CHAPTER 12

DETECTION OF LATTICE DEFECTS BY USING ETCHING TECHNIQUES

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12.1 Introduction

When crystal studies are subjected to the action of some suitable etchants, small geometrical depressions called "etch pits" appear on them. The shape of the etch pits depends upon the nature of the solvent or etchant and the symmetry of the crystal face[1]. Just as the regular geometry and external shape of the crystal are an orderly arrangement in which the units of constructions are built up during growth, so also, when it is attacked by an etchant, the etch figures thus are related to the internal molecular structure[2]. The concept of lattice defects (dislocations) satisfactorily explains the origin of etch pits and their development[3,4].

The studies of dislocations in crystalline solids by etching technique are a subject of considerable interest to many investigators[5-10]. The first convincing evidence that the etch pits nucleate at dislocation sites is given by Vogel et al[5] showed that the number of etch pits at low angle boundaries in germanium crystal corresponds to the grains determined by X-rays. Etch pits are produced at the centres of growth spiral confirming their association with screw dislocations[11]. Further confirmation in this regards is furnished by Lang[12] using X-ray topography showed that the point bottomed pits on diamond surfaces are produced at the emergent point of dislocation lines.

For defect studies, usually the cleavage faces are preferred to the natural ones, because they are free from the usual growth features and other surface markings, which affect the etch patterns produced. The present chapter describes the perfection properties of these crystals by studying dislocation etch pits.

12.2 Experimental

The gel grown transparent and good quality of large RHT crystals are selected for etching study. They are cleaved along (010) planes and the cleavages are first examined by multiple beam interferometry and then subjected to different etchants. They are then cleaned with distilled water and then dried with the help of filter paper. The etched surfaces are examined optically after a thin silver film is deposited on them. They were also examined in the scanning electron microscopy. Usually fresh cleavages are used except for the successive etching experiments. Sutides are made on : (i) the etch patterns produced, on isolated cleavages, (ii) the etch patterns obtained by successive etching, and (iii) the etch patterns produced on matched cleavage faces.

12.3 Observations and Results

12.3.1 Nature of cleavages

The (010) cleavages faces are studied optically and by multiple beam interferometry[13]. They exhibite usual cleavage patterns which are characteristics of soft crystals. A typical matched pair of cleavages is shown in Figures 12.1(a) and 12.1(b). From these figures, it is observed that the cleavages appear almost perfect as in the case of perfectly cleavable crystals. The multiple beam interferometry revealed that these regions are quite flat and the cleavage lines make sharp steps on the faces.

12.3.2 Etching of Isolated Cleavages

Some of the cleavage faces are selected and etched in a 1.0 M formic acid solution for 10 sec. at room temperature. The etch patterns produced on the (010) cleaved surfaces are illustrated in Figure 12.2. Attention is drawn to the following :

1. The shape of the etch pits resembles the shape of the etch pits on the as-grown (010) surfaces.
2. The etch pattern consists of a large number of small micropits randomly distributed and individual isolated point and flat-bottomed etch pits.
3. They are more or less of the same size.
4. Some of the pits occurred in pairs.
5. All the point bottomed pits are eccentric, i.e. the point bottoms of

the pits are not the geometrical centre of the pits, but are displaced from them.

12.3.3 Successive Etching of (010) Cleavages

In order to test that the pits are nucleated at the sites of dislocations, a (010) surface is successively etched for the different periods of time. Figures 12.3(a) and 12.3(b) represent the etch patterns in the same region produced in the 1.0 M formic acid for different period of times. It may be noted that :

1. No new pits are produced on successive etching.
2. The sizes and depths of etch pits increase with an increase in the time of etching, while their size remains unaffected.
3. The structure of the pits remain the same.
4. Some flat-bottomed pits disappear on continued etching.
5. The eccentricities associated with the point bottomed pits increase as the time

of the etching is increased.

The experiment of chemical polishing and re-etching of the same (010) surface show the persistance of the same etch pattern, even after removing a layer of 40 microns. This observation thereby confirm that the pits are nucleated at the sites of dislocations.

12.3.4 Etching of Matched Faces

The effectiveness of this etchant to generate pits at the sites of dislocations is further confirmed by the etch patterns produced on matched cleavage faces. Figures 12.4(a) and 12.4(b) illustrate the etch patterns produced on matched faces etched in 1.0 M HCl solution for 30 sec. It is observed that :

1. There is a one-to-one correspondence in number and positioning of pits on the matched pair.
2. Occasionally, pits having no correspondence are also observed.

3. The bottoms of the point bottomed pits on matched pairs are displaced in opposite sense, though their eccentricities appear to be the same. The inclination of the lines followed by bottoms is found to be the same for matched pairs of pits.

12.4 Low Angle Boundaries

During etching experiments it is frequently observed that the etch patterns consisted of long chains of more or less equally spaced etch pits similar to those observed by Vogel et al[5]. Figure 12.5 illustrates the etch patterns in which a row of elongated etch pits fully resolved, is clearly seen. The spacing between successive etch pits, 1.5 µm and the angle of the tilt calculated from the spacing is 16″. Figures 12.6(a) and 12.6(b) show the exact correspondence of low angle boundaries on the matched faces. Thus, the rows of pits observed represent the low angle boundaries which consists of rows of edge dislocations and that the pits in the boundaries reveal the dislocation etch pits.

12.5 Discussion

The (010) cleavages are quite flat suggests that the crystals might be having fewer dislocations. The fact that by successive etching, the pits grow larger and deeper (although their number does not change) and their bottoms follow linear path indicates that the etch pits nucleate at the sites of dislocation lines terminating on the cleavage faces. This is confirmed by one-to-one correspondence of pits observed on the matched pairs, when they are etched in the same etchant. The observation that some of etch pits in pairs indicates that they are nucleated at the two intersections of a single dislocation loop with the surface under investigations. That the rows of pits observed represent low angle tilt boundaries which consist of rows of edge dislocations and that the etch pits in the boundaries reveal the dislocation etch pits. Interestingly in some cases when (110) faces are etched in formic acid solutions, the etch hillocks produced as shown in Figure 12.7. It is conjectured that the formation of hillocks has nothing to do with dislocation but may be entirely a surface nucleated phenomenon.

12.6 Conclusions

1. RHT crystal possess (010) cleavage plane.

2. 1.0 M formic acid and hydrochloric acid solutions at room temperature are able to reveal satisfactorily the dislocation content of RHT crystal.

3. Well defined etch pits traceable etching of isolated cleavages and matched pairs reveal the sites of dislocations.

4. Almost all the dislocations studied are linear, inclined and parallel.

5. Low angle boundaries are preferentially attacked during etching and hence they are clearly visible.

6. The average dislocation density is 10^3 cm^{-2}. The dislocation free regions

can be clearly seen in the optical micrograph.

7. The as-grown (010) faces revealed the presence of dislocation etch pits.

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Captions of the figures

Figures 12.1(a) and 12.1(b) (X 75)	A matched pair of (010) cleavage faces of RHT crystals.
Figure 12.2 (X 100)	Etch pattern produced by etching a (010) cleavage face in 1.0 M formic acid solution for 10 sec.
Figures 12.3(a) and 12.3(b) (X 80)	Etch patterns of (010) cleavage face after etching at room temperature for (a) 15 sec. (b) 35 sec.
Figures 12.4(a) and 12.4(b)	Etch patterns on matched faces (for 30 sec.).
Figure 12.5 (X 250)	Low angle tilt boundary on (010) face of RHT.
Figures 12.6(a) and 12.6(b)	Correspondence of grain boundary on matched faces.
Figure 12.7 (X 100)	Etch hillock produced on (110) face.

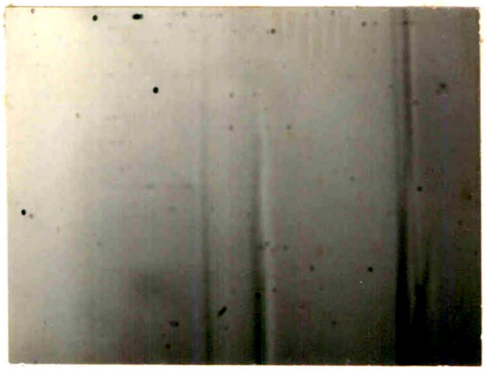

Fig. 12.1(a)

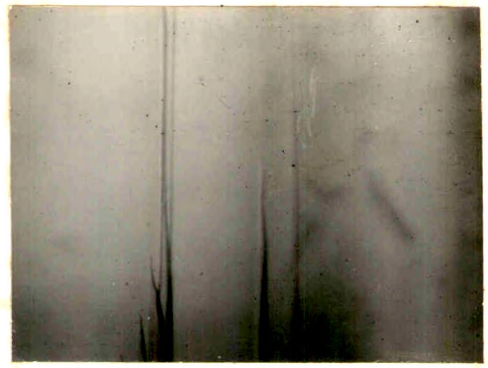

Fig. 12.1(b)

Fig. 12.2

Fig. 12.3(a)

Fig. 12.3(b)

Fig. 12.4(a)

Fig. 12.4(b)

Fig. 12.5

Fig. 12.6(a)

Fig. 12.6(b)

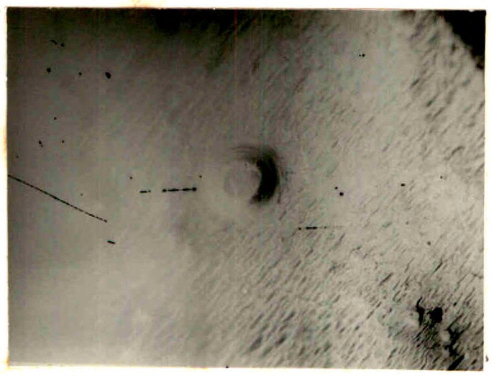

Fig. 12.7