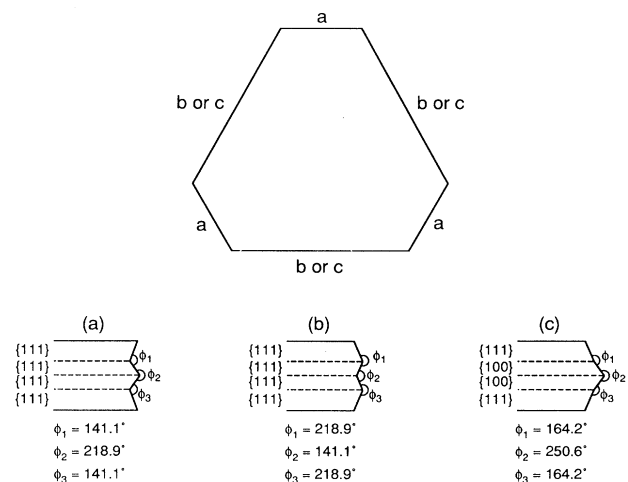
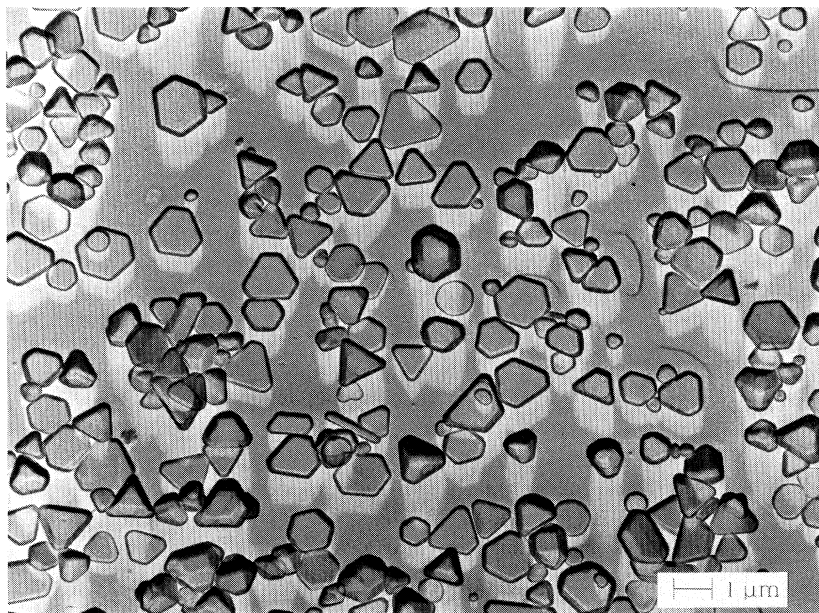


FIG. 3. Alternate side-face structures of a platelet with three parallel twin planes.

(a)



(b)

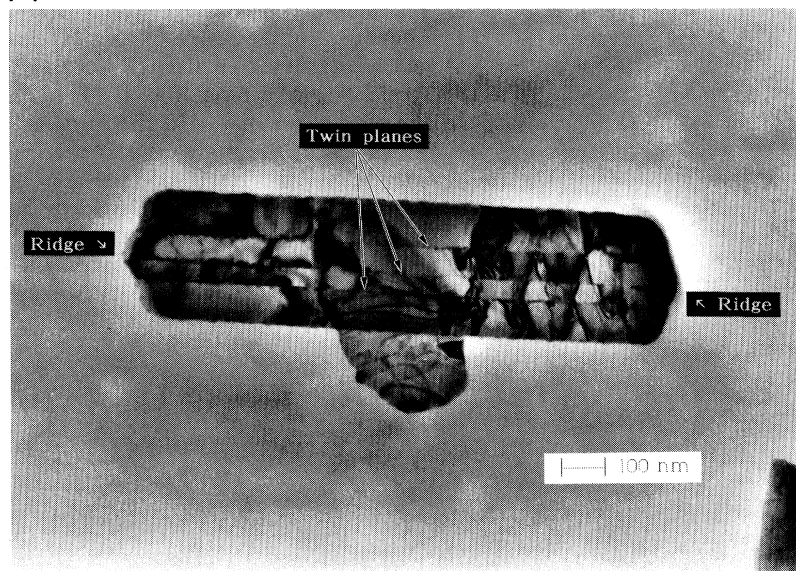


FIG. 4. Experimental evidence of the existence of the rough-smooth side-face geometry: (a) photomicrograph of a carbon replica of the sample of silver halide suspension that was cryosectioned. (b) TEM of a cryoultramicrotomed section of a triply twinned silver halide platelet. Note the ridges on the two side faces.

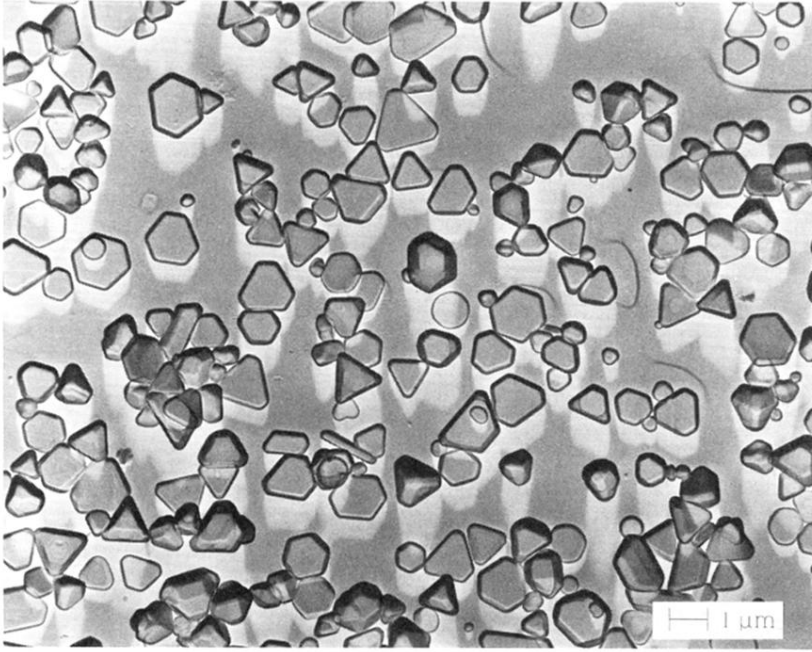
It is recognized that the ball-model simulation of unreconstructed surfaces may be simplistic. The qualitative trends, however, may be correct as seen in the case of silver halides. The new growth mechanism should also operate in the growth of twinned platelets of other cubic lattices. For materials with atomic fcc lattice (e.g., platinum), the above ball-model simulation should be directly applicable. While the coordination number for diamond cubic materials is different, similar considerations should apply. For these materials, $\{100\}$ and $\{110\}$ planes are likely to be atomically rougher than $\{111\}$ planes¹⁷ when analyzed with Hartman and Perdok¹⁸ classification. In fact, unreconstructed $\{100\}$ surfaces may be rougher than the $\{110\}$ surfaces. Geometrically, however, only

$\{100\}$ planes can emerge at the 218.9° ridge (Fig. 1). Unless surface reconstruction or chemisorption of impurities plays a significant role, it is suggested that the growth of twinned platelets of diamondlike materials may also be driven by the "rough-smooth" side faces of the platelets. It is hoped that the results presented here will stimulate a more detailed analysis of this problem with more sophisticated simulation techniques like Monte Carlo or molecular dynamics.

The authors would like to acknowledge J. F. Hamilton for suggesting the ball-model simulation and Dr. J. S. Wey and R. G. L. Bottger for constructive criticisms.

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(a)



(b)

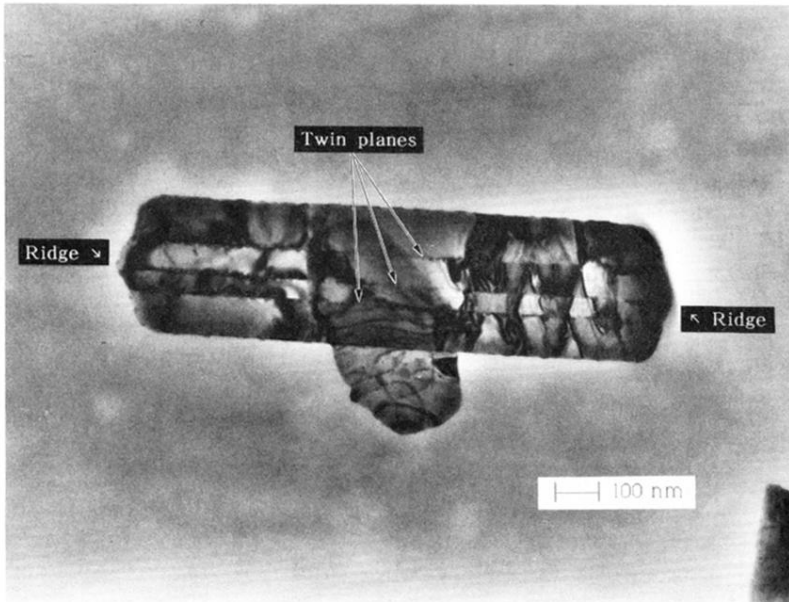


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