Alpha-quartz 3. Origin of cellular structure of synthetic quartz

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MS received 20 March 1979

Abstract. Surfaces of optically flawless and untwinned quartz single crystals, both natural and synthetic, were dissolved both at room temperature and at high temperatures in autoclaves using appropriate etchants. The features that develop have been optically studied, and x-ray transmission projection topographs of some of the specimens from the same natural quartz were also taken and studied. A model has been proposed to explain the anomalies detected earlier by other workers regarding the nature of line defects found in as-grown synthetic quartz, and the absence of lateral strain in the polygonised microcracked layer of the specimens of the present series of experiments.

Keywords. Cellular structure; subgrain boundaries; polygonalisation; frank net; optical twinning; synthetic quartz; alpha-quartz.

1. Introduction

A critical survey and analysis of x-ray diffraction topographic studies of synthetic quartz, and of investigations on the nature, concentration and distribution of common impurities of natural and synthetic quartz carried out by earlier workers has been made (Saha *et al* 1979; Saha and Bandyopadhyay, 1979). It was inferred that a majority (80-85%) of the dislocations present in synthetic quartz are cell-wall dislocations, with a predominantly pure edge, a $\langle 11\bar{2}0 \rangle$, glide component operating on $\{10\bar{1}0\}$ slip planes, the dislocation segments being parallel to the c -axis, and possibly associated with an alternating non-conservative climb component alternately jogging the dislocation lines so as to allow those submicroscopically small segments to make fairly high angle with the c -axis*. It was also inferred that climb is probably caused by precipitation or capture of impurities such as hydrogen, alkali hydroxides or H_2O from the growing medium at suitable defect sites (opened-up discontinuities) of the structure. The present series of experiments

* Recently, Barns *et al* (1978) have pointed out the anomalies in the determinations of Burgers vectors of dislocations in synthetic quartz performed by Lang and Miuscov (1967), McLaren *et al* (1971), and Barns *et al* (1978) themselves. However, the anomalies were pointed out by one of the authors of the present paper (PS), and the climb mechanism was suggested as well to explain the anomalies, during an invited talk at the National Conference on Crystallography held at Vallabh Vidyanagar, Gujarat, India, during February, 1978.

were conducted with both natural and synthetic quartz to obtain more evidence in support of those inferences, as well as to investigate the absence of strain in synthetic quartz because of the accumulation of impurities that cannot be accommodated in the ideal structure. The results obtained, along with the inferences drawn from analysis of previous work, have enabled us to propose a phenomenological model of defect structures likely to be associated with synthetic quartz, which (i) explains the features distinguishing synthetic quartz from untwinned natural quartz, like concentration of certain impurities far in excess of what is required by the charge compensation rule, deterioration of mechanical Q with increase in concentration of impurities, etc., and (ii) provides a mechanism for formation of cellular structure in synthetic quartz without causing detectable lateral strain in the lattice.

2. Experimental

Carefully selected optically flawless and untwinned natural quartz single crystal (Indian and Brazilian) were sectioned into plates parallel to the basal surface, i.e. cut parallel to (0001) with the help of a diamond saw. In the synthetic crystals (obtained from Sawyer Research Products) rods normal to $\{2\bar{1}10\}$, more commonly known as Y-bar rods*, were selected from different areas of the bulk crystals and their relative positions with respect to distance from seed plate noted for future reference. The following experiments were performed :

- (i) Room temperature (RT) etching of (0001)-cut plate of an Indian natural quartz, using 20% HF solution (for 2 hr and later, for 20 hr more).
- (ii) (a) Hydrothermal dissolution (etching in an autoclave of about 200 cc capacity) of five adjacent portions of a (0001)-cut plate of an Indian natural quartz, and another section from an adjacent parallel plate of the same quartz (figure 1), at different temperatures in the range 104°C – 492°C and duration varying from a maximum of 5 hr to a few seconds. Pressure was kept constant at about 374.25 ± 17.02 atm. Etchant $0.5\text{ M Na}_2\text{CO}_3$.
(b) Hydrothermal dissolution of a (0001)-cut plate of a Brazilian natural quartz. Temperature 322°C ; pressure 5,500 psi; duration 75 min. Etching in approx 200 cc capacity autoclave with $0.5\text{ M Na}_2\text{CO}_3 + 0.07\text{ M Li}_2\text{CO}_3$ solution.
- (iii) Hydrothermal dissolution (etching in autoclave of about 6000 cc capacity) of six synthetic Y-bar rods at a pressure of 4400 psi and temperature of 335°C for a few seconds. Etchant $0.6\text{ M Na}_2\text{CO}_3 + 0.05\text{ M LiNO}_3$.

The surface dissolution features were optically examined in a polarising microscope, and later projection transmission topographs of the specimens of the (iia) series of experiments were taken. Some of the latter specimens had to be polished and projection topographs taken again to obtain details of the internal (volume) features which are quite often masked by the surface features, specially for the specimens treated below 200°C .

* Y-bar rods fabricated in this manner will henceforth be referred to as seed plates normal to (0001) to facilitate comparison with other (0001)-cut seed plates.

Figure 1. Schematic diagram showing the location of (0001)-cut plates of an Indian natural quartz. Dotted portions indicate disposition of the natural rhombohedral faces.

3. Optical microscopy

3.1. *RT-dissolution*

The as-cut and dissolved surfaces have been reproduced in figure 2. The finely granular as-cut surface (figure 2a) with two small patches of chipping (one of them indicated by an arrow in all the reproductions) revealed surface microcracks and opening up of some microcrack crevices after short-time etching (figure 2b). The random orientation of the microcracks is very obvious here. Prolonged etching (figure 2c) removed all traces of the entire damaged surface including the microcracks, and an uneven surface covered with large triangular etch pits, showing tails indicating the handedness of the crystal, and some triangular pyramids surrounded by ill-defined subgrain boundaries remain.

3.2. Temperature-dependent dissolution of natural quartz

Except for the as-cut specimen (a) of figure 1 the other six plates from natural quartz were subjected to hydrothermal dissolution at different temperatures keeping all other variables constant as far as practicable. However, the period of dissolution had to be varied for different temperatures since the dissolution rates increase exponentially with temperature. Table 1 gives the original thickness of the plates, the dissolved thicknesses, and dissolution rates assuming linearity of dissolution with temperature. The dissolution rates are empirical, but give some idea of the exponential nature of the curve correlating dissolution rate to temperature. The alphabetical arrangement of the photomicrographs of figure 3 corresponds with designations of the different specimens indicated in figure 1.

A temperature-dependent phenomenon of subgrain boundary formation in an alkaline aqueous environment was observed. With negligible dissolution at 104° C the surface microcracks start becoming coarse (figure 3b). Treatment at 190° C results in progressive removal of the surface amorphous layer (Beilby layer) and opening-up of microcracks of the underlying layer. A certain preferred direction of alignment of the microcracks can also be observed, which is diagonally oriented across the photomicrograph (figure 3c) and which shows similarity in orientation to the cutting-blade markings already in evidence with the previous specimen (figure 3b). However, two more directions are also evident which make an angle of about 120° with the dominant direction of alignment of the microcracks. Very fine polygonal structures are uniformly interspersed between the microcracks, and they indicate initiation of polygonisation phenomenon on the damaged surfaces of the specimens. A sharp change is observed in the sample dissolved at 253° C (figure 3d), where a mosaic pattern of sharply truncated hexagonal shallow basins, of very uniform size and with the trigonal element dominating, can be detected. This feature, and healing up of the microcracks which are so evident in the previous photomicrograph (figure 3c), together with the fact that this specimen has suffered from very little (2 mils) surface dissolution dispels any doubt about the rationality of extensive lateral movement of

Table 1. Original thickness of plates : 1·8 mm (approx 70 mils).

Specimen designation	Dissolution temperature (° C)	Dissolved thickness along <i>c</i> -axis considering both sides of the plates (mils)	Approximate dissolution rate (mils/hr)
(b)	104	negligible	negligible
(c)	190	slight (< 1)	slight
(d)	253	4	4
(e)	287	14	28
(f)	406	61	732
(g)	492	34	extremely high

Figure 2. Room temperature etching of a natural quartz crystal on (0001)-cut surface. (a) as-cut ; (b) etching for 2 hr ; (c) etching for 22 hr.

Figure 3. Temperature-dependent subgrain boundary formation on hydrothermally treated (0001)-cut surfaces of an Indian natural quartz single crystal.

dislocations generated in the damaged portions of the crystals introduced externally by cutting. It may, therefore, be surmised that close to this temperature extensive temperature-dependent surficial plastic movement causing surface polygonisation and subgrain boundary formation takes place. The very sharp boundaries of the polygons and their similar orientation and alignment suggest tight crystallographic control over lateral movement of dislocations during polygonisation of the surface subgrain boundaries.

At a still higher temperature of 287° C (figure 3e), the crystallographically controlled basins, while remaining shallow, broaden out areally (cf. cobble-like *elevated* features on (0001)-cut surface of *grown* quartz) and lose their high relief. They are roughly circular to polygonal in outline and of varying size, but the crystallographic control over the alignments of the edges appears to have diminished. The general surface in totality is now covered with a random distribution of perfectly circular bubble-like depressions (size range 0.4–0.004 mm dia.; density $1.64 \times 10^4 \text{ cm}^{-2}$), and they do not seem to be related to the polygonal basins. Though this specimen has suffered unidirectional dissolution of 14 mils, some similarity with the 253° C specimen (figure 3d) and complete lack of similarity with the heavily dissolved 406° C sample (figure 3f) suggest that the polygonisation effect is entirely surficial and plastic flow has persisted only upto the lowest level of the disturbed layer, if such a level can be distinguished. Below this disturbed layer the crystal will be strained elastically, the magnitude diminishing gradually with depth, on both sides of the (0001)-cut plates.

The 406° C specimen (figure 3f) in striking contrast to the preceding specimen (figure 3e) does not seem to possess any surface relief and the surficial subgrain boundaries of the 287° C-specimen type are entirely missing. Instead, faint, widely-spaced subgrain boundaries can be detected. However, bubble-like depressions as found in figure 3f persist here, their density, so far as can be determined, being of similar magnitude (i.e., $1.60 \times 10^4 \text{ cm}^{-2}$). It can therefore be inferred that the surface disturbed layer has been removed almost completely, and that the faint subgrain boundaries are probably the relicts of volume subgrain boundaries of the natural crystal. At the final stage of dissolution at 492° C (figure 3g) the volume subgrain boundaries and the bubble-like depressions have become very much fainter, i.e., they can be distinguished only with an out-of-focus arrangement of the microscope though only a 34-mil thick layer of this specimen has dissolved as compared to a 61-mil thick layer of the previous one (table 1).

The natural Brazilian (0001)-cut plate of figure 4e, however, shows that high relief and sharp trigonality of the subgrain boundaries are maintained at a temperature as high as 322° C in contrast to lack of similar features in the 287° C Indian specimen (figure 3e). Moreover, the bubble-like depressions are almost entirely lacking in this specimen. The absolute dissolution and dissolution rate of this specimen, however, are comparable to those of specimen (e) of the 2a series of experiments.

3.3. Temperature-dependent dissolution of synthetic quartz

The diagrammatic sketch of figure 4 shows the locations of the cross-sectional areas of the synthetic Y-bar specimens investigated with respect to the $\{2\bar{1}10\}$ -

surface of the parent synthetic crystal. The different growth zones of any Y-bar synthetic quartz and the seed plate on which it is grown are clearly brought out in such type of sketches or topographs (*vide*, topograph of Takagi *et al* reproduced in figure 5 of Saha *et al* 1979a). It can be seen that specimen marked (1) includes both Z-zone and ($-X$)-zone of growth, whereas specimens (2) to (6) were extracted exclusively from the Z-zones of growth of the mother crystal.

Figure 4a illustrates a portion of the *dissolved* (0001)-surface of specimen (1) within that part of the Z-zone which is normal to the seed-plate area. Parts such as this have been demarcated in the sketch by the two parallel dashed lines skirting the shorter edges of the sectional view of the seed plate.* The shallow surficial polygonal basins in this case, as in the case of all the synthetic samples dissolved at 335° C, are quite similar to those of the natural Brazilian quartz described before (figure 4e), and they are likewise devoid of the bubble-like depressions, found in natural Indian quartz (figure 3e). However, the most characteristic feature of this photomicrograph is the presence of very deep coalescing etch pits arraigned in rows and forming a network of widely spaced subgrain boundaries; a few individual deep etch pits are sporadically distributed in the intervening areas. Figure 4b is a photomicrograph of the same (0001)-surface, but now displaced laterally so as to bring the transitional sector between the Z-zone and the ($-X$)-zone of the mother crystal in the field of vision. The significant features of this figure are (i) the complete absence of the deep etch pits and the network, and (ii) the presence of a straight line boundary demarcating the Z-zone from the ($-X$)-zone. Surficial polygonal basins on the straight line do not appear to have been affected to a great extent by the inclined demarcating plane (of which the straight line is the trace on this surface) except for darkening of the polygonal basins on one side.

It has been verified from a study of many synthetic specimens that the deep etch pits are always confined to those portions of the Z-zones of growth which are normally aligned to the (0001)-cut seed-plate areas of the mother crystals, as has been found in the example cited (figure 4a). Figures 4c and 4d, which are lightly polished opposite (0001)-surfaces of specimen 5, show that the networks formed by the deep etch pits continue through a thickness (after dissolution) of at least 2.286 mm. From those observations it can be surmised (i) that those etch pits are surface manifestations of dislocations intrinsic in the volume of the mother synthetic crystal, (ii) that those dislocations are confined to columnar volumes of the Z-zones of growth overlying the (0001)-cut surfaces of the seed plate of the mother crystal, as found in the projection topographic work of Takagi *et al* (1974) (figure 5 of Saha *et al* 1979a), and (iii) that those dislocations which are confined to the network are the *a*-type cell-wall dislocations identified in topographs of *as-grown* synthetic quartz by Lang and Miuscov (1967) and McLaren *et al* (1971) (Saha *et al* 1979a). It may further be noted from figures 4c and 4d that an approximate 120° alignment is maintained between the cell-wall boundaries defined by those *dislocation* etch pits, but that they have become displaced laterally through the thickness of the specimen. The numerical figures accompanying the sketch of figure 4 give the densities of those deep "volume" etch pits only, of the different specimens. It may be recalled that they are of the same order of magni-

* *vide*, footnote of page 92.

tude (10^2 – 10^3 cm $^{-2}$) as those of the dislocations found in the topographs of *as-grown* synthetic quartz by Lang and Miuscov, McLaren *et al* and Auvray and Regreny (1973) (Saha *et al* 1979a). However, since the deep etch pits tend to coalesce (figure 4a) our density counts are likely to be approximate. Nevertheless, they give some idea of the spreading out of the cell-wall dislocation network as we move away from the seed plate of the parent crystal.

4. Optical microscopic observations

The as-cut surface of natural quartz shows that a finely granulated surface layer is formed with occasional patches of chipping (figures 2a and 3a). This layer, but not the chipped blocks, is probably composed of amorphous material (Beilby layer). Both RT-dissolution and high temperature autoclave dissolution show that this layer is comparatively thin (about 2 mils thick on each sawed surface), and except for the chipped areas can be removed easily (figures 2b and 3c). It appears to be underlain by a microcracked layer which is clearly revealed by RT-dissolution for a short period of time (figure 2b). The unilateral thickness of this layer could not be determined unequivocally but it would be between 20 and 30 mils. Below this microcracked layer the crystal remains strained because of cutting, the magnitude of strain diminishing as we move away from the cut surfaces. These observations are in complete agreement with the mechanism of delayed microcracking of brittle materials at room temperature suggested in literature (Lange 1974).

Hydrofluoric acid, even in 20% aqueous solution, being a strong etchant for quartz does not reveal dislocation etch pits. The pits that can be observed in figure 2c, usually at the tip of the triangular pyramids, are therefore *dissolution* etch pits. The faint subgrain boundaries of the photomicrograph, however, may be relicts of inherent subgrain boundaries* of natural quartz. The microcracked layer underlying the easily removable thin surface layer remains as such during RT-dissolution (figure 2b),[†] but for elevated temperatures begins to open up (due to HT-dissolution) and their preferred directions (possibly due to damage along preferred directions caused by a combination of rotatory and translatory motions of the cutting blade) become very prominent at about 200° C (figure 3c). Fine polygonal structures also appear at about 200° C (figure 3c), and the microcracks heal up completely and extensive polygonised subgrain boundaries develop through localised plastic flow at about 250° C (figure 3d). Thus we find evidence of *extensive* dislocation movement causing plastic flow in the microcracked layer at a temperature somewhere between 200° C and 250° C and continuing at higher temperatures concurrently with its dissolution, *but not at temperatures below 100° C*.

The surficial polygonal basins of the microcracked layer, which is a ubiquitous feature of all HT-dissolution experiments in the range 250° C–335° C carried out on quartz single crystals, whether natural or synthetic, lose their sharp crystallo-

* A distinction is understood to be implicit in the terminologies "grain boundaries" and "subgrain boundaries". The former applies to polycrystalline materials and the latter to single crystals.

graphically controlled outline and high relief even below 300° C in some cases (figure 3e), but retain them in the case of others (figures 4a, 4b and 4e) at a temperature as high as 335° C. Only in the former case it is associated with circular bubble-like depressions suggesting collapsed vacancy loops through which water vapour has been desorbed (figure 3e). Since this feature has been found only in flawless clear natural quartz which in most cases is known to contain not more than $55\text{H}/10^6\text{ Si}$ (see Bambauer's data on rock crystal given in table 1 of Saha *et al* 1979b), there seems to be no other way of accounting for profusion of such bubble-like features in hydrothermally treated natural quartz but to postulate that hydrogen from the solvent was entrapped in the microcracked layer at the polygon boundaries (discontinuities) during extensive plastic movement and polygonisation of this layer at about 250° C. Loss of high relief and diminution of crystallographic control over the outlines of the polygonal basins above 287° C (figures 3e, 3f and 3g) but no significant change in the density of the bubble-like features suggests that water vapour and hydrogen impurities were desorbed at the polygonal boundaries above 287° C in this particular case. However, the temperature of onset of this desorption phenomenon varies from specimen to specimen.

In striking contrast to the synthetic specimens, the deep "volume" etch pits, most of which are high temperature (*approx.* 335° C) surface manifestations of *a*-type cell-wall dislocations of synthetic quartz, are entirely missing in natural quartz. This itself is a further proof that the network formed by those dislocations is in fact the cellular structure so characteristic of synthetic quartz. Very low density of dislocations in *seed plates of natural quartz* on which synthetic quartz with cellular structure has been grown, as has been revealed in a topograph of *as-grown* synthetic quartz by McLaren *et al* (figure 7 of Saha *et al* 1979a), suggests that the polygonal structure which developed in the 200–250° C range on the (0001)-cut and partially dissolved surface of natural quartz is the source of development of cellular structure in synthetic quartz grown on such plates, specially since the polygonal structure is retained (figure 4e) on the (0001)-surfaces at usual *growth* temperatures (300° C–350° C; see Bandyopadhyay and Saha, 1966; Chakraborty and Saha 1973, 1974). Also, the topograph referred to shows a high contrast layer on each of the two (0001)-cut surfaces of the natural seed, suggesting that they are the dissolved remnants of the polygonised microcracked layers just before the onset of growth.

For synthetic quartz seed plates on the other hand, the *already existing* cellular structure probably takes a more dominant role in propagating the cellular structure in the grown portion, as would be evident in other topographs of *as-grown* synthetic quartz of McLaren *et al* (figures 6a and 6b of Saha *et al* 1979a), since they show an almost 1 : 1 correspondence between dislocations in the synthetic seed plate and those of the grown portion. It is likely that many of the dislocations generated in the microcracked layer of the seed plate preferentially migrate laterally to the existing cellular structure of the underlying layer during the plastic flow and polygonisation stage.

The fact that all dislocations in the Z-zones of growth of synthetic quartz (etched surface manifestations of which are the deep "volume" etch pits) are always confined to columnar volumes normally aligned to the (0001)-cut surfaces of the seed plate (figure 4) which also substantiates the topographic work of Takagi *et al* (figure 5 of Saha *et al* 1979a), gives support to the postulate that

Figure 5. Transmission projection topographs of specimen (a) of figure 1.

Figure 6. Transmission projection topography and optical microscopy of specimen (d) of figure 1.

the polygonised microcracked layer of the (0001)-cut surface of the seed plate is the source of development of cellular structure of synthetic quartz.

In order to determine precisely the nature of the polygonised subgrain boundaries on the (0001)-cut and partially dissolved surfaces of specimens of the 2(ii)a series of experiments, they were subjected to transmission projection topographic studies. About two dozens of topographs were taken; however, only some representative topographs have been reproduced in this paper and a few of them compared with the corresponding optical photomicrographs.

5. X-ray transmission projection topography

Figure 5a illustrates an enlarged print of a topograph of as-cut specimen (a) of figure 1. Directions of the diffraction vectors, $g[10\bar{1}0]$ in this case, have been indicated on all such topographs* reproduced in this paper. Figure 5b shows the polished surface of the same specimen (a) taken with the same reflection, that is, with $(10\bar{1}0)$. It would be evident that the surface-cutting blade markings mask the internal features of the specimen, namely, the fault fringes found in natural specimens of quartz by Lang (1967). It would also be obvious from figure 5b that the specimen is singularly free from dislocations.

The upper left photograph of figure 6 is a part of a topograph of specimen (d) of figure 1 after hydrothermal dissolution at 253°C for 1 hr. In relation to the diffraction vector of the previous specimen the reflection used in this case would be $(1\bar{1}00)$. It is evident that the internal features are not obscured in this case since the amorphous layer formed on the surface during cutting has already been dissolved away (*vide*, figure 3d). The sharply defined fault fringes, characteristic of the parent Indian natural quartz from which this and other specimens of this series had been derived, are not seen here. The interference fringes that can be detected and which are parallel to a natural border of the specimen are due to slightly wedge-like shape of the specimen in thickness caused by dissolution. This feature would very much be in evidence in topographs of the highly dissolved specimen (g) to be discussed later. Dislocations are absent as in the previous case, but roughly circular high-contrast features, with a straight or wavy or even zig-zag white line through the middle splitting them into two are sporadically and irregularly distributed all over the specimen. Further magnified photographs of the same selected area of this topograph and of another taken with $(01\bar{1}0)$ reflection have been mounted side by side in the upper right corner of figure 6. It can be seen that the alignment of the white line passing through the middle of the circular high-contrast areas changes with change in direction of the diffraction vector, and is roughly perpendicular to it.

Those peculiar features of the topographs of figure 6 deserve further analysis. They resemble the kinematic direct images of spherical precipitates in thin perfect crystals of silicon [figure 3.15 (d) of Tanner 1976], but with the important distinction that the central white line is not straight. The presence of spherical precipi-

* While using the word topograph in this paper it has been our intention to signify enlarged prints of the actual topographs. The magnification of the actual topographs is $\times 1$ (Lang 1959), since the two types of reflections used for this study, namely, $\{10\bar{1}0\}$ and $\{11\bar{2}0\}$, are normal to the specimen surface. Further magnification is achieved optically.

pitates in our specimens is ruled out because of two reasons, namely (i) those high-contrast circular areas are entirely missing in the topograph of the polished as-cut specimen (figure 5b), and their density is very much less in topographs (figure 7) of the highly dissolved specimen (g), (ii) for the existence of smooth spherical precipitates in highly perfect dislocation-free specimens of natural quartz such as ours (figure 5) the central white lines should *always* be perfectly straight and exactly normal to the direction of the diffraction vector, which is not the case here. It is therefore, our contention that those features are due to local misorientations in the lattice planes caused by high localised strains in the microcracked layer around chipped regions (figure 2). The lower two optical photomicrographs of figure 6 of the two sides of the same area of specimen (d) marked out in the topographs and enlarged at magnification similar to that of the two topographs on the top right corner, suggest that some of the polygon clusters of the microcracked layer may correspond to the high-contrast features, since they show higher relief than the background polygons, and may also be misoriented. To quote from Tanner (1976), “‘Precipitates’ seen in an unpolished sample may well be damaged from cutting with a diamond wheel”.

Figure 7 illustrates two topographs of the highly dissolved specimen (g) of figure 1 after hydrothermal treatment at 492° C for a few seconds (*vide*, optical photomicrograph of figure 3g). The thickness of the plate has been reduced at the middle to about half of the original thickness (table 1) and preferentially at the edges to give rise to wedge-shaped borders. This has caused closely-spaced Pendellösung fringes to appear skirting all around the borders of the specimen and the seventh Pendellösung maximum has given rise to the flat darkened area in the middle of the left-hand topograph. In contrast, we find the sixth Pendellösung minimum in the right-hand topograph giving rise to a white patch in the middle, and this difference is probably caused by different types of reflections used for taking the two topographs. Presence of Pendellösung fringes provides conclusive proof that the parent Indian natural quartz is highly perfect and singularly free from defects, including dislocations (Tanner 1976), other than the very much localised planar defects giving rise to the fault fringes. Also, dynamical black-white image contrasts of some defect clusters are very much in evidence in the upper right-hand edges of the topographs as occasionally found in thin crystals (Tanner 1976). Fault fringes can also be detected, and a sector of one such planar defect, traversing the mid-section of the topographs, goes out of contrast when the fault vector becomes exactly perpendicular to the diffraction vector $g[2\bar{1}10]$, as also detected by Lang (1967).

6. Discussion

The results of our experiments indicate that while cutting any specimen of a brittle material such as quartz with a diamond blade, a shallow Beilby layer forms on the sawed surface which can easily be removed by RT-dissolution using a suitable etchant. Underlying this layer would be a region of microcracking followed by a strained portion of the crystal, the magnitude of strain decreasing with increasing distance from the cut surface.

Yield at room temperature of brittle materials by a delayed mechanism of microcracking below critical fracture stress has already been emphasised by

Figure 7. Transmission projection topographs of specimen (g) of figure 1.

Saha *et al* (1979a). This has also been observed in a semiconductor material, e.g., silicon, below the surface during mechanical polishing (Tanner 1976). Figure 8 is a multiple-cell (0001)-projection of the tetrahedral model of alpha-quartz.* The linked corners of the tetrahedra are the centres of the bridging oxygens, and can therefore be the only places of disruption of either of the two Si-O-Si bonds causing a defect to appear in the ideal tectosilicate structure of alpha-quartz. The dashed enclosures indicate successive concentric columns of increasing diameter of the ideal structure parallel to the c-axis (indicated as (1), (2), (3) and (4) in the figure), where the bonding in the structure will be at its weakest since such boundaries never transgress the fundamental SiO_4 building units. Figure 9 illustrates a conoscopic view of a third of the structure along the c-axis, and column (2) of figure 8 has been indicated as a fence in this figure. Figure 10 gives the data on oxygen density on the surfaces of those cylindrical columns. It is highest for column (1), drops sharply to the lowest value for column (2), and then increases exponentially for successive columns, attaining an almost steady value of $8.55 \times 10^{14} \text{ cm}^{-2}$ for column (30). If a sufficiently narrow hole in the atomistic scale and parallel to the c-axis can be physically punched in the structure, it is likely that the material enclosed in column (2) would be displaced, by gliding along the column surface and therefore in the c-axis direction (cf. pencil glide in b.c.c. iron), since bond density, depending on oxygen density, would be lowest on the surface of such a column. However, this is an impracticable proposition, and what we find in reality are curved microcracks below critical fracture stress and macroscopic "conchoidal" fracture above, caused by propagation of the microfracture over the curved surfaces of the different columns. This is, of course, a very much simplified model of the mechanism of "conchoidal" fracturing of quartz, and the structure will have to be considered in three-dimension to substantiate the model proposed.

The glide directions of the $a \langle 11\bar{2}0 \rangle$ cell-wall dislocations found in synthetic quartz have also been indicated in figure 8. Since these were also identified as pure edge dislocations (*vide*, Saha *et al* 1979a), glide associated with them should be on $\{10\bar{1}0\}$ planes for the dislocation lines to be parallel to the c-axis. However, it can be seen from figure 8 that there is no smooth planar surface in those directions, and alignment of such "planes" in the *tetrahedral model*, which should have the least density of the bridging oxygen atoms, must necessarily have a sawtooth-like appearance due to the projecting corners of the SiO_4 tetrahedra. The oxygen densities on those serrated $\{10\bar{1}0\}$ planes, (i) considering the additional lengths due to the sawtooth projections, and (ii) without considering them, have been indicated by the two horizontal lines in figure 10. It can be seen that though oxygen density of such a serrated plane considering the sawtooth projections [horizontal line marked (b) in figure 10] is as low as the oxygen density of column (2), glide would be impossible because of the serrations.

Figure 11 shows superposition of the structure of alpha-quartz on the structure of beta-quartz in (0001)-projection after ignoring the cumulative effect of volume expansion at the transition temperature (573°C). It would be obvious that for

* All diagrammatic sketches of alpha-quartz of this paper refer to the P3_221 enantiomorph, unless stated otherwise.

Figure 8. Multiple-cell (0001)-projection of the tetrahedral model of alpha-quartz. The large dots indicate the position of the silicon atoms at the centres of the tetrahedra.

beta-quartz the serrations would not be present on the $\{10\bar{1}0\}$ glide surfaces. It is therefore, easy to visualise extensive a-type pure edge dislocation movement in beta-quartz at room temperature, had it been possible to retain the structure below 573°C . In contrast, extensive movement of such dislocations in alpha-quartz appears to be a physical impossibility.

Temperature-dependent plastic flow in the microcracked layer, as observed in our experiments, can therefore be visualised as due to movement of a-type pure edge dislocations generated in the microcracked layer on *smoothened-out* $\{10\bar{1}0\}$ glide planes, the smoothening-out process having been caused by enhanced thermal vibration of the bridging oxygen atoms on such “serrated planes” at elevated temperatures.

The most startling feature of optical microscopic and transmission projection topographic studies of our experimental work is the fact that the network of poly-

Figure 9. Partial conoscopic view along c -axis of the sphere-model structure of alpha-quartz; only a third of the structure has been shown.

gons so prominent on the exposed surfaces of the microcracked layers of specimen (d) under the microscope is totally absent in enlarged prints of the corresponding topographs at similar magnification (figure 6). The topographs were taken on an Ilford G5 nuclear emulsion plates having an emulsion thickness of 50μ , at the research laboratory of M/s. Rigaku Denki, Japan, with their cameras using $\text{AgK}\alpha_1$ radiation. For such high precision work, it has been estimated that vertical resolution would be of the order of 1μ and horizontal resolution about 6μ (Yoshimatsu 1968). Perhaps it would have been better to use L4 nuclear emulsion plates (Tanner 1976) to reduce the grainy background evident in the topographs (figures 5, 6 and 7), but since $b = 4.9\text{ \AA}$ for a-type pure edge unit dislocations in alpha-quartz, $\Delta\theta_{\text{a}}$ being approx. 5×10^{-5} radians for the low order reflections used, namely, $\{10\bar{1}0\}$ and $\{11\bar{2}0\}$, it can be calculated that r , the effective radius of

Figure 10. Oxygen densities of the surfaces of the concentric columns of weak zones in the structure of alpha-quartz of figure 8 and of the $\{10\bar{1}0\}$ serrated surface.

the strain field around the core of the dislocation where intensity or contrast will be enhanced would be approx. $b/\Delta\theta_s$, or, about 10μ (Yoshimatsu 1968). Thus it would be expected that the experimental technique should resolve individual dislocations. Moreover, the average diameters of individual polygons of specimens (d) and (e) being 0.07 mm and 0.13 mm , or 70μ and 130μ , respectively, had the boundaries of the polygons been associated with strain fields of the postulated *a*-type dislocations the networks of the exposed polygonised surfaces of the micro-cracked layers on the two sides of the specimens should have been observed in the topographs, as in the case of the high-contrast roughly circular features of figure 6. Overlap of the networks of the top and bottom surface, however, could have

Figure 11. Tetrahedral model of structure of alpha-quartz superposed on the structure of beta-quartz (dotted tetrahedra) in (0001)-projection after ignoring the cumulative effect of volume expansion.

made recognition of individual polygons in the topographs difficult. Absence of images of the polygons in the topographs of figure 6 therefore indicates that no lateral strain is associated with them, and any theory aimed at correlating this polygonised layer to the development of cellular structure in synthetic quartz must account for absence of lateral strain in this layer, and this has been attempted in the model that is going to be proposed now.

7. Proposed model on the origin of cellular structure in synthetic quartz

Introduction of even a single pure unit *a*-type edge dislocation in the ideal structure of alpha-quartz without causing appreciable lateral strain and total disruption of the lattice is a physical impossibility, even if a Frank net type of dislocation arrangement with $\sum \mathbf{b}_n = 0$ (Cottrell 1964), is proposed; this has been investi-

Figure 12. Proposed model of subgrain boundary (Frank net) formation on the (0001)-cut surface of synthetic quartz.

gated exhaustively by the authors and can be verified by constructing the appropriate models. The only alternative seems to be what has been depicted diagrammatically in figure 12. This is a tetrahedral model of the structure of alpha-quartz with a nodal point of the Frank net at the centre. Three a-type "partials"* meet at each nodal point, so that $\sum_n \mathbf{b}_n = 0$, with $n = 3$. The half-planes of the partials, operating on $\{10\bar{1}0\}$ slip planes, radiate out from the nodal point and are disposed in such a manner that the zones of compression and tension of each of the three partials alternately overlap at the nodal point, and the resultant or residual strain at the core (nodal point) is reduced to zero. The line of the dislocation would therefore be in the direction of c -axis emerging outwardly from each nodal point. Concurrent dissolution during polygonisation of microcracks

* The mechanism of glide movement suggested here prior to formation of Frank net has some of the properties of true partials; however, twin element component of the half-planes distinguishes them from true partials. This fact should be clearly understood even though we have referred to them as partials in later discussions.

due to movement of the partials may have been the reason for opening up of the structure at the half-planes and at the nodal points along the *c*-axis. Complete specifications of the partials would be $\frac{3}{2}a\{11\bar{2}0\}\{10\bar{1}0\}$. However, the partials themselves would not account for the absence of lateral strain. For this it has been necessary to postulate optical twinning on atomistic scale caused by introduction of a single row of oppositely oriented SiO_4 tetrahedra [overlapping in (0001)-projection] in each half-plane at suitable intervals. The half-planes would therefore consist of two parallel, but linked components, namely, a plane of oppositely oriented SiO_4 tetrahedra and a plane of normally oriented SiO_4 tetrahedra (figure 12). Thus, in terms of the mnemonic proposed by Saha *et al* (1979a), the oppositely oriented tetrahedra would be disposed in the manner of the tetrahedra of the P3_121 enantiomorphic form of alpha-quartz (striped tetrahedra of figure 12) in a basic P3_221 lattice (see figure 3 of Saha *et al* 1979a). It would be evident from figure 12 that the materials between the half-planes of the lattice are good compact materials, and do not cause any lateral strain to the lattice.

In our opinion, the following are the supporting features of this model:

(i) Extensive plastic flow in the microcracked layer can be visualised at elevated temperatures, *prior* to the formation of the Frank net. The Frank net essentially pins the partials and prevents glide movement. This may account for the absence of dislocations characterised by deep volume etch pits under the optical microscope in regions outside a columnar volume in the Z-zone of growth overlying the (0001)-cut seed surfaces (figure 4).

(ii) The zone between microcracked layer and the underlying strained but not cracked layer is the place for embryonic stage of formation of half-planes containing the twin elements. This region would therefore be strained in projection. Hence with suitable reflections this region would show up as a region of contrast on the (0001) seed surfaces of synthetic quartz. This has been found in the works of Takagi *et al* and McLaren *et al* (see figures 5, 6 and 7 of Saha *et al* 1979a).

(iii) This model also provides for broken bonds at the half-planes and at the nodal points. Unsaturated oxygens here become the likely places for absorption of hydrogen impurity *independent* of the aluminium impurity content of the crystal, as found in synthetic quartz (Saha and Bandyopadhyay 1979b). Figures 13 and 14 show the method of formation of free O-H groups at the nodal points and at the half-planes. Figure 14b gives their elevation around a hole generated in the half-plane. Only one complete spiral turn of SiO_4 tetrahedra along the *c*-axis has been considered. It can be seen that even with ideal configuration of the tetrahedra each containing a free O-H group, the protons of the two neighbouring groups just touch each other. Proton-proton repulsion will of course increase this distance and those tetrahedra may bend further. The environment of each free O-H group being similar the force constants associated with them are likely to be the same, and the O-H absorption bands that should be observable should therefore overlap at the same wave number (Rao 1963). The very characteristic band of synthetic quartz at 3590 cm^{-1} at room temperature shifted to 3585 cm^{-1} at 78 K, has never been observed in natural quartz, and has probably arisen from the above type of mechanism. The free O-H groups of our model, without considering the proton-proton repulsion, would make angles of $63^\circ 30'$ and of $42^\circ 18'$ with the *c*-axis. However, the actual value obtained would be about

Figure 13. Sphere model representation of the opened-up c -axis channel at the nodal points of figure 12. Absorptions of proton at the unsaturated oxygen bond to form free O-H groups have been indicated here. The small black spheres represent silicon atom of those broken bonds. The dot-dashed lines indicate orientations of the Si-O-H bonds in plan. True scale dimension of an H_2O molecule has been shown in the upper left-hand corner.

73° 30' (polarisation factor = 5.5 with a scatter of 0.9, Chakraborty 1977). It is difficult to assess the effect of proton-proton repulsion, and presence of other impurities in the c -axis channels, on the orientation of free O-H bonds at the half-planes and at the nodal points at this stage.

(iv) This model also explains satisfactorily the presence of water molecules giving a broad underlying absorption band in the IR spectrum, and of alkali hydroxide molecules, in synthetic quartz since figure 13 shows that there is enough space left, even after the formation of the free O-H groups, for absorption of water molecules in the structure.

Figure 14. Disposition of the free O-H groups at the opened-up c-axis channels along the half-planes; (a) plan. (b) elevation.

(v) Though the Frank net pins the glide component in lateral directions, climb can occur during growth in the vertical direction due to absorption of impurities mentioned above, giving rise to lateral shifting of the boundaries of Frank net on submicroscopic scale, and causing the cell-wall "dislocation" lines to be confined within a cone of 25° around *c*-axis.

(vi) This model also suggests that the Frank net of half-planes, when extended upwards into the Z-zone of growth, forms the network of cell-walls characterising the cellular structure of synthetic quartz. The 120° disposition of the rows of deep etch pits found in synthetic quartz (figure 4c) is in support of this contention, since the half-planes of the model (figure 12) are also oriented at 120° to each other. However, lateral shifting of the cell-walls by climb due to incorporation of impurities complicates matters, and the cell-wall boundaries more often than not are not so well-oriented as in figure 4c. Also, since impurities can be incorporated at opened-up places of the structure at the half-planes and at the nodal points, they can give rise to the imperfect thin layers at the cell-walls caused by segregation of impurities, as suggested by Lang and Miuscov (Saha *et al* 1979a). Homma and Iwata (1973) also found concentration of some impurities at the cobble grooves of (0001) grown surfaces of synthetic quartz in their EPMA studies; inhomogeneous distribution of hydrogen impurity, however, will not be revealed by this technique. Also, the fault vector at the cell-walls according to our model would be equal to the Burgers vector of the partials, that is, $\frac{2}{3}a$ or $3.74 \text{ \AA}$, which is of the same order of magnitude as the fault vector ($1 \text{ \AA}$) estimated by Lang and Miuscov (Saha *et al* 1979a).

The main disadvantage of this model is that we have to assume edge-sharing of the oppositely oriented tetrahedra at the half-planes along *two* edges, a feature not found in the crystal chemistry of any silicate structure. While determining the structure of cancrinite Jarchow (1965), however, found instances of one edge sharing. Nevertheless, it can be mentioned here that for optical twinning in quartz, where the twinning plane is $\{11\bar{2}0\}$ (Saha *et al* 1979a), edge-sharing seems to be the only mechanism by which it can form, and the lamellae of such twinning are usually extremely fine in appearance.

8. Conclusions

Some dissolution experiments were conducted with (0001)-cut seed plates of natural and synthetic quartz single crystals at room temperature and at high temperatures (approx. 100°C – 500°C) in autoclaves, and the specimens were examined optically and by x-ray transmission projection topography.

RT-dissolution with even 20% aqueous HF solution being comparatively fast and non-selective for short-time etching, does not reveal dislocation etch pits, and with long-time etching dissolution etch pits rather than dislocation pits become prominent. On the other hand, HT-dissolution at progressively increasing temperature reveals the following interesting features, among others, under the optical microscope :

(i) Removal of surface Beilby layer, and simultaneous coarsening and opening up of the microcracks of the underlying layer at about 200°C ; those two layers constitute the damaged portion of the crystals, damage having been caused by cutting.

(ii) Formation of tiny isolated polygons between the microcracks at about 200° C, and extensive plastic flow and formation of polygonal depressions defining subgrain boundaries in the microcracked layer around 250° C.

(iii) Loss of relief of the polygonal subgrain boundaries at about 285° C in some natural specimens concurrent with increase in dissolution rate; however, in some other natural specimens and in synthetic quartz sharp relief is maintained at a temperature as high as 335° C.

(iv) A network of deep coalescing dislocation etch pits in the Z-zone of growth of synthetic quartz only, restricted to a columnar volume overlying and normal to the natural or synthetic (0001)-cut seed plate area.

From a critical analysis of the above features and of previous work it was concluded that the polygonised subgrain boundaries of the microcracked layer of the seed plate are the source of development of cellular structure of synthetic quartz. Whereas for natural quartz seed plates this seems to be the only source, for synthetic quartz seed plates the existing cellular structure of the seed probably plays a more dominant role in propagating itself during lateral growth.

Since earlier topographic work had revealed that the cell-wall dislocations of as-grown synthetic quartz have the character of pure a-type edge dislocations, plastic flow observed in the microcracked layer at elevated temperatures was analysed in terms of movement of edge dislocations. It was concluded that enhanced thermal vibration of the bridging oxygen atoms at elevated temperatures facilitates movement of edge dislocations generated in the microcracked layer along $\{10\bar{1}0\}$ slip planes in $\{11\bar{2}0\}$ directions.

Transmission projection topographic studies of some of the dissolved natural specimens, however, failed to reveal images of dislocations which gave rise to the polygonal subgrain boundaries. This was interpreted to be due to absence of lateral strain in the specimens which, except for the damage caused by cutting, were found to be highly perfect.

A model has been proposed to account for the absence of lateral strain. According to this model three 'partials' which can be characterised as $\mathbf{b} = \frac{3}{4} \mathbf{a} \langle 11\bar{2}0 \rangle \{10\bar{1}0\}$, meet at nodal points to give rise to a Frank net, with $\sum_n \mathbf{b}_n = 0$ ($n = 3$). The distinctive feature of those "partials" is the presence of an optical twin element in the half-planes. The cell-wall "dislocation" lines emerge outwardly from each nodal point of the Frank net in the direction of the *c*-axis.

It has been possible to explain many of the peculiar features of as-grown synthetic quartz with the help of this model, e.g., fanning out of the pure a-type edge dislocation lines of the cell-walls into a cone of 25° around the *c*-axis, occurrence of stacking fault type of planar defects at the cell-walls, presence of hydrogen and alkali impurities in excess of what is required for charge compensation, and ubiquitous association of a broad underlying isotropic band with the sharp anisotropic OH absorption bands even in the low-temperature infrared spectrum. However, the main difficulty of the model is that a plane of oppositely oriented SiO₄ tetrahedra, sharing two edges with neighbouring normally oriented tetrahedra, has been assumed as one of the two components of the half-planes, and this kind of double edge-sharing is unknown amongst silicate structures.

Acknowledgements

The authors are indebted to the Director, CGCRI, for his kind permission to publish this paper. The wholehearted cooperation of M/s Rigaku Denki, Japan, in taking the x-ray transmission projection topographs of the second series of experiments at their research laboratory at Tachigawa, Japan, during the visit of one of the authors (PS) to Japan in 1970 on a JSPS fellowship is gratefully acknowledged. Special thanks are due to Dr M Yoshimatsu, Research Director, Dr H Maruyama, Miss Takada of the research staff, and Mr S Ishiyama, Mr M Kuboya and Mr Y Nakajima of the administrative staff of M/s Rigaku Denki.

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