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EVALUATION OF STRUCTURAL DEFECTS IN CRYSTALS - A PREREQUISITE TO CRYSTAL GROWTH IN SPACE

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16. Abstract

The task of evaluating the crystals to be grown in space is considered. A need for realizing the relevance of the line defects (such as dislocations and stacking faults), complexes of these and point defects, and impurity segregates is stressed. Techniques for observing these defects are discussed in regard to their applicabilities to the precious space-grown crystals. Etching techniques are partially destructive, but of multiple utility. Their application to gallium arsenide epitaxial layers grown on earth is demonstrated by the experiments done in the laboratory. Precise experimental procedures are given.

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EVALUATION OF STRUCTURAL DEFECTS IN CRYSTALS — A PREREQUISITE TO CRYSTAL GROWTH IN SPACE

SUMMARY

Present work is devoted to evaluation of the crystals to be grown in space. Special attention is given to gallium arsenide (GaAs) which is being considered for the crystal growth experiments on the Skylab I.

A brief general discussion of the structural defects is given to determine a useful and desirable procedure for evaluating a space-grown crystal. Relevance of needed stress on the line defects (such as dislocations and stacking faults), complexes of these and point defects, and impurity segregates in the primary evaluation of the crystal quality is discussed. Techniques for observing these defects are briefly discussed in regard to their applicabilities for studying the precious space-grown crystal. Etching techniques and their potentialities are discussed in detail, since they are considered of multiple use in the crystal evaluation.

Application of the etching techniques in the evaluation of the earth-grown GaAs epitaxial layers is demonstrated from the experiments performed in the laboratory. The etchants used and precise etching procedures are described. A typical stepwise experimental procedure is indicated. The results show that a bi-etching procedure for GaAs is of special utility. An etchant reported in this work is capable of revealing dislocations and the associated defects on all low-index planes of GaAs crystal.

I. INTRODUCTION

During the past 1 or 2 years there has been increasing support for the proposals for growing synthetic crystals under reduced gravity in the unique environment of space [1, 2]. Prospects of being able to grow highly perfect crystals in space are fairly convincing [2]. Since a large program of crystal growth in space has already been launched under NASA, concentrated in-house effort on the development of suitable techniques for evaluation of the crystals is necessary. This would be complementary to the effort in the area for developing the suitable crystal-growth techniques for use in space [2], and, in fact, would help their development.

This work is devoted to the development of the techniques for evaluation of the structural defects in crystals, since these are expected to be influenced markedly by growth in space. Since we can expect only a few crystals that can be grown in space, the space-grown crystals will be highly precious, and a careful evaluation plan requiring minimum damage to the crystal will primarily be desirable. To accomplish this, a section is devoted to briefly discussing the basic concepts of the defects in crystals, and to the common methods of observing them. Later, etching techniques for observing defects like dislocations and stacking faults are discussed in detail, and the utility of these techniques is demonstrated by the experiments performed in the laboratory on the vapor-grown GaAs epitaxial layers. GaAs is chosen because it is being considered as one of the most favorable candidates for processing in space. However, etching techniques of more general applicability are also discussed.

II. STRUCTURAL DEFECTS AND THEIR OBSERVATION

A. Conceptual Considerations

Crystal defects or imperfections in crystals may be classified [3, 4] under three main categories:

1. Point defects – Point defects consist of missing atoms (ions) sites in the lattice (or vacancies) and interstitials. These defects are of thermodynamic origin and can be considered as intrinsic defects. Foreign atoms (ions) substituted at the normal lattice sites or incorporated as interstitials are also considered as point defects. However, their influence on the properties of the crystal is called extrinsic, and for that matter they may be called extrinsic point defects.

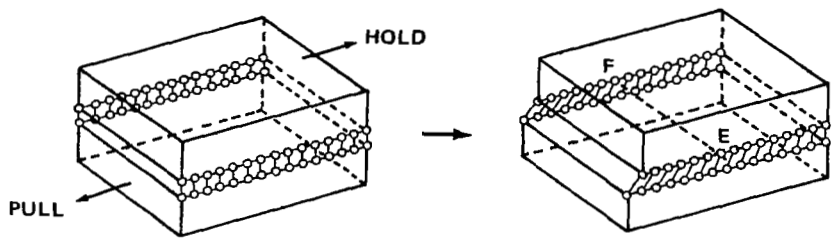
2. Line defects – Line defects consist of purely geometrical faults called dislocations. The concept of these defects arises from the crystallographic nature of the plastic flow in the crystalline materials [3]. In a strained material, the plastic flow occurs by sliding of certain atomic planes called slip planes whose structure remains crystalline during the flow. If we consider plane A of atoms sliding in a certain direction across neighboring plane B, different portions of A, in general, slip over B by different amounts, because the atoms in the crystal are not rigidly bound to each other but are elastically coupled. A boundary may be pictured such that on either side of this, planes A and B have slipped by different amounts. The type of discontinuity making this boundary is called a dislocation. Clearly, a dislocation extends over several interatomic distances.

One distinguishes between two types of dislocations [5] — translational dislocations (such as edge dislocation and screw dislocation), and rotational dislocations which cause lattice distortions to increase toward the center of the dislocation line that usually runs along the crystallographic direction of a rotation axis. To fix the ideas, formation of the edge, screw, and rotational dislocations is illustrated in Figure 1. As shown, EF is the dislocation line; the dislocation line in Figure 1 (c) runs perpendicular to the plane of the paper. It is clear that the rotational dislocations will have a large elastic energy. Consequently, these can be produced under special circumstances [5]. Edge and screw dislocations are those commonly observed in the crystals. A distinction is made between perfect and imperfect dislocations also [5]. To understand this distinction, we have to consider the following:

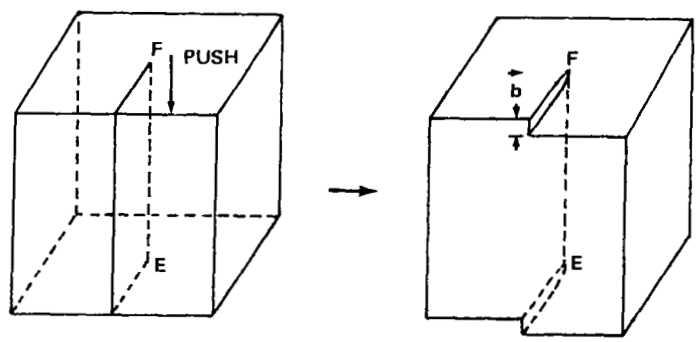
On a perfect lattice plane of the crystal, a route may be traced through nearest neighboring atoms (ions) in such a way that it forms a closed plane loop. Such a route is called "Burgers Circuit." Such a route around a dislocation is incomplete, and a translational vector $\vec{b}$, called the Burgers vector, is needed to form the Burgers circuit [e.g., see Fig. 1 (b)]. Usually, $\vec{b}$ is equal to a period of the crystal lattice, or is a simple multiple of the lattice parameter. Such imperfections are the normal or perfect dislocations. When $\vec{b}$ is not equal to a period of the lattice, one speaks of an imperfect dislocation. Usually, these are not favored due to their high energy. However, for some imperfect translation $\vec{b}$ and along some surfaces, the energy of sticking becomes favorable and the faults in the normal stacking of the lattice planes, known as stacking faults, become possible. There is a close relation between the stacking faults and twinning commonly observed in metals, alloys, and semiconductors.

3. Complex defects — These result due to aggregation of, or complex structure formation by, the above simple defects. Vacancy pairs and aggregates, impurity-vacancy complexes, impurity microprecipitates, dislocation loops, and networks may be mentioned as examples.

It is easily realizable that the point defects would largely influence the atomic and electronic properties of the crystals. Their role can be studied through investigations on the properties such as conductivity, diffusion, optical absorption, galvano-magnetic effects, magnetic resonance, etc. Dislocations and most complex defects cause buildup of significant strains in the crystal which markedly influence the mechanical properties and as well affect the atomic and electronic properties of the crystal by influencing the migration and association of the point defects. It is also to be noted that the dislocations play an important role in the crystal-growth kinetics [3]. Hence,



(a)



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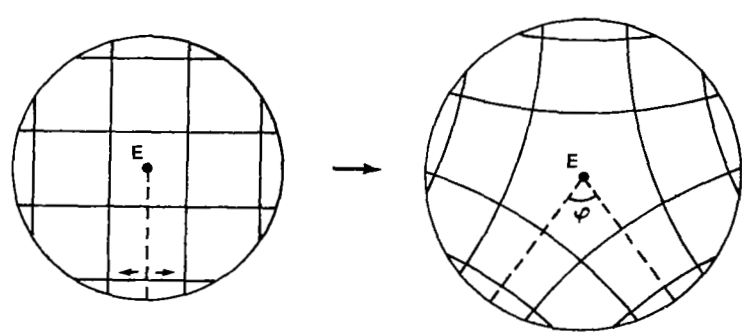

(c)

Figure 1. Formation of (a) an edge dislocation, (b) a screw dislocation, and (c) a rotational dislocation [3,5].

it is logical to concentrate first on the study of the structural defects of types (2) and (3) in expectedly more perfect crystals grown in space. The point defects, though of fundamental importance, are largely the intrinsic property of the crystals (leaving aside the impurity segregation problems). Evaluation of these defects will be necessary subsequently in determining the new applicabilities of the crystals obtained from space.

For the above reasons, the rest of this work is entirely devoted to the evaluation of the line and complex defects with special reference to GaAs, since it is being considered for the first Skylab experiments in the near future.

B. Observation of Line and Complex Defects

Techniques for observing dislocations and their complex structures, and impurity segregates have been described in detail by Verma [3] and Amelincks [6]. The commonly used techniques come under the following heads:

1. Optical.
2. X-ray.
3. Electron microscopic.
4. Etching.

All techniques provide almost direct observation of the defects. Their merit is limited by the limit of achievable resolution. Choice of a suitable technique will depend on several factors, such as (1) the shape and size of the crystal under investigation, (2) cleaving, cutting, and polishing possibilities, (3) permissibility for using destructive techniques, and above all (4) the extent of the details required.

Simple optical topographic techniques provide most direct and nondestructive observation of certain crystal-growth features. X-ray topographic studies can be used nondestructively to obtain finer details. Both optical and X-ray techniques can be used to obtain detailed distribution of the defects in the bulk to the limits of their resolution if the samples can be cleaved and polished. Electron microscopic techniques have proved to be the most versatile and suitable for observing very fine structural details, but they necessarily require small and thin samples (few mm^2 area and few tens of Angstroms in thickness), or require partially destructive and tedious replica

making. Etching, though partially destructive, has provided much detailed information on the structure and distribution of the defects when coupled with suitable optical techniques.

In case of the crystals processed in space, a stepwise procedure to evaluate the quality of the crystal would be necessary[1] to obtain maximum possible information on the effect of the space environment on the crystal growth and crystal perfection. Due to lack of knowledge in this area and the amount of effort and expense involved in growing a crystal in space, each crystal is to be regarded as highly precious. Hence, nondestructive tests will be most desirable as far as possible. As is clear, preliminary optical and X-ray topographic analyses only will be really nondestructive for most materials. These require no special technicality to be mentioned here, being essentially like the common photographic techniques. A planned procedure, though, would be needed , and fundamental knowledge of the scattering and diffraction phenomena will be required for the interpretation. More elaborate optical and X-ray techniques applicable to cleaved and polished samples will be described elsewhere. Etching techniques are considered in this work in some detail because of their possible applicability before cleaving or cutting the space-grown crystal without much loss of the material. The surface studies will be of great relevance in revealing the growth and propagation of the defects in the growing crystal in space.

C. Etching Techniques

1. Principle. In principle, the process of etching is the reverse of the growth process [6]. The technique simply involves immersing of the sample in a suitable medium under appropriate conditions (to be discussed below) to allow dissolution/evaporation of the material. Etching medium may be a liquid (or melt), a solution, or a gaseous chemical reagent. Thermal evaporation of the material may also be used for etching.

Revealing of dislocations and the related defects results from the fact that the removal of the atoms (ions) near the discontinuities in the crystal structure by an etchant occurs at a rate higher than the average rate of removal of the atoms (ions) from the surrounding crystal matrix. Since etching starts from the surface of a given sample, preferential removal of the

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1. A General Procedure for Evaluating the Space-Grown Crystals from the Apollo Flyback Package has been worked out (V. K. Jain, R. C. Ruff, and R. S. Snyder: Unpublished). Typical Suggestive Procedure will be reported here for the evaluation of the GaAs epitaxial layers of unknown characteristics.

material near the defects would give rise to the formation of pits at the emergence points of the dislocations present in the samples. From the distribution and shape of these etch pits, one would hope to obtain information about the structure and distribution of the dislocation type defects. Based on the same principle, the impurity segregates may be revealed as grooves or precipitate clusters on suitable etching.

The pits and their structure after an etching may be studied in an optical or electron microscope by using the common photographic techniques. As mentioned before, applicability of the electron microscope will be greatly limited by the shape and size of the sample.

2. Methods of Etching. It is obvious that etching can be performed in several ways [6, 7]. The etching methods can be described under the following three categories basically:

a. Thermal etching — Preferential evaporation.

b. Chemical etching — Preferential dissolution or removal by forming suitable reaction products using a liquid (or melt) solution, or gas.

c. Impurity decoration and chemical etching — By virtue of the facts that the impurities can decorate along the dislocations, and the segregated impurities may be chemically etched.

Chemical etching has been used most widely in studying dislocations and impurity segregates [6, 7]. Recently [8, 9, 10, 11], thermal etching has gained considerable attention. Thermal etching is of more general applicability than chemical etching and enables the study of dislocation configurations near the melting point of the material. Thus, it is of special significance for understanding the actual crystal growth. The theory of thermal etching has been briefly reviewed by Ejima, Robinson, and Hirth [10]. Applicability of thermal etching is obviously limited by the temperature of decomposition if the material is decomposable. Impurities can segregate along the dislocations preferentially on a heat treatment [6]. The impurity particles formed may be large enough to scatter light and one may be able to see the decoration of a dislocation line by these particles. The impurity decoration can also be revealed by selective etching with an etchant which will either attack the crystal material or the impurity only. It must be pointed out that quite high temperatures may be required to achieve the impurity decoration along the dislocations.

In view of our interest in application to GaAs, which starts decomposing well below its melting point, chemical etching methods will be considered in detail. Any segregation of the impurities along the dislocations during the crystal growth and annealing may be revealed by suitable chemical etching.

3. Search for the Etchant. In general, a search for an etchant for each material for a specific purpose is to be made separately. The primary considerations for a suitable etchant may, however, be summarized as follows [6, 7].

a. Reaction products — Reaction products should be soluble in the etchant liquid or solution, or should be volatile. Hence, the chemistry of the constituent elements must be taken into account, and all possible reactions involved must be checked. In some cases, first products of the etching reaction may inhibit the desired etching. For example, HNO_3:HF solution is an etchant for InSb; but, if very much InSb is etched in the same solution, InF_3 separates out on the sample. A HNO_3: tartaric acid solution overcomes this problem.

As a caution, consideration of the reaction products is very important from the hazards viewpoint also. For example, in case of some III-V compounds, HCl is used as a constituent of the etchant [7]; one of the reaction products with HCl is the Group V hydrides in such cases which are dangerous if inhaled.

b. Etchant's character — Type of the chemical bonding in the material is a guideline in certain respects. If there is covalent bonding, an oxidizing agent will usually be required for breaking the bond. If the material has enough ionic character, the bonds may be attacked by HCl. HNO_3 and H_2O_2 are the commonly used oxidizing agents. Metallic ions like Fe^{3+}, and anions like $Cr_2O_7^{2-}$ have also been used as oxidizing agents. When oxidizing agents are used, it is usually necessary to add a complexing agent to the etchant to keep the ions stable in the solution. For example, in the case of etching of InSb by HNO_3, insoluble antimonyl oxy salts may precipitate in strongly oxidizing solution; HF, HCl, tartaric acid, citric acid, or oxalic acid used as a complexing agent helps in keeping the antimony in solution.

c. Composition of the etchant — Though the composition of an etchant may not be considered very critical, any significant change in the composition will, at least, change the etch rate, and large changes may result in a solution that will not attack the surface of the material; hence, an optimum composition must be found.

d. Etching temperature — Increasing the temperature increases the etch rate unless the stability of the reactants and reaction products is decreased. This may be considered in determining optimum convenient conditions for an etching.

e. Effect of impurities in the etchant — The role of impurities in etching is not well understood at present. There are indications [6, 10] that impurity atmosphere around dislocations helps in revealing the dislocations. It has been found possible [6] to improve the sharpness of the etch pits by adding small amounts of an impurity in the etchant, suggesting that the presence of impurity inhibits the lateral etching rate. However, it has also been shown [7] that the presence of the impurities causes the problem of thermal conversion in GaAs. We feel that it will be safer to use pure etchants as far as possible in the absence of a clear understanding. Only secondary experiments may be performed to investigate the effect of deliberately added impurities on the sharpness of the etch pits on a given material.

4. Information Obtainable From the Etching Techniques. As mentioned before, etch pits formed by etching a surface of the given material sample essentially represent the emergence points of the dislocations present in the sample. From microscopic examination of these pits, the following information can easily be obtained [6]:

a. Density of the singular pits directly gives the density of the dislocations in the sample near the surface examined. Longer etchings may give rise to 2 or more coupled pits, often called dislocation loops, which on continued etching may coalesce. Hence, proper etching time is of importance in determining the dislocation density in a region of interest.

b. Since the etch pits have a certain depth, their shapes can give information concerning the general directions of the dislocation lines as illustrated in Figure 2. Figure 2(a) shows that parallel lines perpendicular to the surface produce symmetrical pits. Figure 2(b) shows that parallel lines inclined with respect to the surface, as in a tilt boundary, produce asymmetrical pits all oriented the same way. Figure 2(c) shows pits formed at the emergence points of a hexagonal grid of dislocation; the pits are asymmetrical and successive pits are oriented differently.

c. A flat-bottomed pit would indicate that the dislocation giving rise to this pit has moved after first etching. After the dislocation has moved, the pit develops laterally, but no longer in depth, as illustrated in Figure 3. Thus, the flat-bottomed [Figs. 3 (a) and 3 (b)] pits represent the intermediate positions of the dislocation; the final position of the dislocation is marked by the centered pit shown in Figure 3 (c). Whence, the dislocation movement in the sample can be studied.

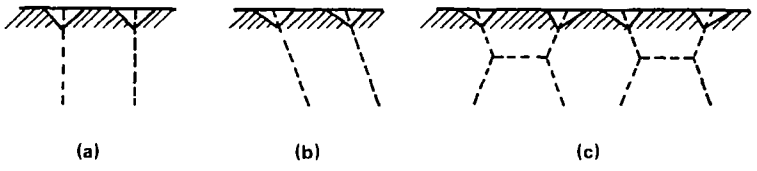

Figure 2. Asymmetry of etch pits due to inclination with respect to the surface of the dislocation lines giving rise to them [6].

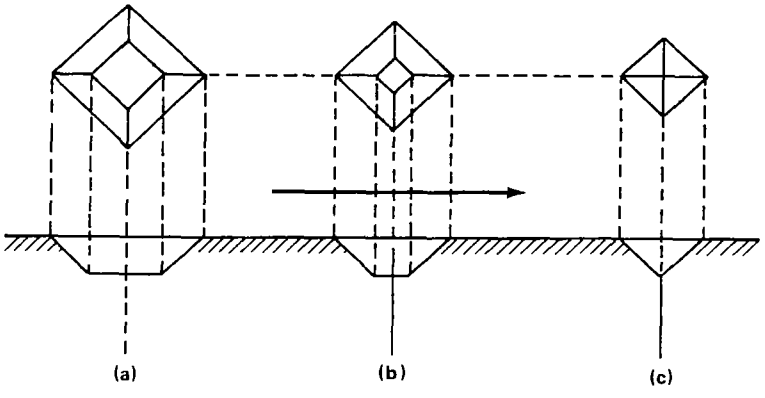

Figure 3. Etch pits due to moving dislocation [6].

d. Debris left by moving dislocations may consist of the aggregates of point defects or of dislocation dipoles broken up in small elongated loops. Consequently, etching at the debris is discontinuous and may be identified.

e. In some cases, dislocations parallel to and close to the surface produce grooves along their length. This is specially observed if the dislocations have acquired an impurity atmosphere (due to unavoidable impurity segregation or intentional decoration with impurity).

f. It is expected that imperfect dislocations, like stacking faults, may also be revealed as etch pits or impurity segregates along them. Regions of other discontinuities, like grain boundaries, will also be etchable and may be revealed.

g. Gradual removal of the surface layers by polishing or cleaving with subsequent etching every time may be used to determine the defects configuration in the bulk of the sample.

III. APPLICATION OF THE ETCHING TECHNIQUES TO GaAs

A. Experimental

The utility of the etching techniques will be demonstrated by the experiments performed on vapor grown epitaxial layers of GaAs[2]. The chemical etching has been used.

1. Etchants. The etchants used are the same as used by Abrahams and Buiocchi [12]. The principal etchant, which selectively attacks dislocations on the Ga{111}, As{111}, {100}, and {110} planes of GaAs, was discovered by these authors, and will be called "AB etchant." It has the composition

2 ml H_2O : 8 mg $AgNO_3$: 1 g CrO_3 : 1 ml HF.

The components are added and mixed in the order listed. If the order is changed, dissolving of $AgNO_3$ is found difficult. Also, it must be noted that the composition of the etchant, as given, is optimum with regard to the formation of a well-defined etch structure.

A second etchant, called "RC-1 etchant" has also been used [12]. This etchant is a modification of an etchant originally used by Richard and Crocker [13], and hence has been called RC-1 by Abrahams and Buiocchi. It produces etch pits on Ga{111} and As{111} planes only. It is prepared[3] by making a 2.4×10^{-3} molar solution of $AgNO_3$ in a mixture of 5 H_2O : 2 HF : 3 HNO_3. Reagent grade chemicals have been used in preparing both the etchants.

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2. These were obtained through the courtesy of Mr. T. C. Bannister of the Space Sciences Laboratory. Unfortunately, the growth conditions of the epitaxial layers are not available, since they were not grown at this center.

3. The amount of $AgNO_3$ for 500 ml of the solution (250 ml H_2O : 100 ml HF : 150 ml HNO_3) is 0.204 g.

2. Etching Procedure. Etching with the AB etchant can be performed at room temperature or at slightly higher temperatures (~65°C). During etching, the solution must be continuously stirred because a precipitate, identified as Ag_2CrO_4 [12], forms as the reaction proceeds; continuous stirring helps in the uniform attack of the specimen surface. It is obvious that the same solution should not be used more than a few times. Etching time required for revealing well defined etch pits and structure is about 10 minutes at 65°C [12]. At room temperature, about a 45 minute etching time has been found adequate which we have used in our experiments for convenience in operation. It may be mentioned here that the minimum necessary time may, in general, vary with orientation and doping of the sample, and with the manner of surface preparation. Hence, for interest in the etching rate and influence of the etching time on the etch pits, a range of etching time from about 30 to 60 minutes may be used. Etching with the RC-1 etchant can also be performed at room temperature. Only about 3 minutes are adequate for revealing the etch pattern, and no stirring is required.

3. Adopted Detailed Experimental Procedure. In accordance with the previous discussion a stepwise procedure was adopted to study the GaAs samples, as described below:

a. The GaAs samples had one shiny surface with a dull opposite surface. The shiny surface was assumed as the epitaxial layer side, and the dull surface as the substrate side. A typical sample measured 3.8 × 3.8 mm^2 (150 × 150 $mils^2$) in area and 0.64 mm (25 mils) in thickness. The thickness d_S was measured at a corner of the sample to avoid damaging the surface at large.

b. A topographical picture of the epitaxial layer (shiny surface) was taken with a metallograph at 15 x and 100 x.

c. The sample was quick cold mounted[4] to avoid any external heating. The epitaxial layer side was kept upwards with care to obtain the layer surface in the plane of the mount as closely as possible (Fig. 4). The thickness d_M of the mount was measured at a corner of the sample, as shown in Figure 4, to be able to approximately determine the thickness of the layer removed in polishing before an etching.

d. The surface of the sample was polished in the usual manner using aluminum oxide powder of 0.01-μm fineness suspended in water

4. Quickmount obtained from Fulton Metallurgical Products Corporation, Pittsburgh, was used.

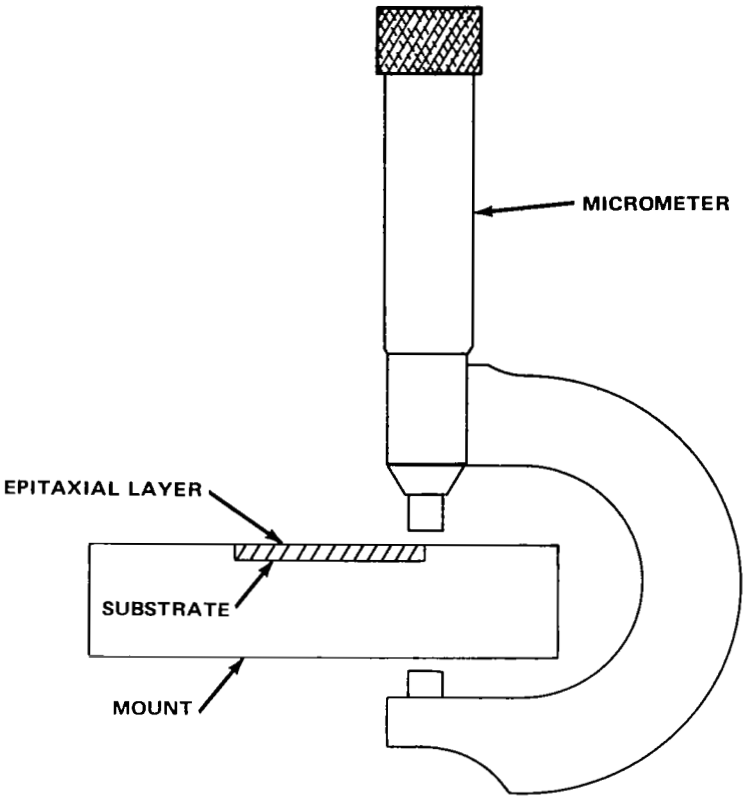


Figure 4. Mounted GaAs sample.

with glycerine added as a lubricant. About 20 hours of polishing were required to obtain a smooth surface. After polishing, the sample was thoroughly washed with water, rinsed in absolute alcohol, and dried. It is recommended that as a precaution, after alcohol rinse, the sample may also be rinsed in acetone to remove all glycerine, and finally washed with alcohol and dried.

e. First etching was performed with the AB etchant at room temperature for 45 minutes with constant magnetic stirring. The etch pattern was photographed using the metallograph at several magnifications as found necessary according to the observed structure details.

f. The sample was repolished as in step d., and etched with the RC-1 etchant at room temperature for 3 to 4 minutes without stirring. The etch pattern was photographed as usual.

g. The sample was polished once more, and its X-ray Laue diffraction pattern was taken. In general, it will be more desirable to have this step after steps b. and d. In the present case, X-ray diffraction was

used mainly as a support to the inference on the orientation of the sample that could be obtained from the etching experiments alone.

h. After X-ray diffraction, the thickness d_M was measured, and the sample was etched with the AB etchant again to compare the etch pattern in the bulk of the epitaxial layer with that near its surface (obtained in step e.).

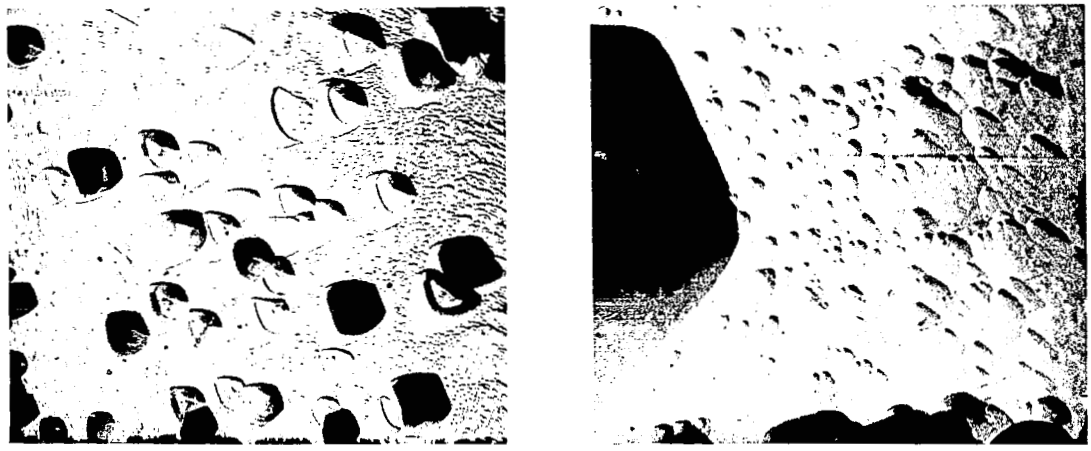
i. Finally, the sample was removed by dissolving the mount material in acetone to measure the actual thickness d_S of the sample after the polishings and etching. The thickness of the material used in the experiments from the d_S and d_M measurements compared within an accuracy of better than 2 percent.

Many of the above experiments were performed on several samples to verify the reproducibility of the results and consistency in the characteristics of the available samples. In one case, the characteristics of the substrate side (dull surface) were determined by both etching and X-ray diffraction measurements for comparison with the characteristics of the epitaxial layer.

B. Results and Discussion

Optical topography of a typical, as received GaAs epitaxial layer is shown in Figure 5(a) at 15 X. It shows the familiar growth pyramids commonly observed [14] on the GaAs epitaxial layers. An enlarged view of the developing growth pyramids in the right-hand lower corner of Figure 5(a) is shown at 100 X in Figure 5(b). Presence of the growth pyramids indicates the occurrence of excessive twinning [14] during the growth, and their distribution indicates that the vapor deposition was probably not uniform over the whole area of the growing layer.

Typical etch patterns after etching the epitaxial layer with AB etchant are shown in Figures 6 and 7, and the etch pattern after subsequent polishing and etching with RC-1 etchant is shown in Figure 8. It is seen that the two etchants give entirely different etch patterns. According to the detailed investigations by Abrahams and Buiocchi [12], both etchants should give similar etch patterns if the epitaxial layer was $<111>$ oriented. Hence, an immediate conclusion that can be drawn is that the epitaxial layer under investigation was either $<100>$ or $<110>$ oriented. A careful comparison with the results of Abrahams and Buiocchi on the $\{100\}$ and $\{110\}$ surfaces of GaAs (etched by the AB etchant) further suggests that the epitaxial layer probably was



(a) (b)

Figure 5. Typical growth features on the epitaxial GaAs layer — (a) 15 X and (b) 100 X.

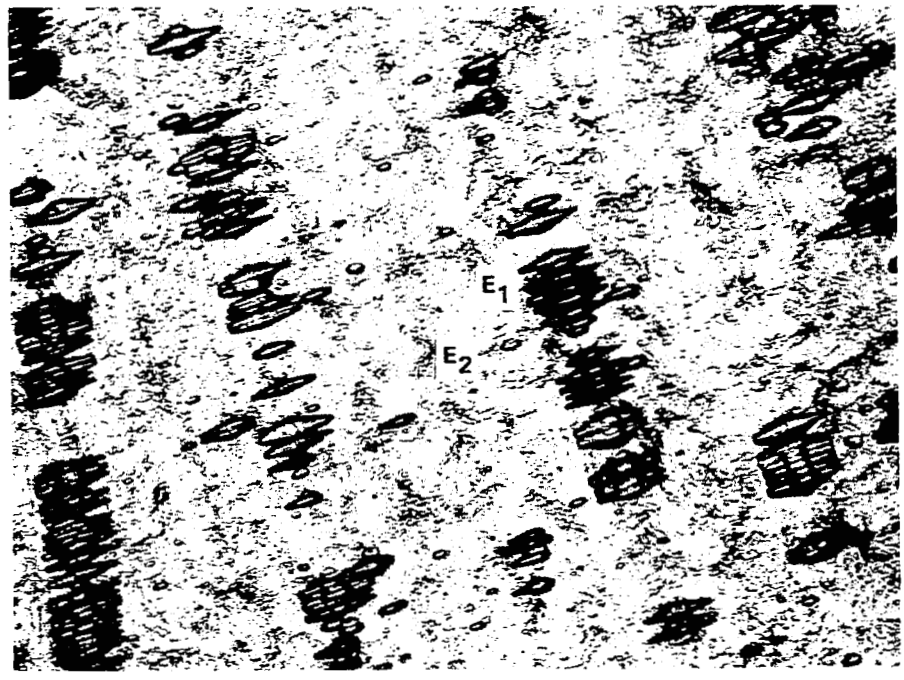
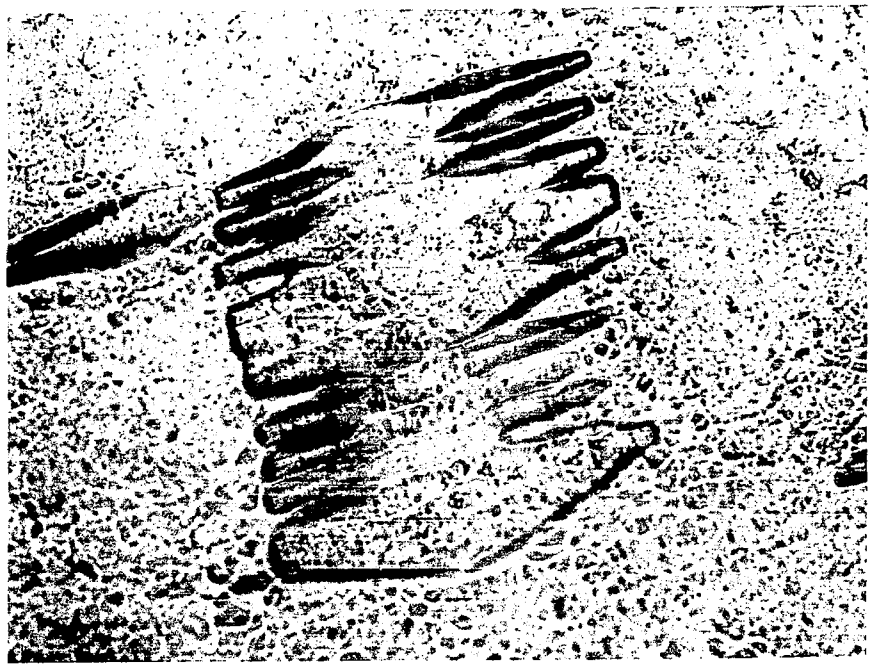
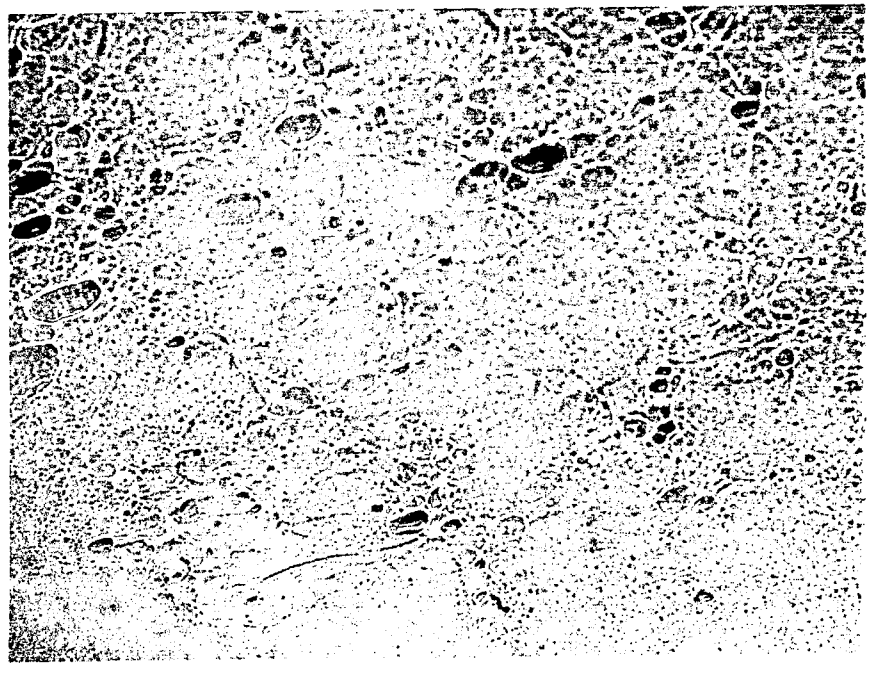


Figure 6. Typical etch pattern after etching the GaAs epitaxial layer with AB etchant at 100 X.



(a)



(b)

Figure 7. Etch pattern type in Figure 6 at 500 X — (a) E_1 and (b) E_2.

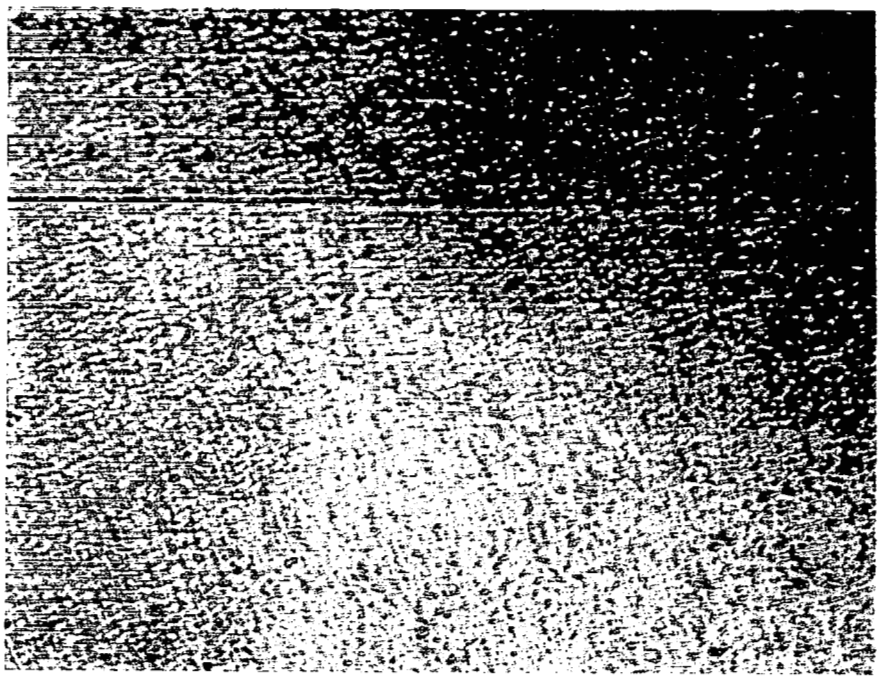


Figure 8. Typical etch pattern after etching the GaAs epitaxial layer with RC-1 etchant at 500 X.

<100> oriented. This inference was confirmed by the X-ray Laue diffraction pattern. A remark may be made about the fine grainy structure observed after etching with the RC-1 etchant (Fig. 8). This structure is irregular, and was similar throughout on the etched sample. The RC-1 etchant does not reveal dislocations on the {100} plane in GaAs. It seems that the fine etch structure observed by us may have been due to unavoidable stains caused in polishing. Results of Abrahams and Buiocchi on the RC-1 etched {111} faces of GaAs also show a grainy structure in the background of the etch pits due to dislocations.

Now, from the etch patterns produced by the AB etchant (Fig. 6), two distinct patterns, marked E_1 and E_2, are readily identified. E_1 type pattern is indicative of the decoration of the dislocations by impurity segregates, the dislocation lines being nearly parallel to the surface of the epitaxial layer. However, the elongated detailed structure of the E_1 type region [Fig. 7 (a)] suggests that the dislocation structures in these regions may have been complicated (consisting of dislocation pileups or stacking faults); or, alternatively, movement of dislocations may have occurred (Fig. 3). The structure in the regions of type E_2 [Fig. 7(b)] clearly shows the formation

of dislocation loops, and the existence of more dislocations [seen at bottom of Fig. 7(b)]. The loops formed in these regions appear to be largely due to joining of circular etch pits formed at the emergence points of dislocations running perpendicular to the surface of the epitaxial layer.

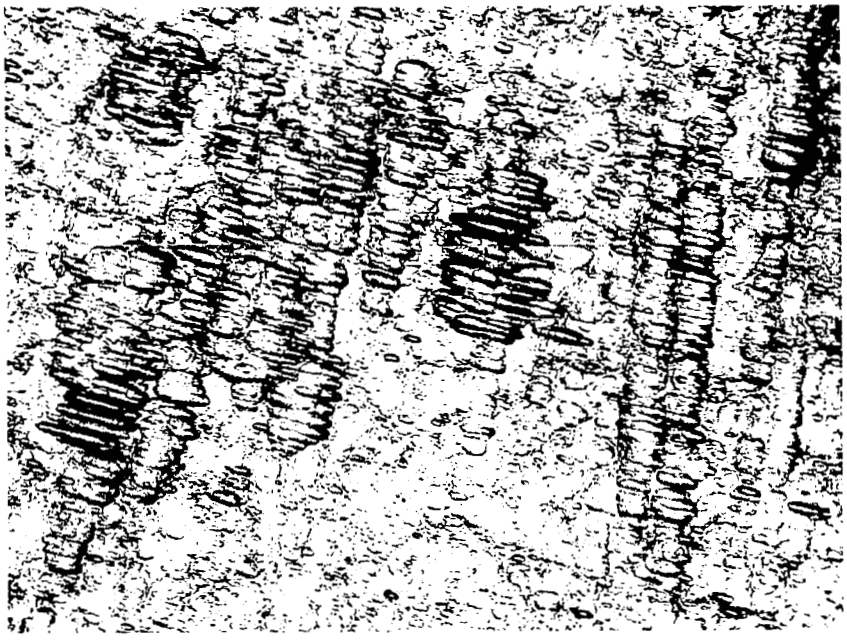
The etch patterns produced by the AB etchant on three samples studied were found to be similar with a variation in the relative dominance of the E_1 and E_2 type structures. In general, E_2 type etch structure was found dominant. Further, in the same sample, appearance of the E_1 type etch structure gradually decreased with depth from the surface of the epitaxial layer, as shown in Figure 9; in traveling a distance of 0.43 mm from the surface of a typical sample into the interior, the E_1 type etch structure almost vanished.

Since the dislocation structures varied appreciably in the interior of the epitaxial layer as compared to that on the surface, it was felt interesting to compare the etch pattern in the epitaxial layer with that produced on the substrate surface. The substrate also showed <100> orientation by X-ray diffraction. Etch pattern with AB etchant of a substrate surface is shown in Figure 10, which shows E_2 type predominant structure. It also shows the presence of some loops similar to vacancy loops [5, 6]. Presumably, these might have acted as source of more dislocations in the vapor deposited epitaxial layer on the substrate. Thus, our investigations support the belief [15] that the imperfections present in the substrate surface propagate in the growing layer, and the surface contaminations and distortions result in the nucleation and growth of several other imperfections, also stressing the need for having good substrate (or seed) in the epitaxial crystal growth.

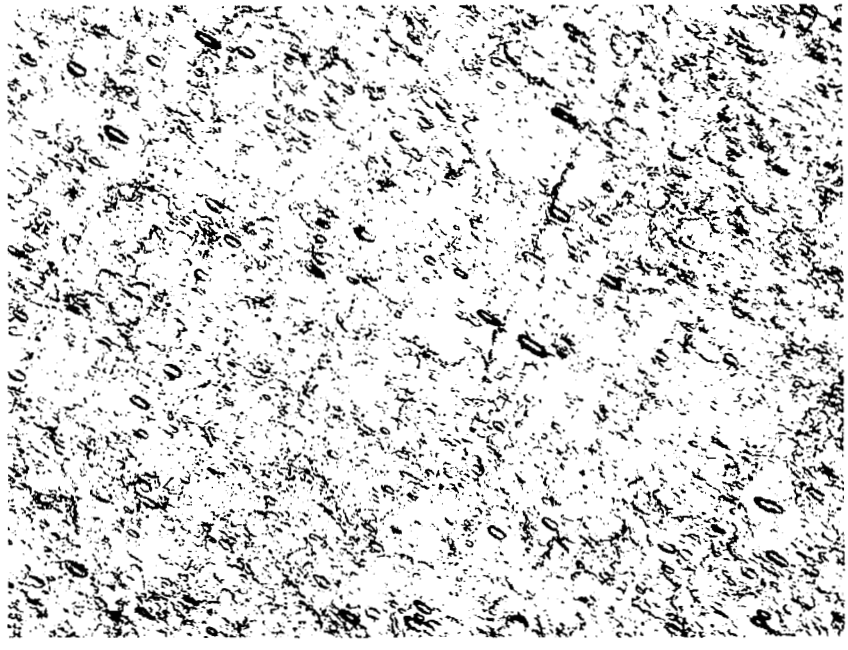
The experimental results presented clearly show that a qualitative comparative study of the quality of the GaAs crystals or epitaxial layers can preliminarily be made from the simple etching techniques used by us. The etching techniques coupled with more sophisticated optical [3] and electron microscopic techniques [6] may subsequently be used after cleaving the samples to obtain more detailed information with regard to the nature of the dislocations and the associated Burger vector's length.

IV. CONCLUSIONS

From careful considerations on various structural defects found in the real crystals and on the techniques for observing these defects it has been shown that the etching techniques have considerable importance in the evaluation of the space-grown crystals. In primary evaluation of the quality

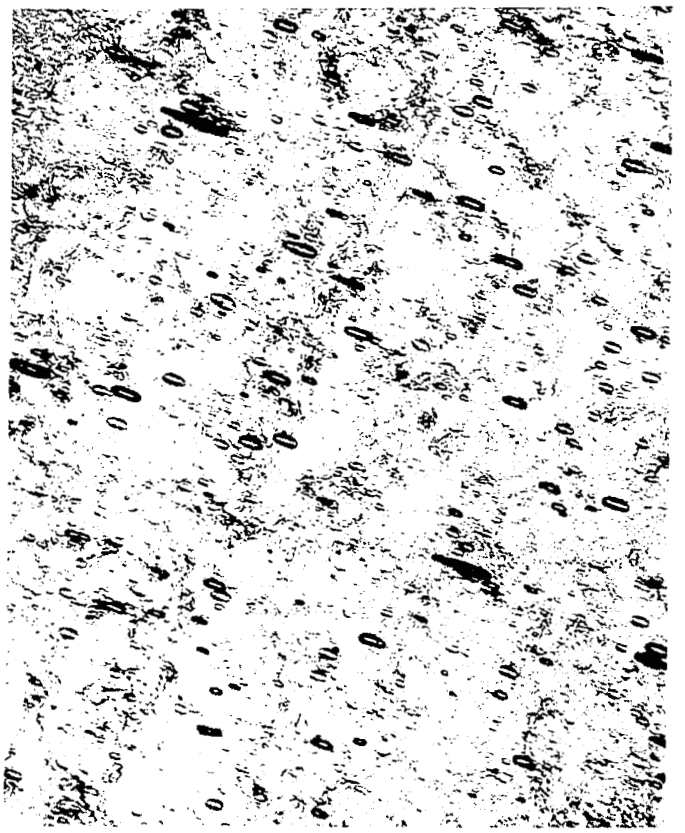


(a)



(b)

Figure 9. Effect of depth inside the GaAs epitaxial layer on etching with AB etchant — (a) after polishing 0. 2 mm thickness and (b) after polishing 0. 43 mm thickness. 100 X.



100X

Figure 10. Representative etch pattern of the {100} GaAs substrate surface after etching with AB etchant.

of the crystal, the importance of these techniques may be ranked next to the nondestructive optical and X-ray topographic studies. In subsequent detailed evaluation of the defects, like dislocations and stacking faults, the etching techniques can also find substantial application.

The use of simple optical topographical analysis in observing certain growth features has been briefly demonstrated by revealing the growth pyramids on the epitaxially grown GaAs.

Application of suitable etching techniques to epitaxial GaAs layers has clearly demonstrated that the dislocation, dislocation structures, and impurity segregates can be revealed easily, and a comparative study of their distribution in the grown crystalline sample can be made. The principal etchant used is capable of revealing these defects on all low-index planes of GaAs.

In the case of GaAs, by following a bi-etching procedure, more useful information can be obtained. In the samples used in our investigations, it was possible to infer the orientation of the epitaxially grown layer which was confirmed by the X-ray diffraction studies.

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Marshall Space Flight Center, Alabama 35812, February 26, 1971

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