Edge Dislocation by Etchant on Cleavage Planes of Glycine Potassium Sulphate (GPS) Crystal

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ABSTRACT

The grown crystals of glycine were used for edge dislocation. Etchant A [85% formaldehyde, 13% distilled water, 2% nitric acid (analar grade)] and etchant B [Propionic acid and formic acid in the volume ratio 9:1] reveals the sites of edge dislocations on (010) cleavage planes of glycine Potassium Sulphate (GPS) crystals. Ethyl alcohol (not less than 99%) was used as rinsing agent. It is found that the etchant B is superior to etchant A, as the surface dislocation with etchant B along [110] direction is less than with etchant A. n-propyl alcohol with distilled water in the volume ratio 3:1 is reported as chemical polishing agent which remove the surface layer at about 0.4 μm. min^{-1}. The structure of isolated pits form on the surface and of those formed along low angle grain boundaries is the same, which suggest that pits are probably formed at the site of edge dislocations. The density of pits of low angle grain boundary remains the same after removing the surface layer of about 4 μm. The implications are discussed.

Keywords: Organic compound, dislocation, GPS crystals.
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INTRODUCTION

Glycine (NH_2CH_2COOH) is a non essential amino acid, which is hydrophilic polar in nature. Understanding and controlling solution crystallization and polymorphism has been an area of active research for many decades [1]. Amino acid are widely used as model systems in these studies because of their well established physical properties ability to crystallize in a range of polymorphs [2]. The simplest amino acid, glycine, crystallize in three distinct polymorphic forms at atmospheric pressure α, β and γ [3]. Recently, additional polymorphs of glycine that formed under high pressure have been reported [4, 5]. Crystallization from solution has been the subject of intense research in recent years. The nucleation of crystals from solution is of great important in industries, since it is the primary method for the preparation and purification of industrially

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important chemicals, such as pharmaceuticals, explosives, dyes and photographic materials. Crystallization is also used for the synthesis of single crystals of proteins, amino acids etc., as well as very small crystals whose large surface area make them important for gas sensing catalysis among other purpose. The early stage of the formation of the particles from solution can play a decisive role in determining the properties of solids and its initial stage.

Referring the work of Konstantionva [6], Dunning [7] has shown that information concerning the line defects present in the bulk of the crystals, obtained by etching techniques, helps towards the better understanding of the surface structure of organic solids. Thomas and Williams [8] have shown that crystal dissolution is one of the phenomena of chemical interest which is governed or modified by the presence of dislocations, particularly in organic solids. Then he also tabulated a very good survey of the information available on dislocation in organic solids. Glycine is of interest for such studies as it has some peculiar characteristics such as: i) in the molecular symmetry each hydrogen atom is surrounded by three oxygen atoms and ii) When the proper amount of sulphuric acid is added to an aqueous solution of glycine, ferroelectric crystals of triglycine sulphate can be obtained [6]. Therefore, as initial stage studies of dislocation in glycine crystals, the etchants are reported in this paper.

MATERIALS AND METHODS

Experimental Details:
Thermodynamically, Glycine is most stable under ambient condition. Crystallization of glycine with Potassium Sulphate in neutral aqueous solution is typically hindered by the formation of the kinetically favored α form. A GPS solution that are at or close glycine's isoelectric points of 5.79 favors the formation of neutral Zwitter ionic cyclic dimmers ($^+H_3NCH_2COO^-)_2$, are the elementary building blocks of α polymorph. In contrast, GPS solutions with a pH value for enough from the isoelectric points will promote the formation of cations ($^+H_3NCH_2COOH$ at low pH) or anions ($H_2NCH_2COO^-$ at high pH), resulting in a "self-poisoning" mechanism that inhibits the crystallization of GPS is obtained. Glycine (amino acetic acid, NH_2CH_2COOH) has monoclinic symmetry along (100) [9]. Crystals of GPS were grown from solution by a slow evaporation technique at room temperature. Good transparent crystals of average size 1.2 cm x 0.4 cm x 0.4 cm can be obtained within 13-15 days. Usually freshly cleaved (010) face were etched in the etchant A {85 % formaldehyde, 13% distilled water and 2% nitric acid (annular grade)} for 2 to 6 sec. The etch patterns thus produced on (101) face were observed with a metallurgical microscope "METZER-780". Metaphot is used for dislocation studies on crystal. Whenever necessary, n-propyl alcohol and distilled water in the volume ratio 3:1 were used as chemical polishing agent, which removes the surface layer at about $0.4\mu.m. min^{-1}$.

An etch pattern produced by etchant A on a (010) cleavage plane is shown in the photograph of fig. 1(a). In this figure, XY is the cleavage step and ST is a row of pits. Some isolated pits are marked by L, M, N etc. The structure of etch pits reveals no definite boundary along a [110] direction. The same crystal phase was further etched for 2 second and the resulting etch pattern from the corresponding region is shown in fig. 1(b). It is observed that (i) the isolated pits have increased in size at the same sites, suggesting that the cleavage step has moved on prolonged etching [10] , and (ii) the dissolution of surface along a [110] direction is faster than that along a [010] direction [11].

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Etch patterns on (010) cleavages

(a)   (b)

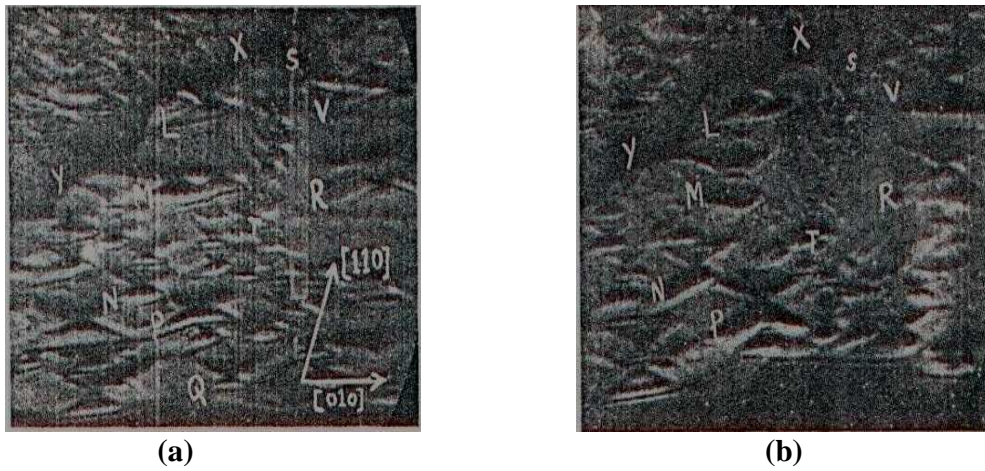**Fig. 1 Etch pattern of GPS crystal.**

(a)   (b)

Fig. 2(a) and (b) Etch patterns on GPS showing one to one corresponds of etch pits produced on matched cleavage planes. (etching time 2 second).

Low-angle grain boundaries on (010) faces:

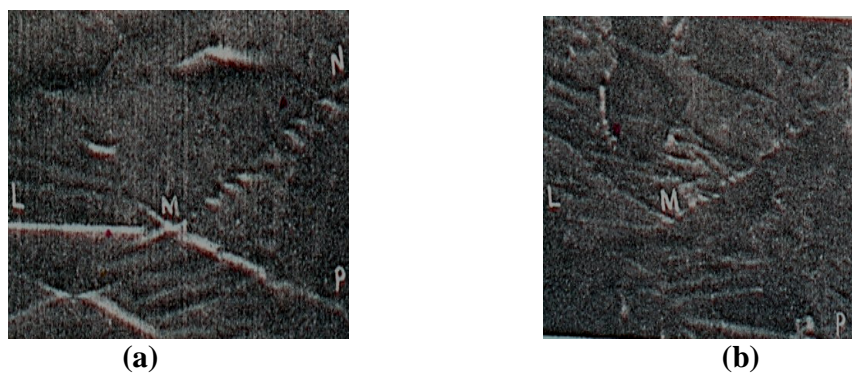(a)   (b)

Fig. 3(a) Low-angle grain boundaries forming a trisection junction observed on (010) plane etched for 6 second, (b) the same trisection junction shown in Fig. 3(a) observed at the depth of about 4 µm for 6 second.

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Fig. 2 shows the etch patterns on the matched faces. It is noted that the row of pits LM, low angle grain boundary XYZ and the isolated pits Q and R observed in fig. 2(a) have an exact correspondence with features on the matched surface, seen in fig. 2(b). From these observations, we conjecture that the etchant A produces the etch pits at the sites of dislocations.

To confirm our conjecture, we made studies on low-angle grain boundaries. It may be mentioned that the rows of equally spaced pits on crystal surfaces can usually be attributed to edge dislocations in low-angle grain boundaries [12]. Hence fig. 3(a) shows three grain boundaries LM, MN and MP forming a trisection junction, similar to those observed on KCl crystal by Patel and Chaudhari [13]. For a stable configuration of such low-angle grain boundaries forming a trisection junction, the relation $n_a = n_b + n_c$ must be satisfied [14], where n_a, n_b and n_c are the densities of pits of the three boundaries. It is difficult to know the pit density of the low-angle grain boundary LM, as both the boundary and apexes of the etch pits are parallel to a [010] direction, to confirm the above relation. The density of etch pits of the of the low-angle grain boundary MN is found to be 0.0422 pits $\mu.m.^{-1}$. The same trisection junction was observed at a depth of about 4 µm [fig. 3(b)] obtained by re-etching the same crystal surface after chemical polishing. It is observed that the density of the pits of the low-angle grain boundary MN remains the same.
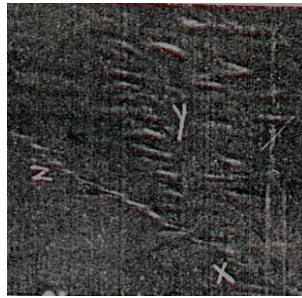

Fig. 4. Trisection junction of low-angle grain boundaries.

Fig. 4 shows another trisection junction of low-angle grain boundaries in which it is possible to confirm the relation $n_a = n_b + n_c$, as none of the low-angle grain boundaries are parallel to a [010] direction. The densities of pits of the low-angle grain boundaries X, Y and Z are 0.01130, 0.01500 and 0.0265 pits/µm. respectively, which satisfies the above relation. Moreover it is seen that the low-angle grain boundary Z disperses at one end (free end). At this end the density of pits decreases. This is in accordance with the observations of Geguzin and Matsokin on NaCl.[15]

RESULTS AND DISCUSSION

Because the etch pits increases in size at the same sites on prolonged etching, the relation $n_a = n_b + n_c$ holds good for the trisection junction of low-angle grain boundaries and the density of pits of the low-angle grain boundary remains the same after the removing the surface layer of about 4 µm, it can be assumed that the etchant A produces the pits at the sites of dislocations. The structure of the isolated pits formed on the surface and of those formed along low-angle grain boundaries is the same, which suggests that these pits are probably formed at the sits of edge dislocations.

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A detailed investigation of the low-angle grain boundaries running parallel to [010] direction is not possible with this etchant, because the apexes of the pits are parallel to [010] direction, which results in the low-angle grain boundary etching as continuous line, as XY in fig. 2(a) and LM in fig. 3(a). The shape of etch pits reflects the slow dissolution rate along the directions parallel to the sides of the pits.[11] Hence the dissolution rate along a [110] direction is faster than that along a [010] direction as seen from the structure of etch pits produced by etchant A. Although this etchant produces the etch pits at the sites of edge dislocations, it fails to reveal much information about the dislocations when they are aligned roughly along a [110] direction. This demands an etchant which will produce the etch pits at the sites of dislocations which a dissolution rate along a [110] direction les than that of etchant A. It was found that propionic acid and formic acid in the volume ratio 9:1 (hereafter called etchant B) produces etch with their sides parallel to [010] and [110] directions.
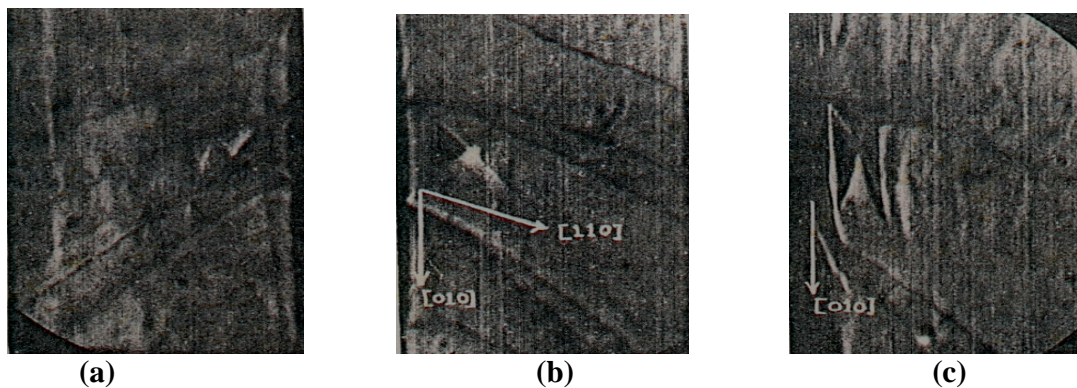

(a)   (b)   (c)

Fig. 5 Photomicrographs of etched pits on GPS.

Figures 5(a) and 5(b) are photomicrographs of match faces etched with etchant B for 30 seconds. It may be noted that the etching time is considerably greater than with etchant A. Exact correspondence is seen in the case of the isolated each pit. Fig. 5(c) is a photomicrograph of the region fig. 5(b) after re-etching the surface in etchant A. From comparison of figures 5(b) and 5(c), it is noted that:

1. Pits produced by etchant B have sides parallel to [010] and [110] directions, while the pits produced by etchant A have longer side parallel to a [010] direction.
2. Etchant B produces etch pits at the same sites as that of etchant A.
3. Pits produced by etchant B have more clearly resolved apexes than those produced by etchant A.
4. The pits produced by etchant A have the depth of about 2-5 µm (etching time 5 second), where etchant B produces the pits of depth of about 1.2-1.6 µm (etching time 20-25 seconds) suggest that the pits produced by etchant B are shallower than those produced by etchant A.
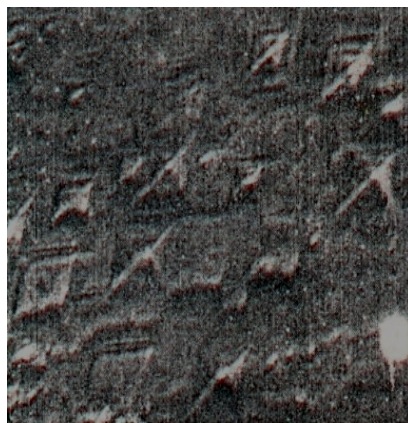
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Fig. 6. Etch pattern on a (010) plane produced by etchant B.

Still more information regarding the dislocations can be obtained from the structure of etch pits produced by etchant B, as revealed from fig. 6. In this case the density of pits is greater than that seen in fig. 5. Along with the pointed bottomed etch pits, some flat bottomed, terraced and small pits are also observed. Such pits are not produced by the etchant A.

CONCLUSION

From the edge dislocations on cleavage face, it is observed that 1) etch pits increases in size of the same site by maintaining their geometry on prolong etching, 2) the etch pits have one to one correspondence on matched cleavage face (110) and 3) The density of pits of low angle grain boundary remains the same after removing the surface layer of about 4 µm. The structure of isolated pits form on the surface and of those formed along low angle grain boundaries is the same, which suggest that pits are probably formed at the site of edge dislocations.

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