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UNUSUAL ETCH PITS IN QUARTZ CRYSTALS

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Abstract

Synthetic and natural quartz crystals have been etched in 48% HF in a manner described by Arnold[7] and have been found to exhibit deep etch tubes which are ribbon-like in shape. Examples of these etch tubes are shown and possible explanations for their formation are given.

Introduction

Recently there has been interest in the structural defects in crystalline quartz and their effect on its physical properties. Bömmel, Mason and Warner[1] have postulated that dislocations exist in quartz. King[2] has suggested that the mechanical properties of quartz are dependent upon its defect structure and has observed differences between synthetic and natural quartz. Cohen[3,4,5] concludes that amethyst and smoky quartz derive their color from defects associated with impurity atoms. The present work was suggested by the discovery of Arnold[6] that concentrated hydrofluoric acid produced deep etch pits, actually etch tubes, in a synthetic quartz crystal obtained from Clevite Corporation. After the present work was completed, the authors discovered similar work had been carried on by a group at Clevite Corporation.[7] Although their results are similar, they differ enough in detail to warrant presentation of our results.

Etch tubes similar to those described below have been observed in minerals such as barite, dolomite, colemanite, apophyllite and topaz. An excellent summary of these observations has been provided by Honess.[8] Miss L. C. Lovell[9] of these Laboratories has recently observed etch pits in apatite which bear a resemblance to those discussed below but which are smaller in size by three orders of magnitude.

Experimental

Several crystals were etched in 48% HF for 48 hours at room temperature. One crystal (#1) was of natural quartz and was cut such that two basal (0001) planes were parallel, making a plate $\frac{1}{2}$ inch thick. Five of the prism faces, $(10\bar{1}0)$, were neither cut nor polished. The sixth prism face had been trimmed with a diamond saw.

A second crystal (#2) was a synthetic stone grown on a Y-bar seed about 3″ long and $\frac{1}{8}$″ square. (The long sides of a Y-bar seed are (0001) and $(11\bar{2}0)$ planes, the ends are prism faces.) This crystal is similar to the one used by Arnold.

A third crystal (#3) was synthetic also and was grown on a CT plate, that is, the large planes of the seedplate were minor rhombohedral faces, $(01\bar{1}1)$.

Three other CT plate crystals and two Y-plate crystals were also etched but were not polished.

After etching, the crystals were washed in distilled water and dried. Crystals #1, 2 and 3 were then polished on two parallel faces so that etch pits could be observed conveniently. Crystals #1 and 2 were polished on two (0001) faces. Crystal #3 was polished on two $11\bar{2}0$ faces.

OBSERVATIONS

1. *The Natural Crystal*

Figure 1 is a photograph of the natural crystal (#1) after etching and polishing. The etch pits appear as small tubes which penetrate three of the $(10\bar{1}0)$ faces of the crystal to depths greater than one centimeter. A close examination of the tubes revealed no particular pattern in their formation, that is, there was no evidence that they formed in rows as is often observed where etch pits are found to originate because of dislocations. Although the tubes are, on the average, perpendicular to the $(10\bar{1}0)$ faces they are seldom exactly so and individuals are often as much as 10° off the perpendicular.

It should be noted that the crystal shown in Fig. 1 had regions of smokiness visible in it. These darker regions appear near the edge of the crystal near five $(10\bar{1}0)$ faces. Since there are etch tubes in three of these regions but not in the other two there appears to be no relation between smokiness and the formation of this type of etch pit.

After photographing the crystal the regions containing the etch pits were cut from the crystal with a diamond saw and the remaining stone was again etched for 48 hours in 48% HF. No etch tubes were observed on any of the faces.

2. *Y-bar Synthetic Crystal (BTL)*

It was noted that in the case of the Y-bar crystal the etch tubes clustered along a line running down the center of the large face which was approximately $(11\bar{2}0)$. These etch tubes all terminate at or near the seed and appear to fan out from the seed in the direction of the $(11\bar{2}0)$ face in the manner of bristles of a worn brush. The etch tubes appearing away from this centrally located cluster all originate at inclusions of impurities which are usually visible under the microscope. Figure 2 shows two inclusions and the etch tubes pointing toward them.

Almost all etch tubes in crystal #2 originate at the $(11\bar{2}0)$ faces. The initial form of the tubes is similar to a normal etch pit much elongated in

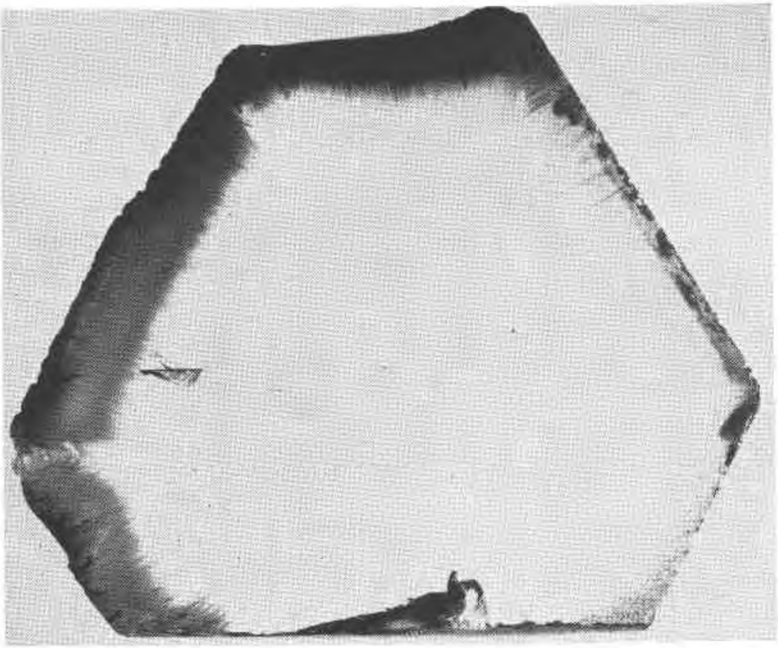

FIG. 1. Etch tubes in natural crystal (2×).

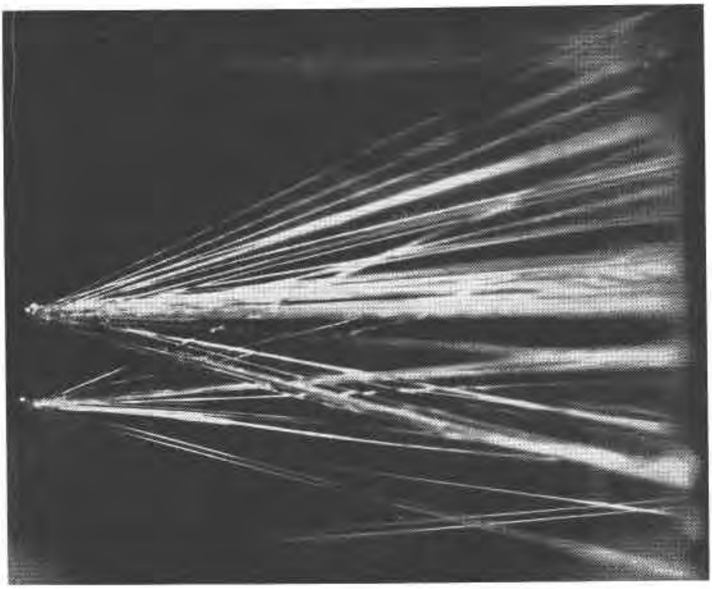

FIG. 2. Etch tubes terminating at inclusions (26×).

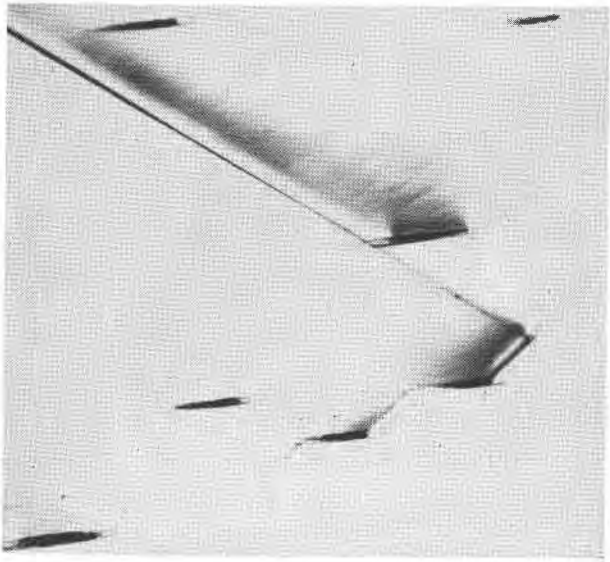

FIG. 3. Etched (1120) surface (100×).

the direction of the *c*-axis of the crystal. The nature of these pits maybe seen in Fig. 3 which shows seven of the pits from which tubes were formed. (The straight lines are cracks which will be discussed later.) The tubes extend below the pits in a ribbon-like form which is sometimes only about one micron wide. The ribbons curve in toward the seed plate in a random but smooth manner. Those ribbons pointing towards inclusions are straight.

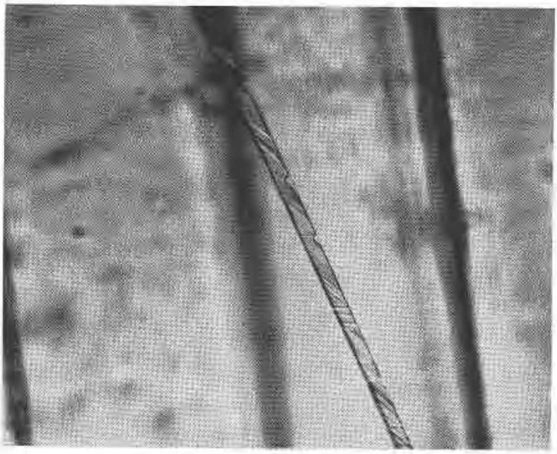

FIG. 4. Magnified etch tubes (67×).

The detailed structure of the ribbon-like tubes is somewhat difficult to photograph, but Fig. 4 shows a tube at 67× magnification. As may be seen the wall of the tube contains a group of parallel etch lines at an angle approximately 60° to the wall and a second group of lines at an approximate angle of 30°. Further observation disclosed that some tubes in addition to having parallel lines at different angles also have irregularly spaced sawtoothed profiles.

In Fig. 5A a typical ribbon-tube is sketched, directed from the surface toward the apex of a cone where an inclusion resides. From this sketch it may be noted that the wall of the tube appears to be discontinuous, an opaque part filling only about one third of the tube near the orifice and the outer edge of the tube being delineated by a single line boundary. In order to substantiate the capillarity of the tube a drop of carmine ink was applied to the surface and later a drop of xylene. Since the index of refraction of the xylene was sufficiently near that of the crystal, as penetration advanced the opacity of the tube lining completely disappeared, leaving the tube bounded by single lines. Upon allowing the xylene to evaporate the part opaque—part transparent pattern in the tubes was re-established. Thus the transparent edges of the tubes were shown not to be trapped solvent but regions where the tubes were very thin and uniformly etched.

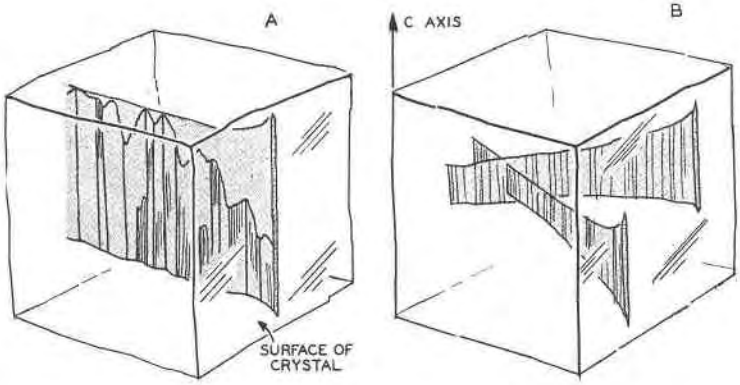

FIG. 5. Sketch of etch tubes originating at a $(11\bar{2}0)$ face.

Occasional instances were noticed where two tubes had intersected. A sketch, Fig. 5B, illustrates one of these pairs. In both sketches it will be noted that the plane of the ribbon-like tubes was parallel to the *c*-axis of the crystal even though the angles the tubes make with the crystal surface are quite different.

It is interesting to compare the observations on this BTL Y-bar crystal with those which Arnold made on a Clevite Y-bar crystal. Arnold observed a much higher density of etch tubes in his crystal. Furthermore, the tubes he observed took a very irregular path from the $(11\bar{2}0)$ face to the seed whereas the BTL Y-bar crystal exhibited etch tubes whose gross forms were smooth curves. The crystals studied by the workers at Clevite appeared much like the one studied by Arnold. This difference probably arises because of the difference in growth conditions. Clevite Corporation uses a sodium carbonate solution to grow quartz while sodium hydroxide are used at these Laboratories. Furthermore, the temperatures and pressures used at these Laboratories exceed those used at Clevite Corporation. A Z-cut crystal grown at General Electric, Wembley, England, was also etched and found to have a much higher density of tubes than the BTL crystal, but the tubes traced smooth curves similar to those in crystal #2.

All synthetic Y-bar and Z-cut crystals, regardless of origin, exhibit a much higher density of etch pits on the slower growing $(11\bar{2}0)$ face, that is, the $-X$ direction. This is also the part of the crystal known to contain more impurities and which *x*-rays darken easily. Under the conditions of growth used at these Laboratories for crystal #2, one $(11\bar{2}0)$ face grew about four times as fast as the other. That is, the rate in $-X$ direction was $\frac{1}{4}$ that in the $+X$ direction. The density of etch tubes in the slow growing $(11\bar{2}0)$ face is about four times that in the opposite fast growing face.

Figure 6 shows a row of etch pits which appears on the slow growing $(11\bar{2}0)$ face of crystal #2. This row contains over 70 pits. None has an etch tube emanating from it. These pits recall those usually attributed to dislocations in metal crystals which are located at small angle boundaries. The long direction of the etch pits is parallel to the *c*-axis of the crystal as was observed in the case of the etch tubes. The presence of the striations and small peaks observed in this photograph is unexplained.

Finally, the cracks in crystal #2 were made by an accidental combination of thermal and mechanical shock. They all make angles close to 53° with the basal plane, corroborating the observations of Bloss[10] and Mrs. Wood[11], which indicate that quartz cleaves parallel to the rhombohedral faces. That this cleavage can be quite perfect is shown by the straight lines formed by the cracks in Fig. 3.

3. *CT Synthetic Crystal* (*BTL*)

As in the case of the Y-bar crystal, in the CT crystal (#3), the direction the tubes take from a given face is always determined by the growth direction. In this crystal the fast growing face was the minor rhombohedral, $(01\bar{1}1)$, face. The etch tubes were all directed toward the seed plate whose largest surface was the minor rhombohedral face. Some of the tubes, as in the case of the Y-bar crystal, terminate at inclusions of impurity. The tubes approach the seed plate at an angle which averages 79°, although angles as low as 67° and as high as 86° were measured. This places the majority of the tubes roughly parallel to one of the major rhombohedral faces.

A striking example of the propagation of the disturbance which leads to the etch tubes from seed plate to grown quartz was observed in crystal #3. Apparently the sodium hydroxide solution used in the hydrothermal method sometimes etches tubes in the quartz seed before growth begins. When growth does begin the etched tubes begin to fill in, but do so rapidly enough that inclusions of solvent are left in the seed. The disturbance causing etch tubes remains and is propagated as the crystal grows even though the surface of the seed appears to be sound. This is shown in Fig. 7 where a group of eight etch pits in the crystal forms the identical pattern of eight partially refilled tubes in the seed. (The seed crystal is the band bounded by two straight lines running from left to right in the lower half of the figure).

From Fig. 7 it can be seen that the tubes etched in the seed are not perpendicular to the seed plane; they make an angle with it about the same as that made by the etch tubes in the bulk of the crystal. The imperfections leading to the etch tubes in the seed and crystal do not lie in a straight line, however, as a close examination of Fig. 7 will show. The etch tubes formed by the HF, which are straight near their origin, make an angle with the seed plate 4° smaller than the angle made by the tubes in the seed with the seed plate. A microscopic examination of the tubes formed by the HF reveals that this 4° angle is caused by a gentle curving of the tubes near the seed and suggests that the etch tubes if elongated to the seed plate would meet the tubes in the seed plate at the same angle to the seed plane. The eight etch tubes were also observed on the other side of the seed.

In Fig. 8 the eight tubes appear with kinks near their origins. The kinks occur at that point because there the capping of the crystal which goes on during growth caused a major rhombohedral face (top of figure) to encroach on the domain of the minor rhombohedral growth. Although it is not obvious from the figure, the kinks in the tubes occur at the point from which they grew toward the $(10\bar{1}1)$ face instead of toward the $(01\bar{1}1)$ face, again demonstrating that the tubes have a strong tendency to follow the direction of growth.

It was also observed that many etch tubes terminated at inclusions (Fig. 7) as in crystal #2. Many terminated at the seed at points where no previously etched tubes could be found in the seed. Most of the tubes etched in the seed before growth had corresponding tubes etched in the crystal, but it could not be established that a tube existed in the crystal for every one in the seed.

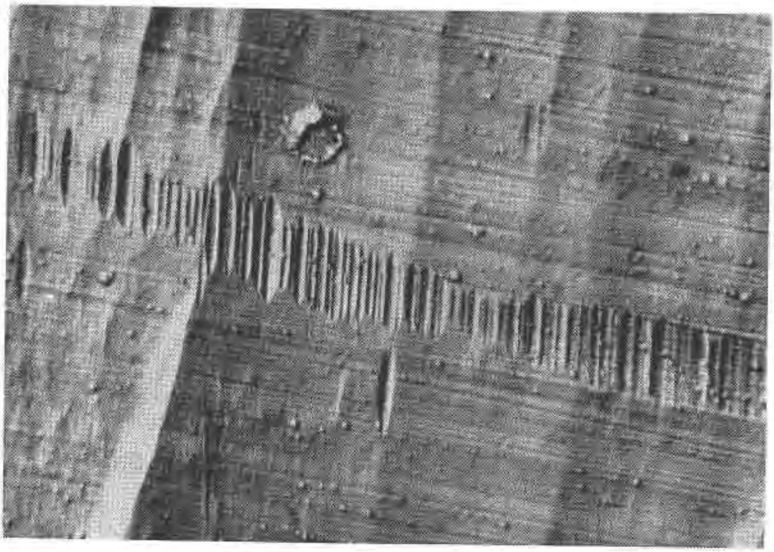

FIG. 6. Row of etch pits without tube formation (110×).

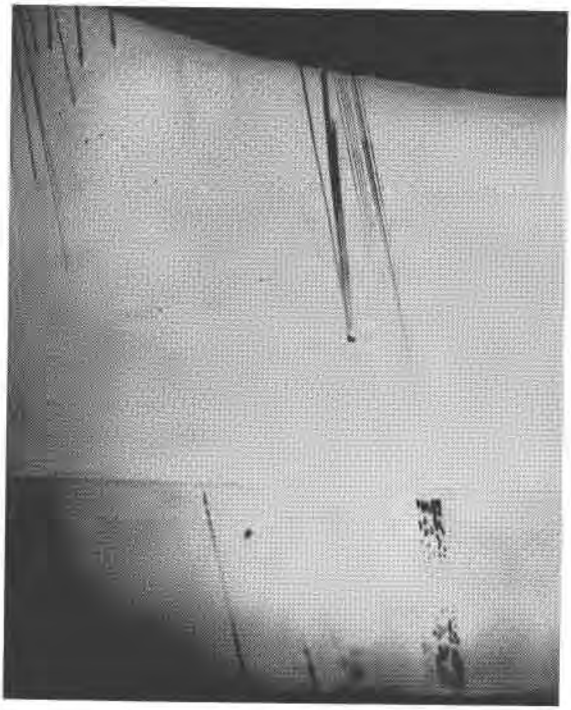

FIG. 7. Example of imperfections in seed continuing through grown crystal (13×).

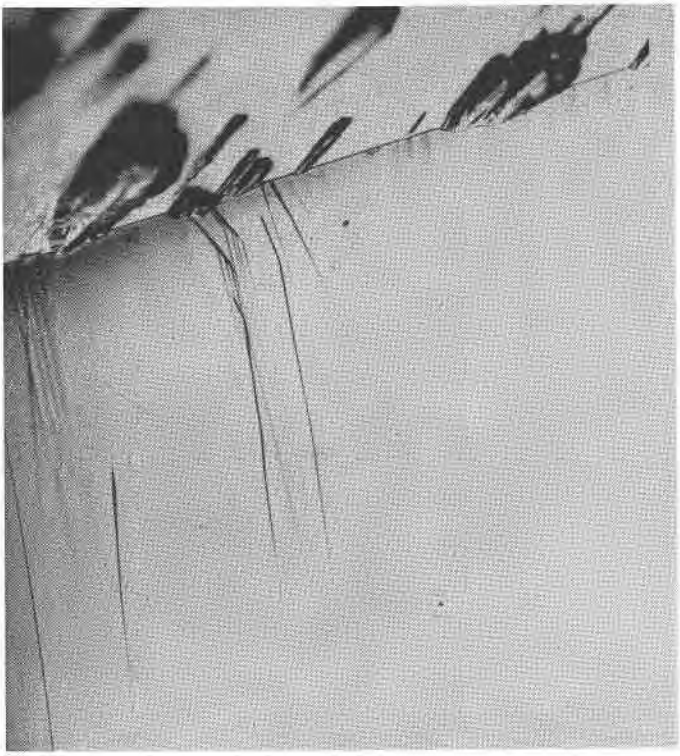

FIG. 8. Demonstration that etch tubes follow direction of growth (15×).

Finally, in no crystal of any type were etch tubes ever observed parallel, or nearly parallel, to the *c*-axis of the crystal.

DISCUSSION

It is apparent that natural and synthetic quartz contain imperfections which, in the presence of HF, cause etch pits to form. These pits are very deep compared to their width; indeed, the rate of solution along the length of the pit is sometimes 10^3 greater than that perpendicular to it. The nature of these imperfections is difficult to ascertain with the meager data presented here, but three possibilities are suggested.

First, the imperfections may be dislocations. If we disregard the difficulty of visualizing the form a dislocation takes in a structure such as quartz, and simply assume that a structure can be set up which satisfies the definition of a dislocation given by Read,[12] then one observation may suggest that the etch tubes are the result of dislocations. The one to one correspondence between partially refilled etch tubes in the seed plate and etch tubes in the grown crystal would be observed if the disturbance causing both were a dislocation in the seed. The dissolution of material around the dislocation in the seed would not "remove" the dislocation, for regrowth would generate it again and further growth would propagate it. This assumes, of course, that no other faults or disturbances occur as the crystal grows to refill the tube etched by the solvent. However, it is not impossible that the imperfections leading to the etch tubes in the seed were different from those causing them in the bulk of the crystal, and dislocations may not have been responsible for either. Thus one hesitates to state that the etch tubes were certainly the result of dislocations without more evidence. Unfortunately, quartz cannot be successfully deformed so that dislocations can be created and observed by decoration and etch in the normal manner. Furthermore, it seems risky to attribute etch tubes to dislocations if one considers the energy distribution necessary around such dislocations. In order to exhibit an etch rate along the length of the tube 10^3 times greater than that perpendicular to it, the lattice along the line of the dislocations would have to be violently disturbed. But the strain resulting from such a disturbance would have to be relieved a short distance from the line of disturbance or the rate of etch perpendicular to the line would also be rapid. The authors hesitate to suggest such a structure exists which would still be described as a dislocation.

A second explanation for formation of the etch tubes involves the non-uniform incorporation of impurities in the crystal as it grows without the formation of dislocations. If the crystal has a tendency to include impurities in pipes rather than uniformly, such pipes could serve as points of easy attack by the HF and the tubes would be formed by nothing more than the leaching out of the impurity. Some support for this point of view may be gleaned from the observation that the tubes are most numerous in faces known to contain the most impurities, such as the slow growing $(11\bar{2}0)$, and are absent in the material known to contain the least, the fast growing (0001) face. Cook[13] observed streaking and spots in a few monochromatic x-ray reflection photographs which he attributed to impurities, thus there is some evidence to show that these impurities are not uniformly distributed in the regions in which they occur. However, Cook found the streaks to be present in a $+X$ growth specimen and not in a $-X$ growth specimen, although $-X$ always contains more impurities. Cook did find that in general the line breadth was greater in the $-X$ growth specimens, indicating more defects of some type. Furthermore, smoky regions which are caused by impurities do not always exhibit etch tubes. Thus, if an impurity is responsible for the etch tubes it is apparently not the impurity which is considered to be responsible for smokiness.[4] Hydrogen, present as hydroxide, is one impurity which could cause etch tubes, but one is hard put to explain why hydroxide ion should not be incorporated into the lattice uniformly. One must, it seems, consider the nonuniform inclusion of impurities as only a possible cause of the formation of etch tubes.

A third explanation of the formation of the etch tubes is that they are the result of a combination of the two possibilities discussed above; i.e., they are caused by the etching of impurities which have precipitated along dislocation lines after diffusing to them. This would account for the great depth and small cross section of the etch tubes. Unfortunately, an attempt to isolate impurities from the etchant failed. Either the concentration of impurities was too small to be observed or the impurity formed a volatile fluoride, such as HF, which was lost.

If we do not attempt an atomistic picture of the defects resulting in etch tubes some aspects of the tubes themselves are interesting. For instance, why should the eight tubes shown in Fig. 7 make a slight curve near the seed which changes their direction of approach to the seed by 4°? One explanation is that because of a higher impurity content near the seed the ratio c/a for the quartz unit cell is slightly different there. This should be detectable by careful x-ray analysis, but attempts by W. L. Bond[14] to observe lattice parameter differences between seed plates and grown quartz on other crystals have so far been unsuccessful.

The directions the etch tubes take are also puzzling. Although they tend to lie in the general direction of growth, they appear to be located at random on the face of origin and to make a multitude of angles with it. In the case of the Y-bar crystal all tubes pointing toward the seed were curved; all tubes pointing toward inclusions were straight. This was true even though the seed and inclusions were in the same region of the crystal. It is very difficult to suggest a mechanism for tube formation which explains this.

Equally puzzling are the great differences observed in the density of etch tubes on different faces and on faces which differ only because quartz is piezoelectric. Thus no etch tubes are observed lying near the (0001) direction in any crystal, and $(11\bar{2}0)$, $(-X)$, always has a high density of etch tubes in Y-bar crystals but none in CT crystals. From the few examples studied one gets the impression that the density of etch tubes is related to the impurity content which, in turn, depends in some way on the polarity of the crystal and perhaps direction of growth. It is known that the purity of quartz grown on various faces, beginning with Y-bar seeds, varies as follows in order of decreasing impurity content: $[11\bar{2}0]\ (-X) > [11\bar{2}0](+X) > [0001]$. The density of etch tubes observed on the faces varies in the same manner. BTL synthetic quartz exhibited pit densities of the order 10 cm^{-2} while the natural crystal had a higher density of the order 10^4 cm^{-2}. These estimates are crude and do not apply to the same crystallographic face. The intersection of two etch tubes which was observed at several points in crystal #2 is another phenomenon which is not explained. If the tubes are caused by dislocations the lines in this case must intersect without disturbing each other. It is hard to believe that two dislocation lines lying in two different but nonspecific directions would intersect without some change in one or the other, or both, being observed.

With so many questions unanswered and so few samples, the authors offer no single explanation for the origin and behavior of the etch tubes. It is hoped that the work done so far will stimulate further research. For instance, it is apparent that the preparation of an ultra-pure quartz crystal is of paramount importance. Then etching experiments and experiments like those conducted by Cook,[13] and King,[2] could be done with the hope of discerning the role played by trace impurities in modifying the properties of quartz crystals.

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