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Etch pit shapes on {110} surfaces of CaF_2 crystals

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Abstract. {110} surfaces of CaF_2 crystals are etched with different concentrations of HCl. It is found that concentrated HCl produces characteristic rectangular pyramidal etch pits and 2 volume percent HCl produces boat shaped etch pits. Such variations in the etch pit shapes on {110} surfaces of CaF_2 crystals with different concentrations of HCl have been explained. Concentrated H_2SO_4 is found to be a suitable chemical polisher for these surfaces, the polishing rate is about 0·1 μ/min.

Keywords. Chemical etching; etch pit shapes; etch pit orientation; chemical polishing; calcium fluoride; etching of CaF_2.

1. Introduction

Etch technique has been one of the useful tools for observing the emergence points of dislocations on crystal surfaces. In the past, enormous work has been done on the etching of cleavage faces of crystals *viz* Gilman and Johnston (1957) on LiF, Hari-Babu *et al* (1966) on NaCl, Patel and Choudhari (1969) on KCl, Patel and Singh (1970) on BaF_2:$BaCl_2$ crystals. These workers have also observed a rotation of the square etch pits by changing either the concentration of etchants or the impurity content in the etchants. Recently, Jain and Murty (1976) have reported the etching of {110} polished surfaces of NaCl single crystals. Evants and Sauter (1961) have described the etching of {110} surfaces of diamond and observed the rotation of boat shaped etchpits by changing the temperature of the air etchant. The etching of {001} surfaces of CaF_2 crystals have already been reported by Jain *et al* (1981). In the present paper the authors have described the etching of {110} surfaces of CaF_2 single crystals and have obtained etch pits of different shapes by changing the concentration of the etchant. An attempt to explain the formation of etch pits of different shapes with a change in concentration of the etchant has also been made here.

2. Experimental procedure

Mechanically polished {110} surfaces of CaF_2 crystals are chemically polished by treating them with concentrated H_2SO_4 at room temperature for 2 hr (Jain 1979).

This reagent dissolves the surface layers of the crystal at the rate of about 0.1 μ/min. These polished surfaces are rinsed in water, subsequently in absolute alcohol and finally in anhydrous ether. The surfaces are then etched by immersing them in concentrated HCl for about 30 min or in 2 vol. % HCl for about one hour. After rinsing, the surfaces are examined with the Reichert universal microscope.

3. Results

The three consecutive stages of etching, polishing and again etching of the same region of a $\{110\}$ surface of a CaF_2 crystal are shown in figures 1, 2 and 3 respectively. Etching of the surfaces with concentrated HCl for 30 min. in each of the two stages of etching as mentioned above, produced the rectangular pyramidal etch pits with their long sides parallel to $\langle 110 \rangle$ and the short ones parallel to $\langle 100 \rangle$ directions as shown in figures 1 and 3. Although the general appearance of the two patterns is similar, the pattern of figure 3 has changed in respect of the four pits on the right side which have come closer and the grain boundaries have shifted towards the left side. From this it appears that the dislocation lines are inclined to the surface. Figure 2 shows the same region after polishing with concentrated H_2SO_4 at room temperature for 30 min. The disappearance of all the pits indicates the effective polishing action of the reagent. Figure 4 shows the boat-shaped etch pits on a $\{110\}$ surface of a CaF_2 crystal when etched with 2 vol. % HCl for one hour. The keels of the boat pits are along $\langle 100 \rangle$ directions.

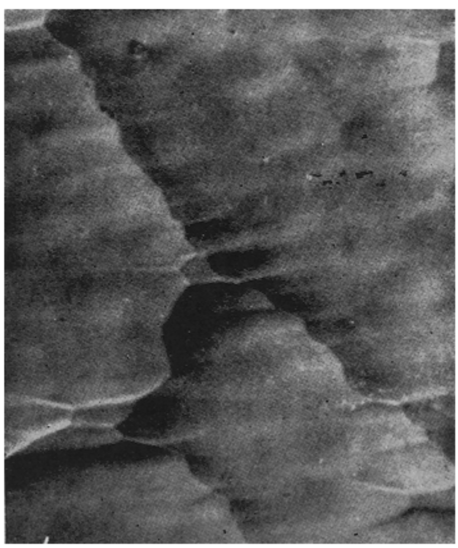
On comparing the etching action of dilute and concentrated HCl, it is found that the pit shapes change on changing the concentration of the etchant. A close observation of the etch pits shows clearly that not only have they changed from rectangular shape to boat shape but their lengths have rotated simultaneously through an angle of 90° (from $\langle 110 \rangle$ to $\langle 100 \rangle$ directions) on changing the concentration of HCl. It may be noted here that etching at intermediate concentrations of HCl was not possible as the solvent eats away the surface at such concentrations.

4. Discussion

Arrangement of atoms on a $\{110\}$ surface of a CaF_2 crystal is shown in figure 5. Considering only the nearest bondings between opposite ions (*i.e.* Ca and F atoms) alone, it can be easily conceived that each Ca atom on the surface is bonded to 6 F atoms (4 in the surface and 2 below the surface) and each F atom on the surface is bonded to 3 Ca atoms (2 in the surface and one below the surface).

A procedure similar to that of Evans and Sauter (1961) has been followed here to consider the formation of a rectangular pit. Imagine the nucleation of a unit rectangular pit on a $\{110\}$ face, outlined by the atomic steps 1 being parallel to $\langle 100 \rangle$ and the steps 2 being parallel to $\langle 110 \rangle$ directions respectively; such a pit grows in size by the retreat of these steps and continues to retain the rectangular shape with its short sides parallel to steps 1 retreating at a faster rate and long sides parallel to steps 2 retreating at a slower rate.

(1)

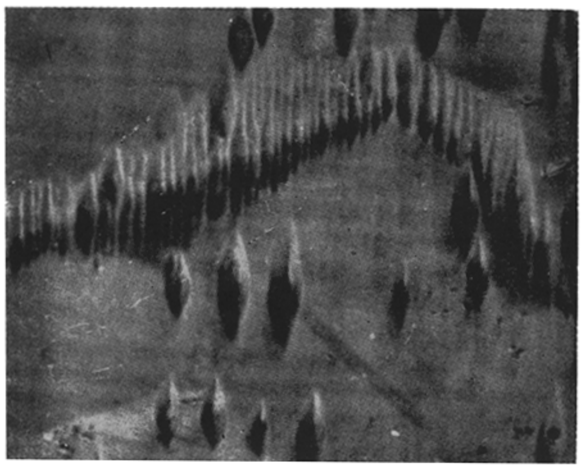


(2)

Figure 1. Rectangular pyramidal etch pits on a {110} surface of a CaF_2 crystal etched for 30 min. with concentrated HCl. The long sides of the pits are along ⟨110⟩ and short sides are along ⟨100⟩ directions. (× 700).

Figure 2. The {110} surface of figure 1 after polishing with concentrated $H_2SO_4$for 30 min. showing the disappearance of etch pits. (× 700).

(3)



(4)

Figure 3. Etch pattern on the same surface of figure 2 when etched with concentrated HCl for 30 min. The etch pits have reappeared with their long sides along ⟨110⟩ and short ones along ⟨100⟩ directions. (× 700).

Figure 4. Boat shaped etch pits on {110} surface of a CaF_2 crystal when etched with 2 vol. % HCl for one hour. The keels of these etch pits are along ⟨100⟩ directions. (× 700).

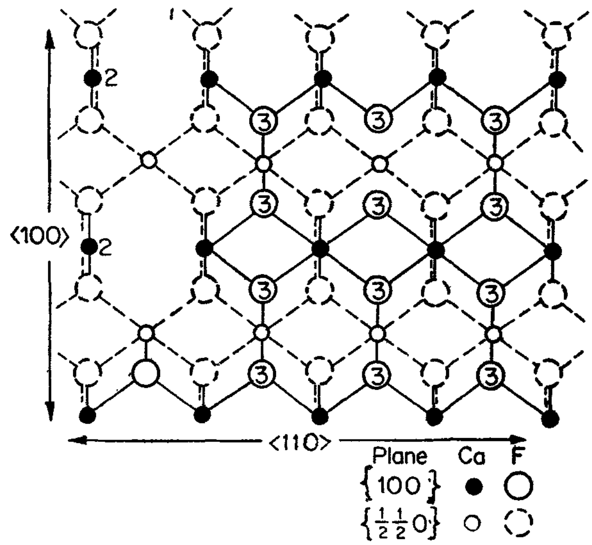


Figure 5. Arrangement of atoms when viewed normal to a {110} surface of CaF_2 crystals.

4.1 *Etching with concentrated HCl*

In the {110} plane of the two atoms Ca and F, the atoms F being larger in size will be attacked first by HCl when it is in concentrated form; as such the steps 2 retreat by the removal of two rows of F atoms (with 3 bonds in each row), followed by a row of Ca atoms (with 2 bonds), thus involving breaking of 8 bonds. Likewise steps 1 retreat by the removal of one row of F atoms (with 3 bonds) first and then a row of Ca atoms (with 2 bonds). Thus, steps 1 involves 5 bonds for their retreat through a distance which is $1/\sqrt{2}$ times the distance traversed by the steps 2. The effective number of bonds involved for the retreat of steps 1 may therefore be regarded as $5/(1/\sqrt{2})$. This shows that the binding energy of steps 2 is more than that of steps 1, hence steps 2 move slower than steps 1 which explains why the rectangular pit has its long sides parallel to ⟨ 110 ⟩ and short sides parallel to ⟨ 100 ⟩ directions.

4.2 *Etching with 2 vol. % HCl*

When 2 vol. % HCl is used as an etchant, due to its high degree of undersaturation, general dissolution of the surface takes place and lower layers of the surface also get affected. Selective etching not being possible, the formation of boat-shaped etch pits cannot be considered in terms of lateral displacement of atomic steps over the surface. Evans and Sauter (1961) have explained their formation as the results of the tendency of depressions to assume a shape bounded by the surfaces with the slowest etch rates, in order to stabilize themselves. But the definite outlines of the boat pits of figure 4 give an indication that inspite of the general dissolution of the surface, the mechanism of lateral retreat of atomic steps might have also come into play a role in the final formation of the boat shaped etch pits; these atomic steps seem to be parallel to the directions of some higher indices. Of course, the lateral retreat of the above atomic steps cannot be attributed to their binding energies, but there is a possibility that the reaction products might have played a role in controlling their relative retreat velocities by way of inhibiting them in the final stage of formation of the etch pits, and as such the etch pits have boat shapes with the definite outlines.

References

Evans T and Sauter D H 1961 *Philos. Mag.* **6** 429

Gilman J J and Johnston W G 1957 Dislocations and mechanical properties of crystals, (New York: John Wiley) Eds. Fisher J C, Johnston W G, Thomson R and Veerland Jr T 116

Hari Babu V, Sirdeshmukh D B and Bansigir K G 1966 *Philos. Mag.* **14** 1067

Jain L C and Murty T S 1976 *Indian J. Pure Appl. Phys.* **14** 67

Jain G C, Krishnamoorthy R and Murty T S 1981 *Indian J. Pure Appl. Phys.* **19** 1012

Jain G C 1979 *Studies of hardness and elastic-plastic properties of crystals* Ph.D. Thesis University of Jabalpur

Patel A R and Choudhari R M 1969 *Indian J. Pure Appl. Phys.* **7** 341

Patel A R and Singh R P 1970 *Indian J. Pure Appl. Phys.* **8** 30