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ETCHING AND INHIBITION OF THE $\{111\}$ SURFACES OF THE III-V INTERMETALLIC COMPOUNDS: InSb*

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Abstract—In oxidizing etching media, the $\{111\}$ surfaces of InSb are much less reactive than the $\{\bar{1}\bar{1}\bar{1}\}$ surfaces as determined by direct dissolution rates and by etching of spheres. Related to this difference in reactivity is the fact that dislocation etch pits appear on the $\{111\}$, but not on the $\{\bar{1}\bar{1}\bar{1}\}$ surfaces. Inhibitors such as stearic acid and primary amines decrease appreciably the dissolution rate of only the $\{\bar{1}\bar{1}\bar{1}\}$ surfaces. Furthermore, etching inhibitors lead to the formation of new dislocation etch pits on the $\{111\}$ and also on the $\{\bar{1}\bar{1}\bar{1}\}$ surfaces. Similar effects were observed in GaAs. These phenomena are discussed in terms of the atomic configuration of the surfaces involved and the relative reactivity of the group III and group V atoms.

INTRODUCTION

WITH the introduction of intermetallic compounds to semiconductor science and technology, surface studies of these materials have become of interest. The surfaces of the III–V compounds (zinc-blende structure) present unusual characteristics as a result of the crystallographic polarity along the $\langle 111 \rangle$ direction. It is well known, for example, that dislocation etch pits can ordinarily be revealed on the $\{111\}$ surfaces of these compounds but not on the $\{\bar{1}\bar{1}\bar{1}\}$ surfaces. WAREKOIS and METZGER(1), employing X-ray diffraction techniques, have recently identified the $\{111\}$ surfaces terminating with group III atoms and those terminating with group V atoms.† It is now generally accepted that the $\{111\}$ surfaces developing dislocation etch pits are the A surfaces, whereas those developing no dislocation etch pits are the B surfaces.

The authors(2) have recently discussed these and other differences between the two types of $\{111\}$ surfaces. They have also reported on the influence of the polar $\langle 111 \rangle$ direction on the etching behavior of the $\{110\}$ and $\{100\}$ surfaces of InSb.(3) In these reports an attempt was made to interpret the observed etching behavior on the basis of bonding and electronic configuration.

In the present paper the differences between the A and B surfaces of InSb are pursued further, and new effects of etching inhibitors leading to the development of dislocation etch pits on both A and B surfaces are presented. An interpretation of these results is advanced.

EXPERIMENTAL

The specimens employed in this study were cut from high-purity single crystals of InSb grown in the $\langle 111 \rangle$ direction by the Czochralski method (rate of rotation: 10 r.p.m.; rate of pulling: 1·9 cm/hr). The parallel sides of wafer specimens were ground to within 1° from the $\{111\}$ orientation as determined by X-ray diffraction. Regular tetrahedrons (with an edge of approximately 1 cm) having either only A or only B faces were also prepared by grinding. In InSb(4) as in the case of other III–V compounds the A and B surfaces have been identified by X-ray diffraction techniques.

The InSb spheres (approximately 1 cm in diameter) were prepared by placing specimens of roughly cubical shapes on a tube mounted on a horizontal wheel. The specimens were rotated

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† In the III–V compounds it is customary to designate the group III atoms as A atoms and the $\{111\}$ surfaces terminating with triply bonded A atoms as A surfaces. Similarly the group V atoms are designated as B atoms and the $\{111\}$ surfaces terminating with triply bonded B atoms as B surfaces. This designation will be used in the present paper.

manually in a direction opposite to the rotation of the wheel.*

The two principal etchants employed were: (a) 2 conc. HNO_3 + 1 conc. HF + 1 glacial CH_3COOH (in parts by volume); and (b) 0·2N Fe^{+++} in 6N HCl. For convenience, etchant (a) will be referred to as modified CP–4 and (b) as Fe^{+++} etchant. In the case of InSb, the modified CP–4 generally leads to chemical polishing whereas the Fe^{+++} etchant acts preferentially leading to well defined etch figures.

Etching experiments

Dissolution rates. At room temperature, the dissolution rate of InSb in strongly oxidizing media, including the modified CP–4 and the Fe^{+++} etchant, is controlled by the diffusion rate of the oxidizing species to the InSb surface. The apparent activation energy for dissolution is approximately 5 kcal/mole, typical of diffusion controlled processes. Consequently, no differences in dissolution rates were observed between the A and B tetrahedrons. At lower temperatures however, differences in dissolution rate exceeding one order of magnitude were observed, as shown in Fig. 1. Here, the dissolution rate of the A surfaces becomes a chemical activation process with an apparent activation energy of approximately 25 kcal/mole. The dissolution of the B surfaces remains under diffusion control down to, at least, 0°C.

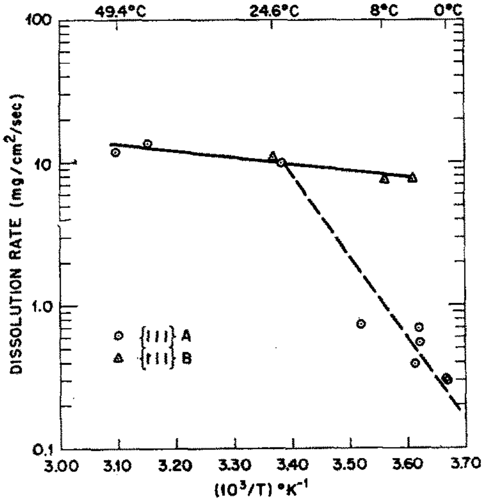

FIG. 1. Dissolution rate of InSb as a function of temperature in modified CP–4.

Etching characteristics. Although, at room temperature, no difference in dissolution rates was observed between the A and the B surfaces, the microstructure of the A and the B surfaces etched in modified CP–4, was found different. For example, the familiar dislocation etch pits were observed on the A but not on the B tetrahedrons.

In the Fe^{+++} etchant, the etch figures of the A and the B surfaces were strikingly different. The etch figures on the B surfaces formed arrays of well defined or overlapping equilateral triangles oriented along and bounded by ⟨110⟩ directions. The etch figures on the A surfaces were irregular or regular hexagons usually much larger and less well defined than the corresponding triangular figures of the B surfaces. The hexagons were also bounded by ⟨110⟩ directions. A typical example of the etch figures on the A and B surfaces of an {111} wafer is shown in Fig. 2.

The above differences in etch figures can serve for the unmistakable identification of the A and B surfaces even when, due to very low dislocation densities, dislocation etch pits are not revealed on the A surfaces of InSb. In this connection it is of interest to point out that triangular figures (not as well defined as in Fig. 2) persist on the B surfaces even when the A surfaces appear chemically polished.

Etching of spheres. Single crystal spheres can provide a simple means for obtaining general information on the orientation dependence of etching. This is true even if the overall etching rate is controlled by transport phenomena in the etchant.

InSb spheres were etched in several media and at various temperatures. In no case did the A faces develop since they are the slowest reacting ones. Consequently, octahedron shapes resulting from the development of all of the {111} faces, as in the case of germanium,⁽⁵⁾ were never observed. The orientation of the spheres was determined by X-ray diffraction and preferential etching techniques. Figure 3(a) shows a sphere etched in modified CP–4 at room temperature. The pitted triangular area corresponds to a B face. Four such

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* This method was suggested to us by G. A. WOLFF of the U.S. Army Signal Research and Development Laboratory.

areas developed around the sphere and were connected by pitted strips corresponding to the {100} planes. Independent tests showed that in the modified CP–4 etchant the {100} surfaces are approximately as reactive as the B faces.

In 1 part 30 per cent $H_2O_2 + 1$ part conc. $HF + 4$ parts H_2O (by volume), in addition to the four B faces, four sets of three {100} faces were observed. One of these sets is shown in Fig. 3(b). The faces of each set converge to an A {111} pole. In the Fe^{+++} etchant each of the four B faces were formed at the intersection of three {100} faces (Fig. 3(c)); in addition, four sets of six faces were developed (one such set is shown in Fig. 3(d)); three of the six faces are {100} and three are {110}. The six faces converge to an A {111} pole.

Inhibition experiments

Some of the etching experiments described above were repeated in the presence of etching inhibitors in the hope that etching inhibition might contribute to the understanding of the etching mechanisms. Tetrahedral specimens, as above, were employed for determining the dissolution rates.

The following inhibitors were employed: stearic acid, amylamine, butylamine and propylamine. About 0·5 per cent of a given amine was added to the etching solution. Since the solubility of stearic acid is very small, a slight excess of this inhibitor was added to the etchants.

In the modified CP–4 at O°C containing any of these inhibitors, the dissolution rate of the A surfaces was found to be $0{\cdot}31 \pm 0{\cdot}04$ mg/cm^2/sec; a rate of approximately $0{\cdot}52 \pm 0{\cdot}08$ mg/cm^2/sec was obtained in the absence of inhibitors. In the case of the B surfaces, the dissolution rate decreased very markedly in the presence of an inhibitor; i.e. from approximately 7·8 mg/cm^2/sec to $0{\cdot}36 \pm 0{\cdot}04$ mg/cm^2/sec.

The fact that the dissolution rates of the A and B surfaces became virtually equal in the presence of inhibitors was also reflected in the etching of spheres; their shape was not altered detectably even after prolonged etching. Thus, although no independent experiments were performed, it would appear that the dissolution rates of the {110} and {100} surfaces are inhibited to approximately the same values found for the A and B surfaces.

It is of interest to note that the differences in microstructure between the A and B surfaces (Fig. 2) become far less pronounced in the presence of inhibitors as seen in Fig. 4.

Dislocation etch pits on the A *and* B *surfaces.* The most striking effect of the etching inhibitors is the appearance of dislocation etch pits on the B surfaces and the appearance of new pits on the A surfaces. A preliminary account of this observation has already been reported.(6) The etch pits ordinarily appearing on the A surfaces appear also in the presence of inhibitors, but their size is appreciably smaller than that observed under the same conditions in the absence of inhibitors. Typical examples of an A and a B surface etched in modified CP–4 with and without an inhibitor are shown in Fig. 5–I (all of the inhibitors pointed out above lead to the same results).

The following experiment was performed in connection with the etch pits developing in the presence of inhibitors: An {111} wafer approximately 3 mm thick was etched in modified CP–4 containing no inhibitor. The A and B surfaces were replicated on Faxfilm and then the wafer was re-etched (without grinding) in modified CP–4 containing an inhibitor. The A and B surfaces were again replicated. Etching in modified CP–4 containing an inhibitor and replicating were repeated nine times until microscopic holes appeared through the wafers. The thickness of the wafer was monitored with each etching. Large areas of the surface replicas were mapped on composite microphotographs using suitable reference points.

In the successive etchings, it was possible to follow through the wafer many of the new pits appearing on the A and B surfaces. In these cases, the pits followed a line intersecting the {111} surface at an angle of 60°, characteristic of dislocation lines in the zinc-blende structure. (An error of ± 2° was associated with these determinations.) In many instances it was possible to find one-to-one correspondence between the new pits on the A and those on the B surface. Furthermore, some of the holes finally formed on the wafer, could be traced to individual pits (Fig. 5–II). No direct correspondence was found between the ordinary etch pits on the A surface and new pits on the B surface.

Although only a limited number of the new pits was traced through the wafer, there is no doubt that they are associated with dislocations.

It should be pointed out that the appearance of new pits in the presence of inhibitors was observed not only in the modified CP–4, but in a number of other etching media. Furthermore, by adding inhibitors in the GaAs etching employed by SCHELL(7) (10 ml conc. $HNO_3 + 30$ ml H_2O), etch pits appeared on both A and B surfaces of a GaAs wafer.

DISCUSSION

In a previous communication(2) an atomic model was proposed to explain the overall differences in behavior between the A and the B surfaces of the III–V compounds. The model is based on the assumption that the sp^3 tetrahedral bonding of these compounds extends to the surface atoms. The B atoms on a B surface must then have a dangling (unshared) but filled s–p orbital (Fig. 6(b)). In the case of the A surface atoms, (Fig. 6(a)), there are no electrons available for the fourth s–p orbital. A reasonable consequence of this is that the electronic configuration of the A surface atoms is distorted from the tetrahedral symmetry. On this basis it was anticipated and experimentally verified that less perfect crystals of InSb are grown in the A{111} direction than in the B{111} direction.(8)

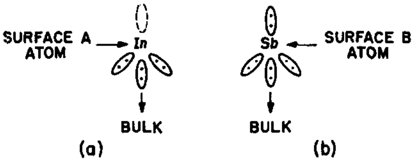

FIG. 6. Atomic model of the A and B {111} surfaces.

Regarding the chemical reactivity of the A and B surfaces, it was argued that in reactions where oxidizing (electrophilic) agents are involved B atoms are more reactive than A atoms because they have an unshared pair of electrons available for oxidation.

The dissolution process under consideration is far too complex and the available information rather limited to allow a quantitative development of the dissolution mechanism. Certain aspects of the mechanism, however, can be pointed out at this time.

The growth and dissolution of crystals are generally considered to proceed through the propagation of atomic or molecular steps along the exposed surfaces.(9–11). In the case of the III–V compounds, such steps are expected to be diatomic layers as shown schematically in Fig. 7. In other words, the surface configuration with singly bonded atoms is considered unstable; if it were stable, the A and B surfaces would behave alike. Thus, the rate determining (slow) partial reaction* of the dissolution process is not associated with the breaking of the single bonds between the atoms of layers II and the substrate, but primarily with the bonding between layers I and II. This conclusion is consistent with the atomic model of the {111} surfaces pointed out above. It is being assumed, of course, that no drastic structural changes occur at the surfaces, since such changes are not readily visualized at this time.

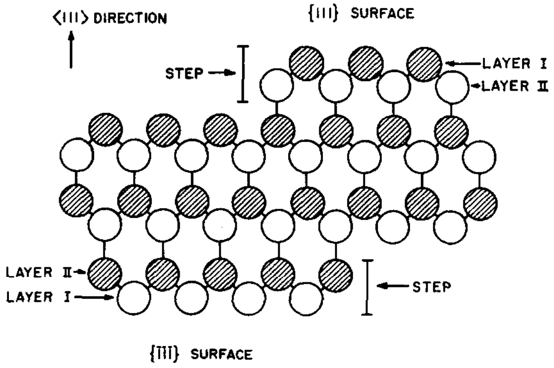

FIG. 7. Two-dimensional representation of the zincblende structure with surface steps.

The rate of motion of the diatomic steps (v_s) across the surface is an important parameter in the dissolution process.(10, 11) Atomic pits (created by the removal of one atom from layer I) or kinks (created for example by the removal of two adjacent atoms from layer I), such as shown in Fig. 8, can be considered as nucleation points for steps (no reference is made to crystal edges, since the crystal surfaces are assumed to be relatively large). If, over a given {111} surface, the rate of

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* The term "partial reaction" will be used in lieu of "step" from the chemical kinetics standpoint. The term "step" will be retained for designating a physical step as in Fig. 7.

formation of atomic pits or kinks (v_n) is relatively large ($v_n > v_s$), then it would lead to the unstable surface configuration with singly-bonded atoms. Thus, it is necessary that $v_s \geqq v_n$. No reliable conclusion can be drawn as to the relative magnitudes of v_s and v_n. However, in view of the fact that the dissolution rate of the B surface is much greater than that of the A surface, it can be stated that

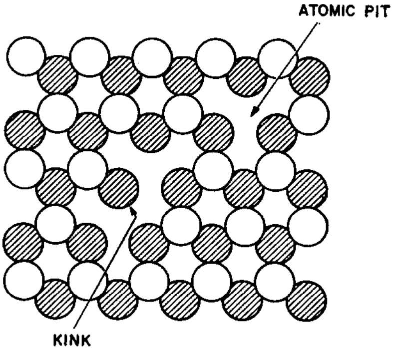

FIG. 8. Representation of an {111} surface with an atomic pit and a kink.

$$v_n^{\mathrm{b}} > v_n^{\mathrm{a}}$$

where the superscripts a and b refer to A and B surfaces. This relationship probably reflects the marked tendency of the B faces to develop well defined etch figures.

Etching at dislocations

There are two types of edge dislocations present in the III–V compounds; i.e. α dislocations, having a row of A atoms and β dislocations, having a row of B atoms. VENABLES and BROUDY(12) have shown that on the {110} and the {111} surfaces of InSb the ordinarily observed dislocation etch pits are associated with only one type of dislocation. If their work is viewed in the light of WAREKOIS'(4) identification of the InSb crystallographic polarity, the observed dislocation etch pits are associated with α (In) dislocations. Such dislocations in intersecting the A surfaces terminate with a doubly bonded surface atom. This atom is apparently attacked faster than the other surface atoms. Thus, it is reasonable to expect that the rate of nucleation (v_d^{α}) along the dislocation line (exposing at any given time a doubly bonded atom) exceeds v_s^{a}, which is a condition necessary for the formation of a dislocation etch pit. On the other hand, β dislocations in intersecting the A surfaces terminate with a trivalent atom. Thus, it is not surprising that the rate of nucleation along the β dislocation (v_d^{β}) does not exceed v_s^{a}. The elastic strains associated with edge dislocations do not appear to play a significant role in the etching of the III–V compounds.

Regarding the B surfaces, v_s^{b} is apparently so large that it is not ordinarily exceeded by v_d^{α} or v_d^{β}.

Inhibition

In acid solutions, the primary amines employed as inhibitors form positively charged ammonium ions and are expected to adsorb preferentially (although not exclusively) on the B surface atoms, which have an unshared pair of electrons (see also model Fig. 6). It is believed that this is the primary reason for the marked decrease in dissolution rate of the B surfaces in the presence of inhibitors and the virtual lack of inhibition in the case of the A surfaces. Preferential adsorption on the B atoms can also be argued for the case of stearic acid. Although the substantial decrease in v_n^{b} is apparent, it is not clear to what extent v_s^{b} is affected. The fact that the surface dimensions of the α dislocation etch pits on the A surface decrease (but not their depth) suggests a decrease in v_s^{a}, although the overall dissolution rate of the A surfaces is only slightly decreased.

Regarding the new dislocation etch pits developing on both the A and B surfaces in the presence of inhibitors, their formation is apparently related to a decrease in v_s^{a} and v_s^{b}. These new etch pits can be associated with β dislocations on the A surface and with α or β dislocations on the B surfaces. There are indications that some of the new pits may be associated with screw dislocations. Any further discussion on the formation of these new pits must be postponed until more is known about the nature of the dislocations with which they are associated.

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