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HILLOCKS ON FIRST-ORDER PRISM FACES OF SYNTHETIC QUARTZ

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ABSTRACT

Square-shaped growth hillocks observed on first-order prism faces of synthetic quartz are illustrated. These hillocks interact with growth layers from other initiating centres and lead to the modification of the shapes of such hillocks. Pits replace hillocks on etching and polishing and re-etching. Pits at the centres of hillocks are related to linear defects, probably screw dislocations. Possible twin boundaries bound areas of differing hillock orientation.

INTRODUCTION

Prism faces of natural quartz crystals are characterised by horizontal striations perpendicular to the *c*-axis. Van Praagh and Willis (1952) reported tetragonal growth pyramids on such faces, where the longer edges of the pyramids were shown to constitute such striations. Joshi (1959) reported vertical striations parallel to the *c*-axis of first-order prism faces of synthetic quartz. In order to understand the mechanism of growth of first-order prism $\{11\bar{1}0\}$ faces in particular and synthetic quartz crystals in general, we carried out a detailed topographical study of $\{11\bar{1}0\}$ faces of over a hundred synthetic quartz crystals grown on different types of seed plates. This paper deals with the mechanism of the formation of hillocks observed on these faces.

Daly (1899) has reported hillocks on hornblende and interpreted them as etch hillocks. Honess (1927) refers to raised hillocks on the surface of a crystal and according to him the hillocks are not a result of an etch phenomenon. Hillocks observed by Williams (1932) were of the layer type and were interpreted as growth hillocks. According to Buckley (1951) all natural hillocks should be treated as produced by growth when they show a degree of symmetry corresponding to that of the face. He goes to the extent of saying that practically all symmetrical figures that are hillocks are growth hillocks. Hillocks on prism faces of natural quartz have been reported by Zimonyi (1957). Batterman (1957) observed hillocks on germanium surfaces. He showed that they are real projections produced during the etching process, and possess the symmetry of the crystal face on which they occur. According to him hillock formation is not related to internal structure but is a surface nucleated phenomenon and such hillocks do not correlate with dislocations intersecting the crystal surface. The faces bounding the hillocks were interpreted as limiting etch planes. Augustine and Hale (1960) also reported characteristic hillocks on prism faces of synthetic quartz and attributed them to growth. By etching experiments they showed that each hillock is replaced by a corresponding pit. Meckel and Swalin (1959) reported sputter-produced hillocks and attributed them to imperfections where the sputtering rate is comparatively smaller than elsewhere. Haneman and Chung (1963), however, attributed hillocks to impurity clusters of low sputtering rates. Meckel (1966) correlates hillocks on germanium to screw dislocations. Joshi and Vagh (1966) reported hillocks on first-order prims $\{10\bar{1}0\}$ faces of cultured quartz and explained them as a result of dissolution. In their case the surface surrounding the hillocks was mottled and highly rough.

Observations

Correlation of growth hillocks with linear defects. Crystal faces were thoroughly cleaned and were silvered in a vacuum coating unit. These faces were then examined under a metallurgical microscope, using optical techniques, including light profile (Tolansky 1952) and the multiple beam interferometry (Tolansky 1948).

It may be mentioned that practically every first-order prism face that we examined had some kind of hillocks, although their density differed in different cases. All these faces were remarkably plane, brilliant and lustrous, showing no sign of any etching.

Figure 1 is a photomicrograph showing a number of closely spaced hills. They look like cones or shells and are oriented. Figure 2a illustrates some square-shaped hillocks. Examining on a higher magnification one can see very clearly the growth layers composing such hillocks (Figure 2b). It seems there are a large number of growth centres in this case. One more case of densely populated square hillocks is shown in Figure 3. These hillocks are also strictly oriented. Parachute-like hillocks are illustrated in Figure 4a. It is suggested that these hillocks are also square shaped but because they are partly covered over, unevenly, by the growth layers from some other growth center from the top-right corner of Figure 4a, they assume parachute-like shapes. The modification of such growth layers as they move past these hillocks endorses this suggestion.

This face (shown in Figure 4a) was then etched with 20 percent hydrofluoric acid vapour at room temperature for 30 hours. The resulting etch pattern thus obtained is illustrated in Figure 4b. Here it is seen that most of the growth fronts of Figure 4a are washed off and each hillock of Figure 4a is replaced by a corresponding etch pit. This suggests that the hillocks correspond to some kind of dislocations on the crystal face, which may probably be screw dislocations. To investigate whether or not such dislocations penetrate into the body of the crystal the face was subjected to prolonged etching. Figures 4c and 4d illustrate etch pat-

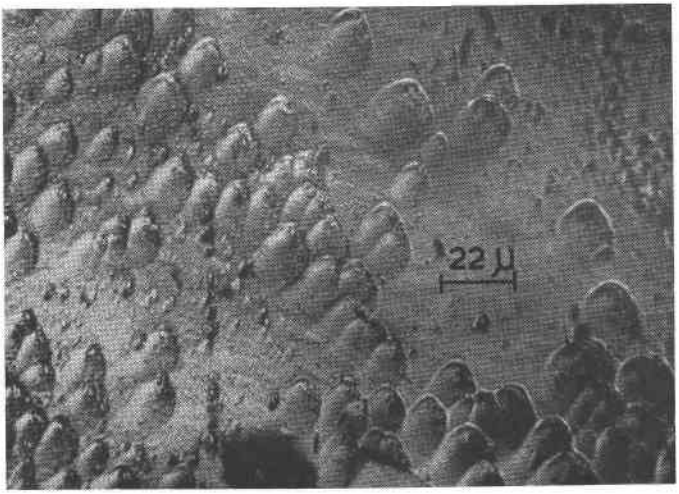

FIG. 1. Cone-like closely spaced hillocks.

terns produced on the same region when etched in the same etchant for 50 hours and 80 hours respectively. It is seen that the point-bottomed pits of Figure 4b, which correspond to hillocks of Figure 4a, have gone deeper and have increased in their lateral dimensions, while the flat-bottomed pits have disappeared. This proves that the hillocks correspond to (nucleate at) dislocations and that the latter do penetrate into the body of the crystal.

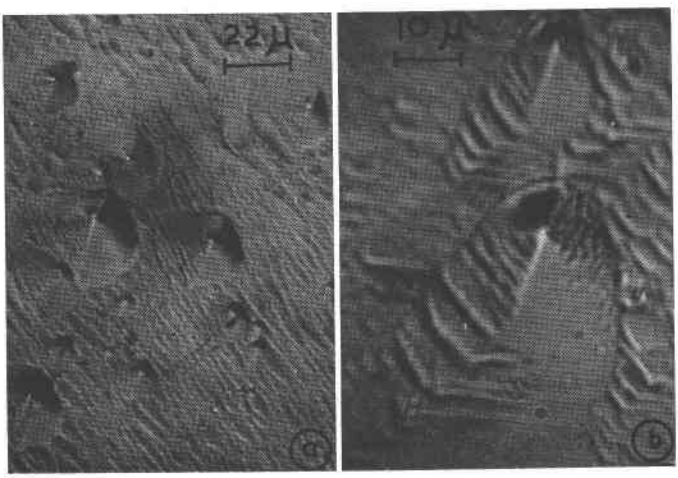

FIG. 2. Square-shaped hillocks. a Isolated square hillocks. b Square hillocks at higher magnification with a number of growth centers.

In some cases, however, hillocks are closely spaced and are arranged in the form of an array as shown in a photomicrograph of Figure 5a. This region of Figure 5a was etched in 20 percent hydrofluoric acid vapour at room temperature for 32 hours and the etch pattern so obtained is illustrated in Figure 5b. Here once again each hillock of Figure 5a is replaced by a pit. This face was then polished till all the etch patterns were completely removed. It was then re-etched in a solution of 6 gm of KOH and 3 cc of water at 280°C for 50 minutes. The resulting etch pattern is shown in Figure 5c. The deeper pits are at the same positions as those of pits in Figure 5b. The face was then polished again till

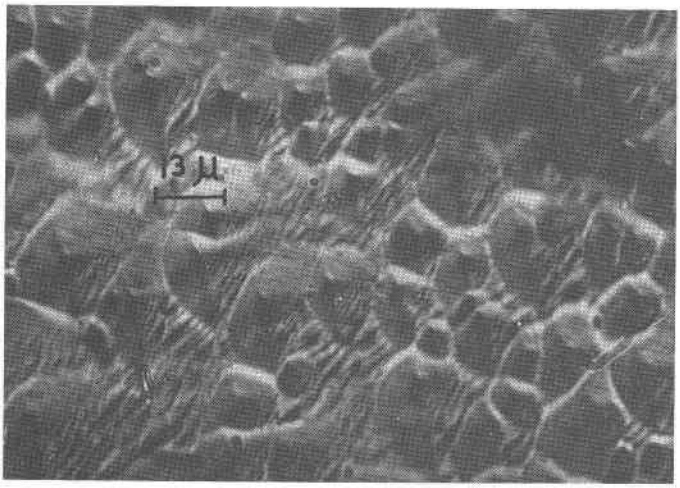

FIG. 3. Closely spaced intergrown square hillocks.

the whole etch pattern was removed. These two polishings removed about 25 microns thickness of the crystal face. It was then etched in 20 percent hydrofluoric acid vapour at room temperature for 24 hours. Figure 5d shows the etch pattern thus obtained. Once again we see that the pits along the line correspond to pits along the lines in Figures 5b and 5c, and hence they correspond to hillocks of Figure 5a. For pits in Figure 5d the etching time was restricted to a short interval (24 hours only) to prevent the intergrowth of etch pits so that they can be resolved individually to correlate them with pits and hillocks of Figures 5b and 5a respectively. These results prove that the dislocations at which the growth hillocks nucleate penetrate into the body of the crystal.

Variety of growth pyramids. On some faces a number of small, closely spaced hillocks were observed along parallel directions as shown in a photomicrograph in Figure 6. Here, practically each hillock is characterised by a black dot at the centre. These directions are found parallel to the edge between the $\{1\bar{1}0\}$ face and the rhombohedral face. These directions are also parallel to the striations seen in the lower-right of Figure 6. The latter are growth fronts of hexagonal growth pyramids which are very common on $\{1\bar{1}0\}$ faces (a detailed study of such pyramids and associated features will be communicated elsewhere). These striations are inclined at about 42° with the edge between the $\{0001\}$ plane and the $\{1\bar{1}0\}$ face. In some cases isolated hillocks are also observed as illustrated in Figure 7. Here one boundary of the hillock is rounded and hence these hillocks are not perfect squares. Growth layers composing these hillocks are visible. One more such case of hillocks is il-

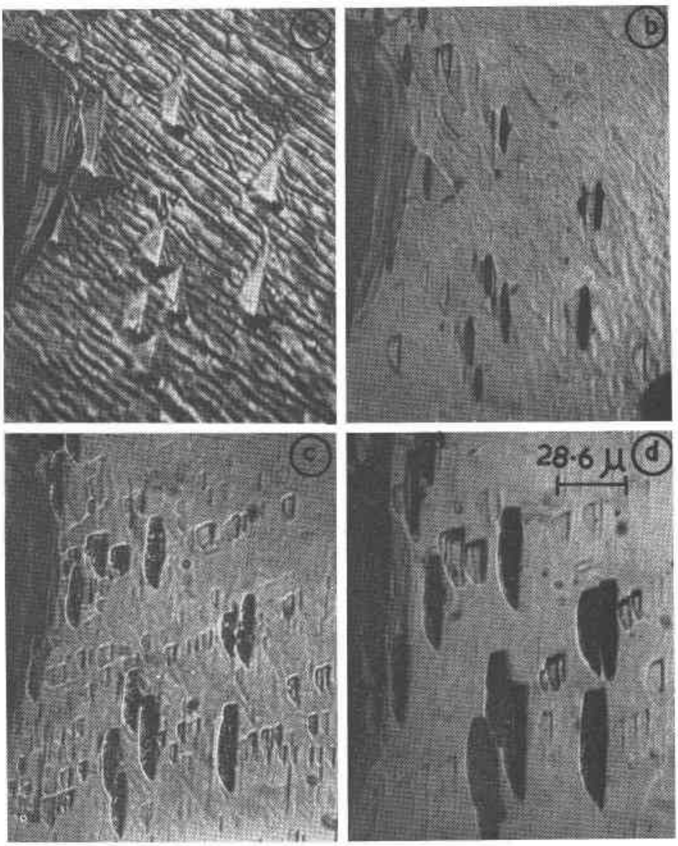

FIG. 4. Parachute-like hillocks. Hillocks in (a) etched into pits by HF acid vapour for (b) 30 (c) 50 and (d) 80 hours respectively.

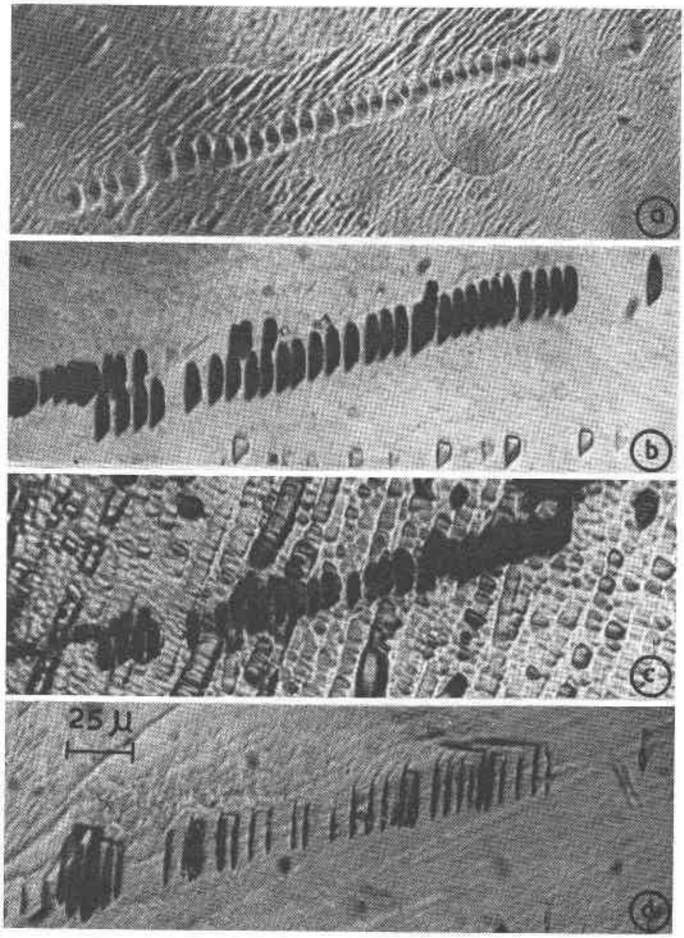

FIG. 5. An array of closely spaced square hillocks in (a); replaced in (b) by pits by etching in HF vapour; new pits in (c) produced after polishing and re-etching in KOH, showing exact correspondence with hillocks of (a) and pits of (b). In (d), pits produced after polishing and re-etching in HF vapour showing correspondence with hillocks of Fig. 5(a) and pits of Figs. 5(b) and 5(c).

lustrated in Figure 8a, for which the corresponding multiple beam interferogram is shown in Figure 8b. These fringes reveal the profile of these hillocks. At times the centers of initiation of hillocks are closely spaced with the result that growth hillocks in such cases intergrow forming complex growth forms as illustrated in Figures 9 and 10. Here also growth fronts of layers composing the hillocks are visible.

Figure 11a illustrates isolated hillocks. Some hillocks are so small

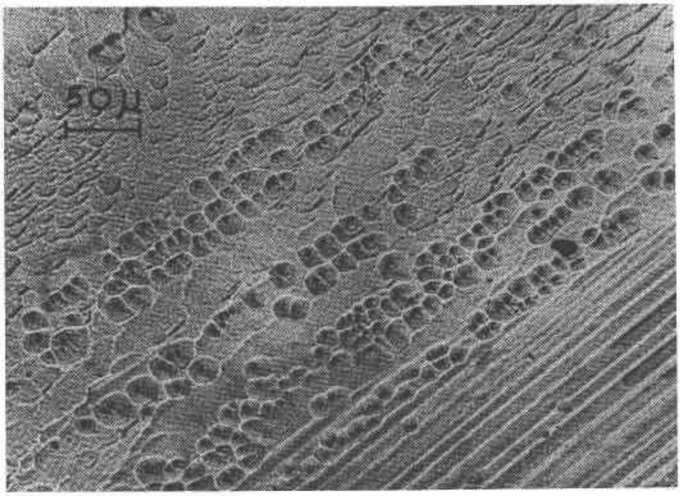

FIG. 6. Very small closely spaced hillocks parallel to striations.

that only their centers of initiation, characterized by black dots, are seen. On etching this region of figure 11a in a solution of 6 gm KOH and 3 cc of water at 280°C for 50 minutes it is found that each hillock, big or small, is replaced by a pit as shown in Figure 11b. Smaller hillocks have left no trace after etching whereas the traces of bigger ones are clearly seen in the figure. It is interesting to note that besides the formation of pits at the sites of hillocks they occur at other places also. Every type

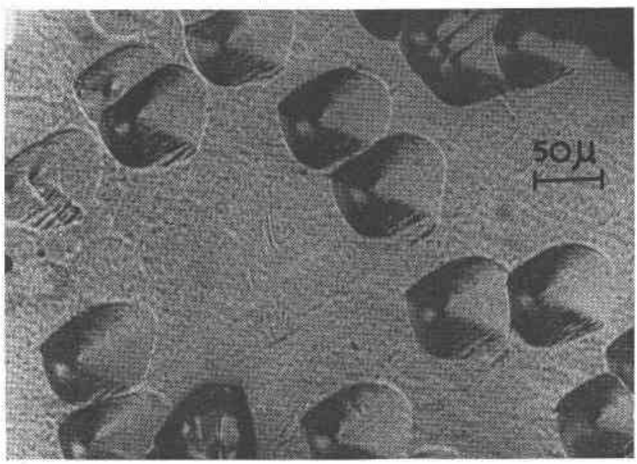

FIG. 7. Isolated hillocks with one side rounded.

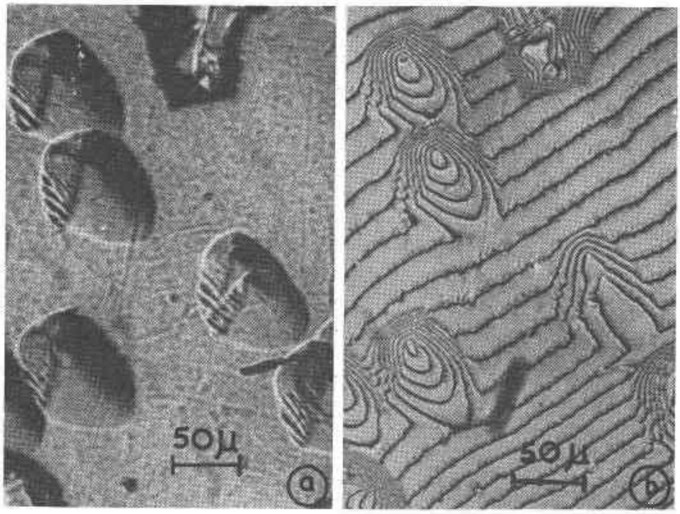

FIG. 8. Square hillocks slightly elongated to one side: (a) photomicrograph, (b) interferogram.

of dislocation may not give rise to a hillock whereas the etchant may also reveal other defects which are not responsible for the nucleation of hillocks. The surface round about the hillocks illustrated in Figures 7, 8a, 9, 10, 11a seem to be apparently devoid of growth layers from other initiating centers.

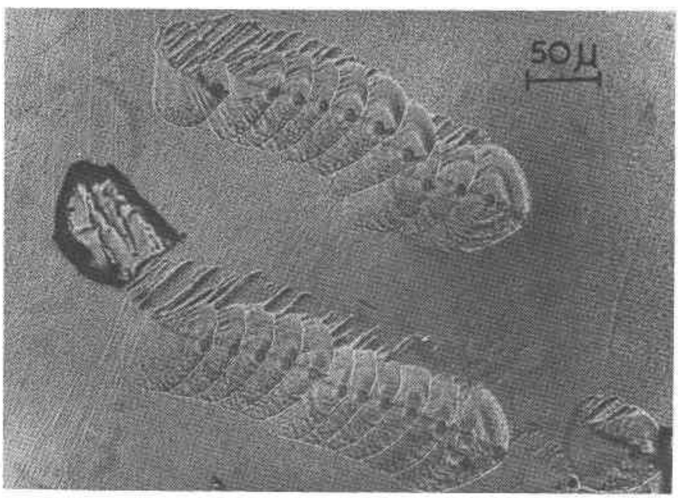

FIG. 9. Rows of closely spaced hillocks revealing growth layers on them.

Twin boundaries. On some faces irregular boundaries were observed such that the hillocks within and outside the boundary have different orientations. One such case is illustrated in a photomicrograph in Figure 12. The hillocks outside the boundary are oriented at 90° to those within. It is suggested that this line of discontinuity is a twin boundary. Figure 13a illustrates one more case of such a twin boundary and Figure 13b its corresponding multiple beam interferogram. Here (Fig. 13a) the hillocks outside the boundary are oriented at about 60° with respect to those within. The crystal was then etched with the solution of 6 gm of KOH and 3 cc of water at 380°C for 50 minutes. The etch pattern thus produced is illustrated in Figure 13c. Once again each hillock within and

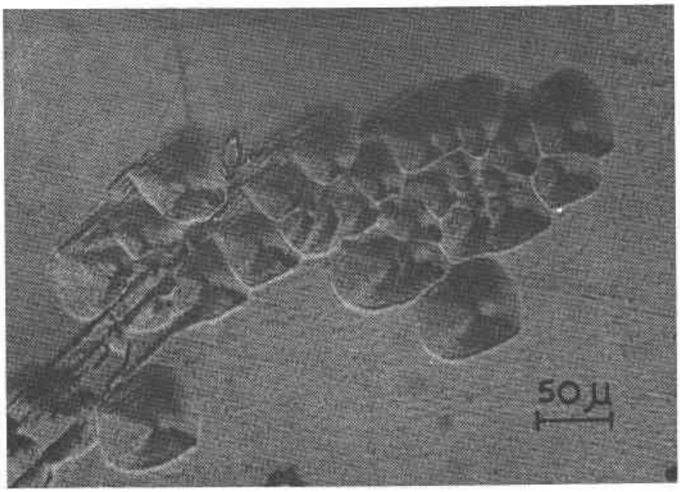

FIG. 10. Aggregate of clusters of hillocks.

outside the boundary, is replaced by an etch pit. It is interesting to note that the pits corresponding to hillocks outside the boundary are oriented at about 60° with respect to those within. Figure 13d represents distorted etch pits on a small portion of the twin boundary of Figure 13a. These observations presented in Figures 13a, b, c, and d endorse our suggestion that this line of discontinuity is a twin boundary.

DISCUSSION

Observations presented here are the first of their kind, at least for first-order prisms of quartz, and hence demand an adequate explanation. Since practically no face studied under the present investigation is left without hillocks, we conclude that formation of such hillocks is a natural phenomenon rather than an exception. Some of the hillocks are

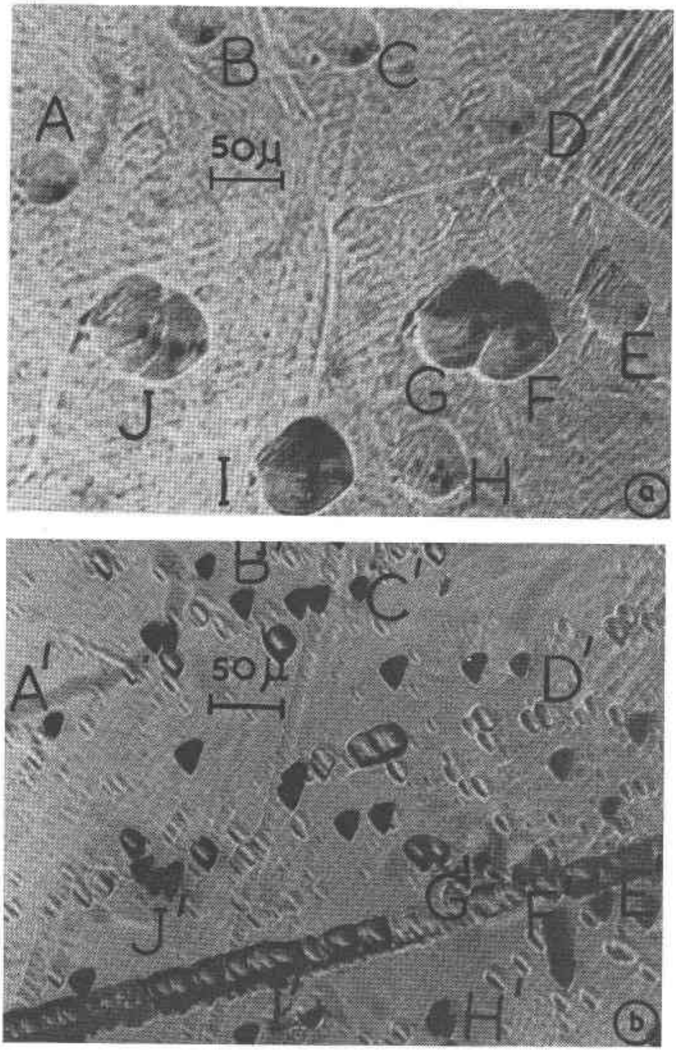

Figure 11. Hillocks in (a) replaced by pits in (b) Etchant KOH.

found partly covered over by growth layers from some other initiating centres, as is evidenced by the bending (retardation) of growth fronts as they move past and engulf such hillocks as illustrated in Figure 4a. Such a process leads to queer shaped (parachute shaped) pyramids of Figure 4a.

Photographs 5b, c and d illustrate the positioning of the pits at the hillocks of Figure 5a. This correlates hillocks with linear defects penetrating into the body of the crystal. These linear defects may be dislocations of the screw nature, but because we are not able to resolve the growth layers of these hillocks and show them of the spiral nature, we are not in a position to say anything conclusively in this regard. Spiral growth hillocks on prism faces have, however, been reported by Joshi and Vagh (1964). Unfortunately we have not been able to observe a single spiral on the $\{11\bar{1}0\}$ faces which we examined.

From the observations of the closely spaced hillocks shown in Figures 1, 2a, 3, 6, 9 and 10 we suggest that in some cases a large number of initiating growth centers become active, some for a short time or probably towards the end of the growth as should be the case for the seemingly

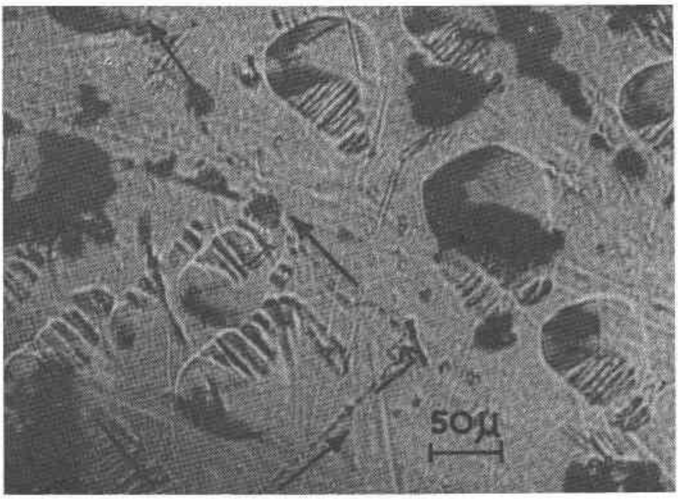

FIG. 12. Hillocks oriented at 90° within and outside an irregular boundary.

very small hillocks of Figure 6. We are given to understand that during the complete process of growth of synthetic crystals the autoclaves are opened to refill them with mother liquor and nutrient etc. and then shut again for further growth. For mother liquor used for these crystals the supersaturation increases with the fall of temperature and hence the cooling down process of the autoclave before it is opened, at each stage, should be favourable for enhancement of growth. From this fact we are inclined to suggest that at least some of the hillocks should have been a result of growth towards the end of each stage. Hillocks thus formed may be partly covered over by growth layers from other initiating centers which become active in the next stage. Hillocks presented in Figure 4a could be attributed to such a process. The apparent absence of any growth fronts in the regions round about the hillocks presented in Fig-

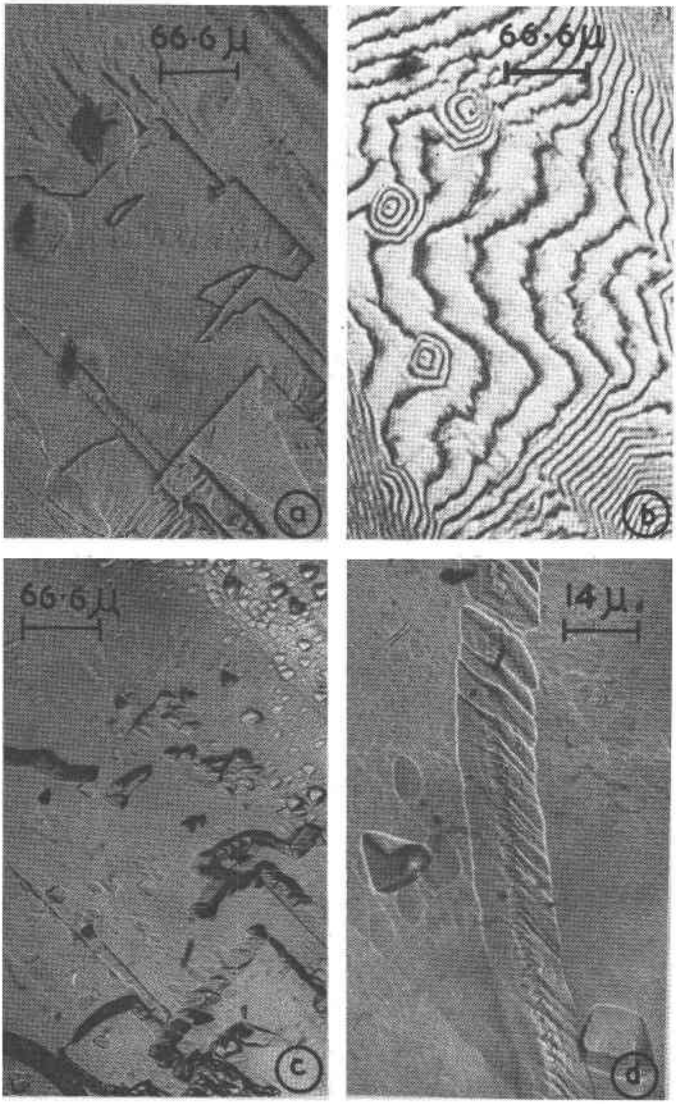

FIG. 13. Irregular boundaries: (a) Hillocks oriented at 60° within and outside an irregular boundary. (b) Interferogram over (a). (c) Etch pits oriented at 60° within and outside the boundary and replacing the corresponding hillocks of (a) Etchant KOH (d) Distorted etch pits on a portion of the line of discontinuity of (a).

ures 1, 7, 8a, 9, 10 and 11a indicate that these hillocks should have been formed towards the end of the growth at the last stage of growth after which the crystals are taken out of the autoclave.

The irregular boundaries within and outside which the growth hills are oriented at 90° and 60° with respect to each other, shown in Figures 12 and 13a respectively, are suggested to be twin boundaries. This is confirmed by etching this region shown in Figure 13a. The twin boundary is preferentially etched as shown in Figure 13c. The orientations of pits inside and outside the boundary differ by the same amount (60°, Figure 13c) as is for hillocks within and outside the boundary (Figure 13a). The observation of distorted pits on this irregular line of discontinuity is an additional evidence in favour of it to be a twin boundary. The profile of the hillocks on the twin boundary is shown in Figure 14, which also

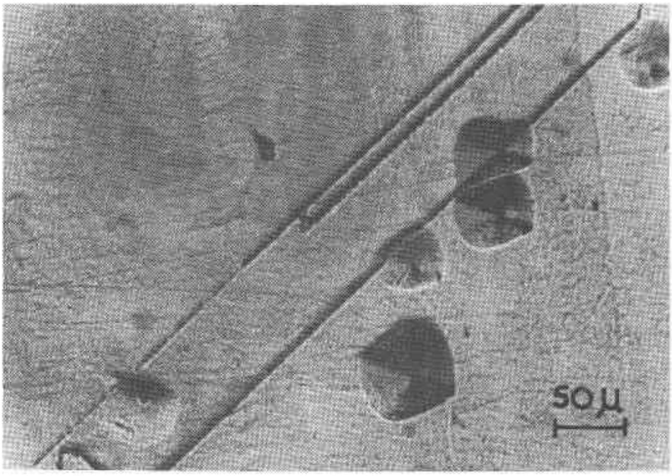

FIG. 14. Profile of hillocks at the line of discontinuity.

endorses the view that these lines of discontinuity are twin boundaries.

We are of the opinion that growth takes place, at least in the beginning, parallel to the surfaces of the seed plate. When the other faces develop, independent growth on them may also then be expected. Observations of growth hillocks on all $11\bar{1}0$ faces, without exception, support this view. From our present investigation we hold the opinion that growth on first-order prism faces takes place mainly by two-dimensional nucleation and spreading and piling of layers. This, however, does not preclude growth by spiral mechanism at screw dislocations. The striations observed are growth fronts of the growth hillocks on the faces. Faces $\{10\bar{1}0\}$ are the slow-growing faces whereas faces $\{11\bar{2}0\}$ are the fast-growing ones. Second-order prism $\{11\bar{2}0\}$ faces seldom occur on natural quartz but are available on synthetic quartz crystals. The growth and development of the commonly observed rhombohedral and the first-order prism faces take place at the expense of the seldom faces like the basal planes and second-order prisms, and if growth is allowed to take place fully both these types of faces may eventually be wipped off. In this respect one may call such faces as the transitional ones.

Hillocks presented here are strictly oriented, bear symmetry to the prism face on which they occur and on some of them edges of the growth layers composing them are clearly visible. These observations lead us to conclude that they are really growth hillocks. The faces are remarkably brilliant and lustrous as against the rough and mottled surfaces reported by Joshi and Vagh (1966), which rules out the possibility of any appreciable etching or dissolution, and hence this fact rules out the possibility that the hillocks presented here could be etch hillocks. Replacement of each hillock by an etch pit (using both acidic as well as alkaline etchants), successive stages of etching the region with isolated hillocks and the repetition of the etch pattern on a series of etching and polishing experiments show that the growth hillocks reported are formed at the sites of dislocations intersecting the crystal face. It is conjectured that these sites at which the preferential growth takes place may be the points of emergence of screw dislocations from within the crystal. Correlation of hillocks with dislocations shows that the formation of the hillocks observed here is related to the internal perfection of the crystal.

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