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## The Anodic Dissolution Reaction of InSb: Etch Patterns, Electron Number, Anodic Disintegration, and Film Formation<sup>1</sup>

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### ABSTRACT

The etching behavior of the inverse {111} planes of undoped, semiconducting, n-type, InSb single crystals was explored. Depending upon the etchant, including anodic dissolution, various etch patterns were obtained on the inverse planes. In general the etch pits on the In{111} plane were round, and the face was shiny, whereas the face of the inverse plane was dark and rough. The rates of dissolution in the electrolytes used were very low, especially in absence of oxidizers. The components dissolve as  $\text{In}^{3+}$  and  $\text{Sb}^{3+}$ . At current densities above 40 or 60  $\text{mA cm}^{-2}$  (on  $\text{Sb}\{\bar{1}\bar{1}\bar{1}\}$  or  $\text{In}\{111\}$ ), growth of a black, colloidal film of  $\text{Sb}_4\text{O}_5\text{Cl}_2$  containing very fine metallic Sb particles occurs on both planes. The Sb particles result from the partial disintegration of InSb. Upon heating the film in vacuum, recrystallization occurs and the Sb aggregates to form larger particles. An explanation is offered for the different behaviors of the inverse {111} planes.

The chemical and anodic dissolution reactions occurring on various planes of III-V semiconductors in several electrolytes have been studied by Gatos *et al.* (1, 2), Pleskov (3), Dewald (4), Gerischer (5, 6), Harvey (7), Straumanis *et al.* (8, 9), and others. Dewald attempted to explain why the {111} inverse faces of InSb in an aqueous solution of KOH behave differently. Anodic oxide films of varying composition with the ratio of Sb:In close to one at the surface of the crystal planes were formed during electrolysis.

The aim of the present investigation was, therefore, to check once more the etch patterns formed on the inverse {111} faces of InSb, to determine the valences of the ions (In and Sb) going into solution in acidic electrolytes, to look for disintegration phenomena and film formation, and determine the composition of the films.

#### *Electrodes and Their Treatment*

The electrodes were prepared as for GaAs by mounting InSb wafers (~ 2 mm thick and 8 to 12 in diameter) into Teflon holders provided with a screw cap and Cu lead wires (9). The wafers were cut from single InSb crystals obtained from the Monsanto Company (St. Louis, Missouri), grown in the [111] direction by the Czochralski or the gradient-freeze technique. They were n-type with no intentionally added dopants, and the impurity level was less than 1 ppm. The {111}, {110}, and {100} directions were established from Laue x-ray back reflection patterns. Deviations from these faces were adjusted by successive grinding to give the desired orientation on the Laue patterns.

These faces had a mirror-like appearance after mechanical polishing (Fig. 1a). To remove mechanical surface damage, they were subsequently treated with

CP-4 (2, 4) (mixture of concentrated acids  $\text{HNO}_3$ , HF, and  $\text{CH}_3\text{COOH}$ ) for 2 sec, washed, and dried. Although still mirror-like, the faces showed a slight undulation in the interference microscope (Fig. 1b).

This etchant and several others, including anodic dissolution, were used to check the previous results and to determine which of the {111} faces was In {111} and which Sb  $\{\bar{1}\bar{1}\bar{1}\}$ . The distinction is based on x-ray work and its comparison with the results obtained by etching (1, 10, 11).

### Results

*Etching.*—The two inverse {111} planes of InSb, following etching for 5 or more sec in CP-4, showed the expected results: one side of the wafers was glossy, exhibiting round, flat etch pits—(In{111}), and the other was dark and rough—(Sb $\{\bar{1}\bar{1}\bar{1}\}$ ).

The  $\text{HNO}_3$ -HF etchant (1:1 of the concentrated acids) worked similarly: rounded etch pits appeared on the glossy side, as on the Ga{111} side of GaAs (8) but on the inverse Sb $\{\bar{1}\bar{1}\bar{1}\}$  side, irregular triangular etch pits appeared (Fig. 5).

The HCl- $\text{FeCl}_3$  etchant produced a different kind of pattern, especially after prolonged treatment (Fig. 2a and b and Fig. 3).

Anodic etching led to round or rounded, triangular pits on the In{111} face. These pits grew in size with the time of etching and finally merged together as observed by Gatos and Lavine (1). The anodic dissolution in 2N HCl lasted 15 to 45 min ( $10 \text{ mA/cm}^2$ ) and 60 min in 1N  $\text{HNO}_3$  containing 1N tartaric acid. Figure 4 shows a surface which displays merging, round etch pits.

The Sb $\{\bar{1}\bar{1}\bar{1}\}$  plane becomes rough after etching displaying irregular triangular etch pits (Fig. 5) and frequently pits within pits.

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\* Electrochemical Society Active Member.

Key words: inverse {111} planes, self-dissolution rates,  $\text{FeCl}_3$  etchant, colloidal Sb,  $\text{Sb}_4\text{O}_5\text{Cl}_2$ .

Fig. 1. Interference rings on InSb faces, 165X; a—highly polished; b—etched with CP-4 for 2 sec.

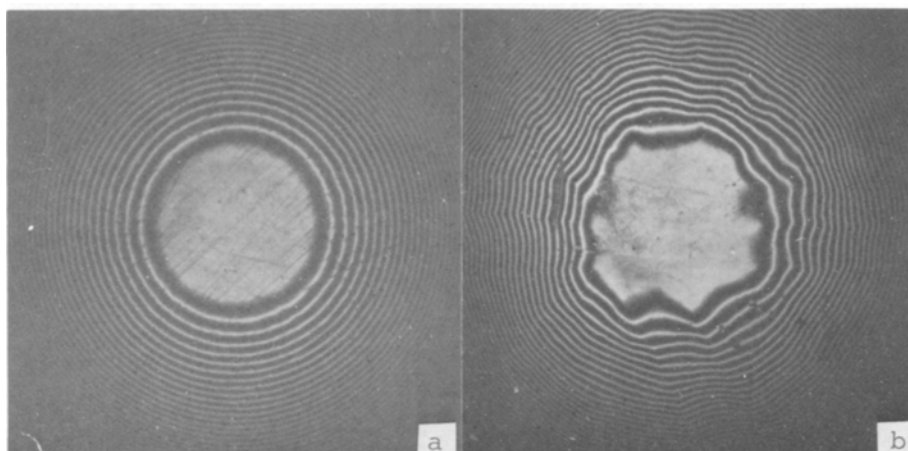


Fig. 2. a—In{111}, etchant: 6N HCl-0.2N FeCl<sub>3</sub>; 20 min; 80°C; 970X. b—In{111}, etchant: 2N HCl-0.5N FeCl<sub>3</sub>, 24 hr; 25°C; 90X.



Anodic or chemical etching, excepting FeCl<sub>3</sub> additions, produced round pits on In{111} faces. The latter were then treated with the HCl-FeCl<sub>3</sub> etchant. Dense triangular etch pits, as pictured on Fig. 2a, developed on these faces; even the walls of the deep round pits (Fig. 4) consisted of triangular steps. Thus, sub-microscopic steps, which might have been present on the walls of the round pits were developed to microscopic size by the HCl-FeCl<sub>3</sub> etchant. No superimposed pattern was observed on the Sb{111} face.

The main characteristic in distinguishing the two inverse faces is, therefore, the shiny appearance of In{111} and the dark, rough one of the inverse face. Consideration of etch pits only for recognition may be

misleading as the etch pattern changes with the nature of the etchant, its concentration, and time of etching.

*Apparent electron number of InSb.*—Since some of the anodic dissolution experiments were continued up to 24 hr, it was necessary to know the self-dissolution rate of the InSb used in the various electrolytes. These rates are summarized in Table I, which clearly shows that the self-dissolution rate of InSb in pure 2N HCl is nearly zero. It increases considerably in the presence of oxidizers. There is some difference in the dissolution rates of the inverse {111} planes.

The electron number determinations were, therefore, carried out in 2N HCl and in tartaric-HNO<sub>3</sub> acid (Table I). The results can be read from Fig. 6, which

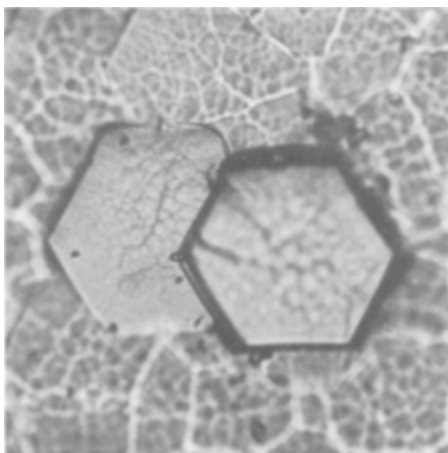


Fig. 3. Sb{111}, etchant: 6N HCl-0.2N FeCl<sub>3</sub>; 20 min; 80°C; 970X.

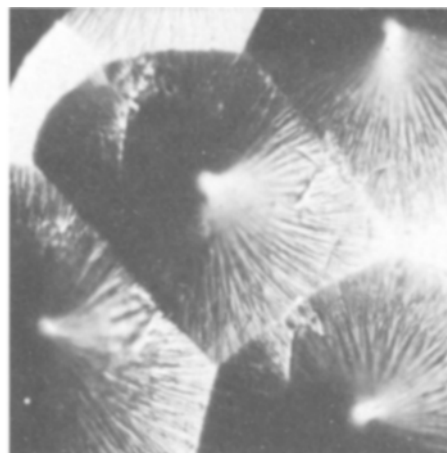


Fig. 4. In{111} etched anodically in 1N HNO<sub>3</sub>-1N H<sub>2</sub>C<sub>4</sub>H<sub>4</sub>O<sub>6</sub>; 10 mA/cm<sup>2</sup>; 60 min; 500X.

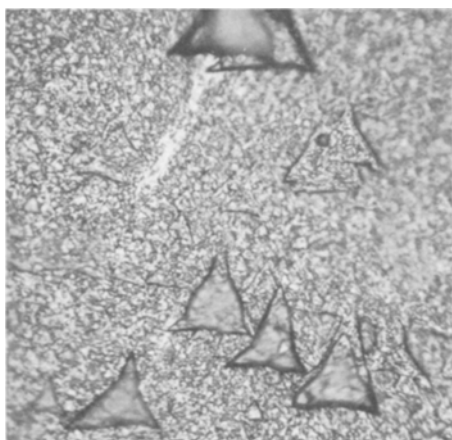


Fig. 5. Sb(111); the same etch as in Fig. 4 or simple HNO<sub>3</sub>-HF etchant.

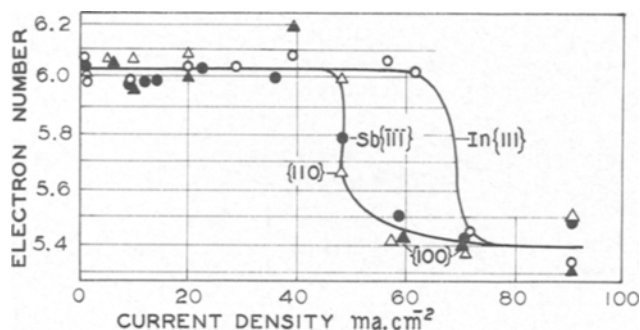


Fig. 6. Apparent electron number of InSb as a function of current density. The faces In(111), Sb(111), {110}, and {100} were dissolved anodically in 2N HCl.

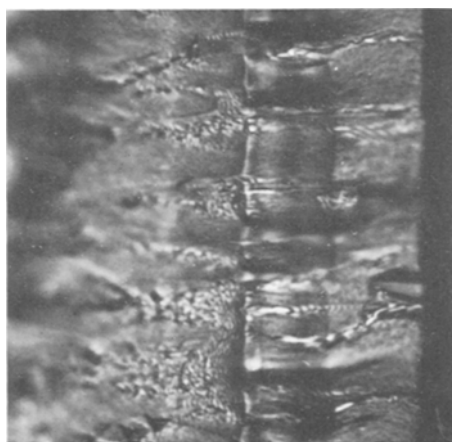


Fig. 7. Cross section of the black film formed on In(111) of the InSb electrode. 2N HCl; 70 mA cm<sup>-2</sup>; 970X.

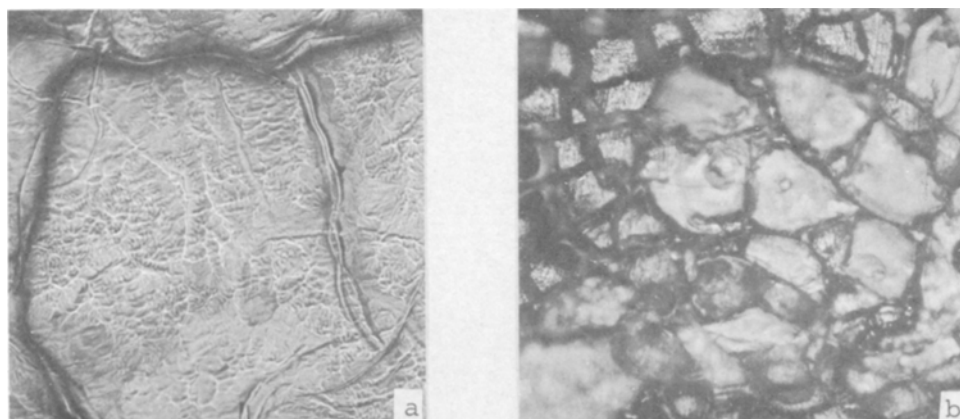


Fig. 8. Black film resulting from anodic dissolution of the In(111) face of InSb in 2N HCl at 70 mA cm<sup>-2</sup>; 970X. a—Substrate side; b—Electrolyte side.

Table I. Self-dissolution rates of InSb in various electrolytes in air  
Estimated accuracy:  $\pm 0.02$

Face	Electrolyte	Time, hr	Self-dissolution rate, mg cm <sup>-2</sup> day <sup>-1</sup>
In(111)	2N HCl	24	0.00
Sb(111)	2N HCl	24	0.00
In(111)	{ 1N H <sub>2</sub> C <sub>2</sub> H <sub>3</sub> O <sub>6</sub> 1N HNO <sub>3</sub>	30	0.07
Sb(111)	the same	30	0.04
In(111)	{ 2N HCl 0.005N FeCl <sub>3</sub>	45	1.06
Sb(111)	the same	45	1.33
In(111)	{ 2N HCl 0.01N FeCl <sub>3</sub>	37	2.25
Sb(111)	the same	37	2.60

indicates that up to current densities below 50 mA cm<sup>-2</sup> the electron number is 6.00 within error limits. Since In goes into solution as In<sup>3+</sup> (12, 13), Sb must do the same. The In(111) face seems to be more resistive than the inverse and the {110} and {100} planes, as it tolerates current densities up to 60 mA cm<sup>-2</sup>. At higher current densities, the apparent electron number decreases, that is more In or Sb goes into solution than predicted by Faraday's law. This can be attributed to the formation of ions of lower valency (14), increased local corrosion and/or anodic disintegration (15-18). However, no particles were observed separating from the InSb anode, only the formation of a film at current densities above 40 to 60 mA cm<sup>-2</sup>.

**Anodic film formation and disintegration.**—The films formed on the anode at elevated current densities were nearly black, but displayed a mother of pearl luster. They had a stratified structure (Fig. 7) and were colloidal in nature as they did not produce x-ray diffraction lines. The electron diffraction method was not used.

The same kind of film was produced on both inverse {111} planes. The film could usually be removed from the crystal surface by a soft brush. The substrate side of the film appeared more even than the electrolyte side (Fig. 8a and b).

To investigate the composition of the films, fragments were heated in vacuum at 350°C for about 2 hr. As a result of this treatment, an x-ray diffraction pattern consisting of many sharp lines was obtained. The position of these lines coincided with those of a powder resulting from anodic dissolution of pure Sb in 2N HCl and with those of a precipitate obtained by (aqueous) hydrolysis of SbCl<sub>3</sub>. According to Mellor (19) and the ASTM cards, the composition of the white precipitate is Sb<sub>4</sub>O<sub>5</sub>Cl<sub>2</sub>. Since the Sb is trivalent in this compound, this is a further confirmation for the trivalency of Sb ions going anodically into solution from InSb.

The above x-ray patterns exhibited some weak, additional lines. To identify them, the black anodic

film fragments were heated in vacuum above 650°C (melting point of Sb-630°). At that temperature the black and the white material separated. The latter proved to be  $Sb_4O_5Cl_2$ , while the former appeared as molten spheres, identified as metallic Sb.

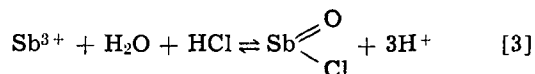
### Discussion

Since no reducing species were in the black anodic deposits, metallic Sb must have already been present as very fine particles.

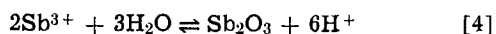
The explanation of the anodic behavior of InSb is then as follows. Both components dissolve anodically as trivalent ions



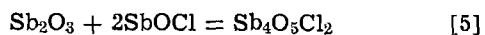
Although the  $\text{In}^{3+}$  pass directly into solution, the  $\text{Sb}^{3+}$  ions hydrolyze, particularly at increased current densities (above 40 to 60  $\text{mA cm}^{-2}$ ), as a sufficient amount of  $\text{H}^+$  cannot penetrate to the surface of the anode



or complete hydrolysis may occur



The oxychloride as well as the oxide or hydroxide  $\text{Sb}(\text{OH})_3$  are relatively insoluble and adhere to the anode as layers consisting of crystallites of colloidal dimensions. A further reaction may occur on the surface and after heating



Simultaneously, during heating, the colloidal product is converted into a crystalline one, detectable by x-ray diffraction.

Since metallic Sb is much more noble than In, the Sb atoms of the InSb have a tendency to retain their valence electrons whereas In is readily oxidized and goes easily into solution. Consequently, especially at increased current densities, the In atoms surrounding the Sb atoms dissolve and some of the latter embed themselves into the oxychloride film (Eq. [5]), which is simultaneously formed according to Eq. [3] and [4] by a part of  $\text{Sb}^{3+}$ . The oxychloride film prevents the Sb atoms from collecting into particles larger than colloidal (20). As a consequence, the white, possibly transparent film turns dark, and the electron number (or the apparent valency) drops. Thus, partial disintegration of the Sb on the surface of the InSb occurs, and the resulting product does not produce x-ray interference lines. The film formation process may proceed periodically, starting where there is a weakness in the thin film or where a breakdown of the film takes place. A film of stratified structure results (Fig. 7). Upon heating in vacuum, the colloidal particles of the oxychloride and the Sb grow separately to form larger entities which can now produce x-ray diffraction lines.

That the  $\text{Sb}\{111\}$  is more susceptible than  $\text{In}\{111\}$  to partial Sb disintegration (Fig. 6) depends evidently on the characteristic structure of these inverse planes. According to Galaev and Gorelik (21), the bond strength on the  $\text{Sb}\{111\}$  plane should be weaker

than on the  $\text{In}\{111\}$  plane. Consequently, the former is easier to destroy; its hardness is less; and the outer Sb atoms are more remote from the In atomic layer than on the inverse side (21). This explains why the partial Sb disintegration on  $\text{Sb}\{\bar{1}\bar{1}\bar{1}\}$  and on  $\{110\}$  and  $\{100\}$  planes starts at lower anodic current densities than on  $\text{In}\{111\}$ .

Finally the weaker bond strength on  $\text{Sb}\{\bar{1}\bar{1}\bar{1}\}$  suggests that this plane should be attacked by etchants at a faster rate than the inverse plane. Table I shows the correctness of this conclusion. The difference in the rates of corrosion of the two inverse  $\{111\}$  planes in  $\text{HNO}_3$ -tartaric acid is, however, within the limits of error.

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Any discussion of this paper will appear in a Discussion Section to be published in the December 1971 JOURNAL.

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