The Chemical Etching of GaSb in Br_2-Methanol Solutions

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ABSTRACT

The Br_2-methanol system has been found to give good results for chemical polishing etching of GaSb except for the {111}Ga plane. The etching rates for {100}, {111}A, and {111}B of n-type and p-type GaSb have been studied as a function of Br_2 concentrations. The etching rates for {100} and {111}B planes of GaSb follow the same linear track in a plot of etching rate *vs.* Br_2 concentration. By comparing the activation energies for the above etching process and the temperature dependence of viscosity of liquid methanol, the above etching process is shown to be a diffusion-controlled reaction. The etching of the {111}A plane of GaSb, however, is preferential with a reaction-limited etching rate. Further experiments show that the etching rates for {100} and {111}B GaSb are similar to these for {100}GaAs, InAs, and InP as expected for diffusion-limited processes.

Since Fuller and Allison[1] first presented Br_2-methanol solution as a chemical polish etchant for III-V semiconductors, this etchant has been widely used. Although some drawbacks exist such as aging effect of the solution,[2] the Br_2-methanol etchant is essentially a universal agent not only for preparing smooth semiconductor surfaces but also for minimizing the amount of interface material left at the surface.[3] Relatively little work has been done in studying the etching process of the Br_2-methanol system. The etching rates of GaAs in Br_2-methanol solutions have been investigated by Tarui *et al.*[4] They found that the etching rate increased with increasing Br_2 concentration, but not in a strictly linearly proportional mode, up to about 5% by weight of Br_2, and the rate then started to level off. They also indicated that different crystal planes etch at different rates, with the rates in the order {110} > {111}As > {100} > {111}Ga for a 1% Br_2 solution by weight, so they concluded that the etching characteristics of GaAs in the Br_2-methanol system was preferential. However, this solution is used as a chemical polishing etchant, not only for III-V semiconductors including GaAs but also for II-VI semiconductors,[5] and for most crystallographic planes (except the {111}A plane), whereas preferential etches tend not to be used for polishing purposes.

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The major purpose of this work was to study the etching behavior of GaSb in the Br_2-methanol system. A linearly proportional relation of etching rate to Br_2 concentrations, which is the feature of diffusion-controlled etching processes, was observed up to a Br_2 concentration of about 8% by weight. The etching rate data of Tarui *et al.*[4] for n-type {100}GaAs follow almost the same track as the etching rates for n-type {100}GaSb measured in this work, except for some experimental points within the range they examined. However, we repeated the measurement of etching rates for n-{100}GaAs and found much stricter linearity than reported by Tarui *et al.* From a study of the temperature dependence of etching rates for {100}GaSb an activation energy was determined and shown to compare to the temperature dependence of the viscosity of methanol. This further confirmed that diffusion of Br_2 though a stagnant boundary layer of methanol is the prime controlling factor for the etching process, although diffusion of the reacting products may also be involved.

The etching rates of n- and p-GaSb {100} planes were found to be similar as was the etching rate for the {111}B (Sb) plane. However, the {111}A (Ga) plane has a much lower etching rate which suggests that the surface reactivity is a controlling factor, as {111}A GaAs.

Experimental

The major samples used in this study were either n- or p-type {100}GaSb with doping concentrations ranging
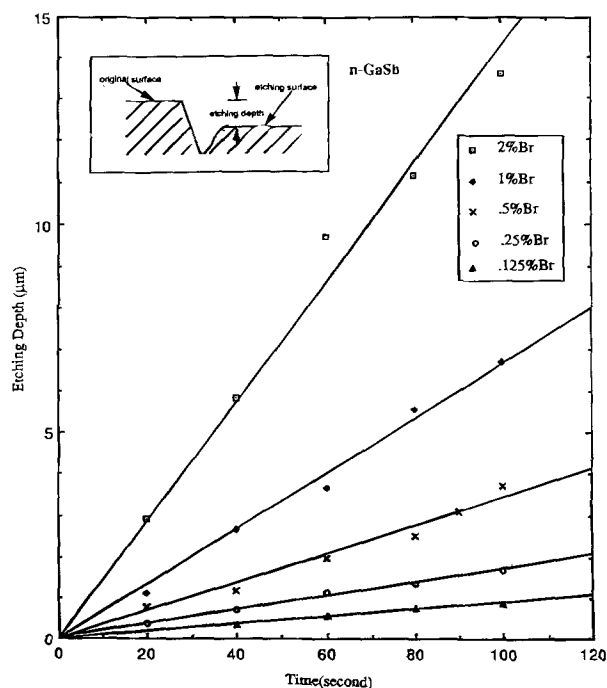

Fig. 1. Etching depth with time for n-GaSb {100} in various Br_2 concentrations by volume.
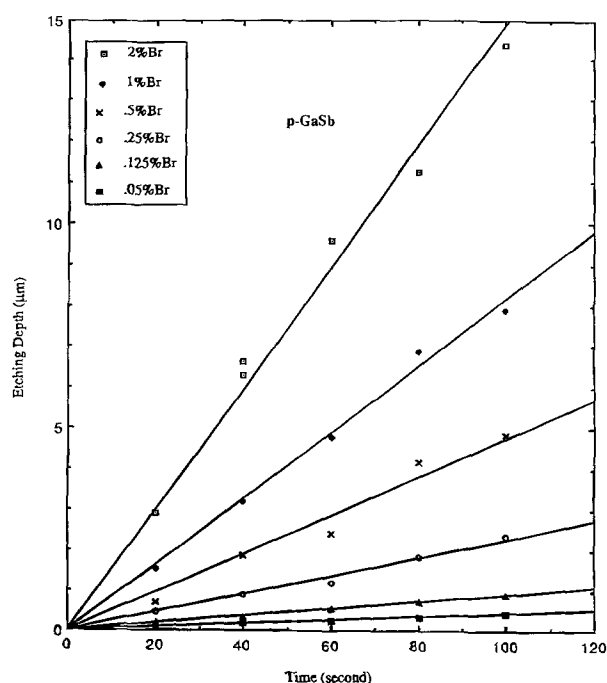

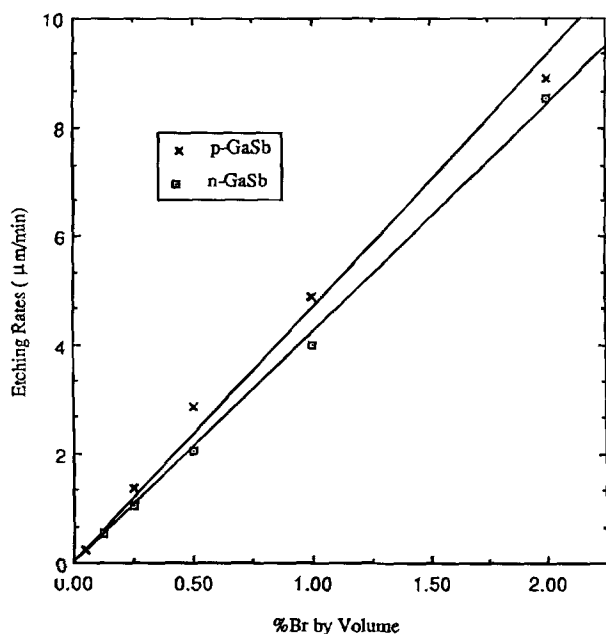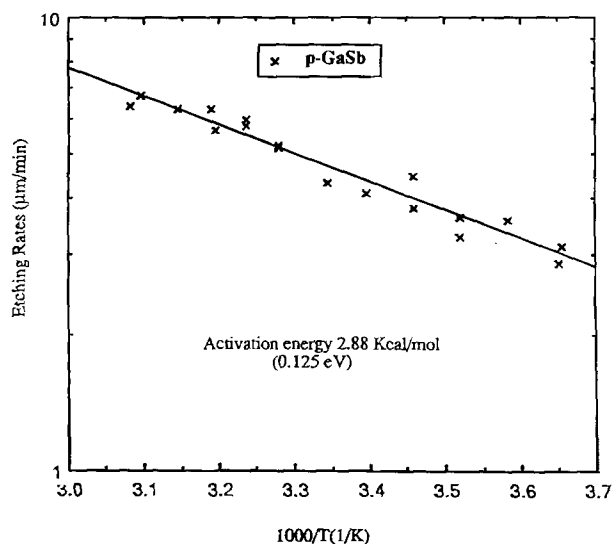**Fig. 2. Etching depth with time for p-GaSb {100} in various Br_2 concentrations by volume.**
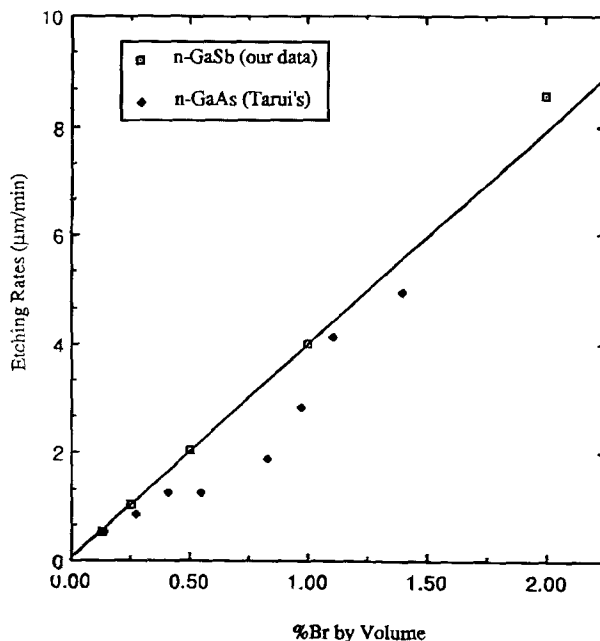
Fig. 3. Etching of n- and p-{100}GaSb.

Fig. 5. Comparison of our data with the data from Tarui *et al.*[4]

from 10^{17} to 10^{19} cm^{-3}. For comparison samples of n-{100}GaAs with doping concentration 2.5×10^{18} cm^{-3} p-{100}GaAs with $1-3 \times 10^{19}$ cm^{-3}, n-{100}InAs with 1 to 2×10^{18} cm^{-3}, p-{100}InP 2×10^{18} cm^{-3}, and undoped p-GaSb 1.5° off {111} toward the {211} plane were examined. All samples are obtained as polished wafers from various vendors. The samples were cleaned with trichloroethane, acetone, and methanol, sequentially, then etched in 0.5% Br$_2$-methanol by volume for about 5 min to remove about 10 μm of surface layer that might affect the etching rate measurement because of polishing damage.

It is generally recognized that Br$_2$-methanol solutions age in strength because of slow reaction of the Br$_2$ with the solvent (other organic solvents have been found to react even faster). In order to minimize the aging effect of the Br$_2$-methanol solution,[6] the following precautions are desirable: (*i*) the etching solutions should be freshly prepared before each experiment and not used after 8 h have elapsed; (*ii*) the solutions should be stored in amber bottles, since light accelerates the aging process; and (*iii*) the beaker and the sample should be dried thoroughly before the etching process.

For our studies the Br$_2$ concentrations in methanol were varied from 0.05 to 2% by volume corresponding to concentrations from about 0.5 to about 8% by weight. The samples were sliced into small pieces of about 3×7 mm for most of etching experiments, and half of the sample was masked by black wax or photoresist. The etching process was done in a small beaker of about 1 in. in diameter, which could be put in the center of an insulated cup during the study of temperature effects. The samples were put on the bottom of the beaker face-up. The solution was agitated manually by rotating and swinging the small beaker continually at about two times per second. Most experiments were performed at room temperature except where mentioned. After removal of the black wax or photoresist, the heights of etching steps were measured using a Tencor Instrument, Model 200. Several factors will affect the measured accuracy of etching rates. Under carefully controlled conditions, the experimental error is within ±10%.

When photoresist lithography was used, SiO$_2$ was deposited by sputtering, forming striped windows parallel to

Fig. 4. Etching rates as a function of temperature for {100}GaSb in 1% Br$_2$-methanol.
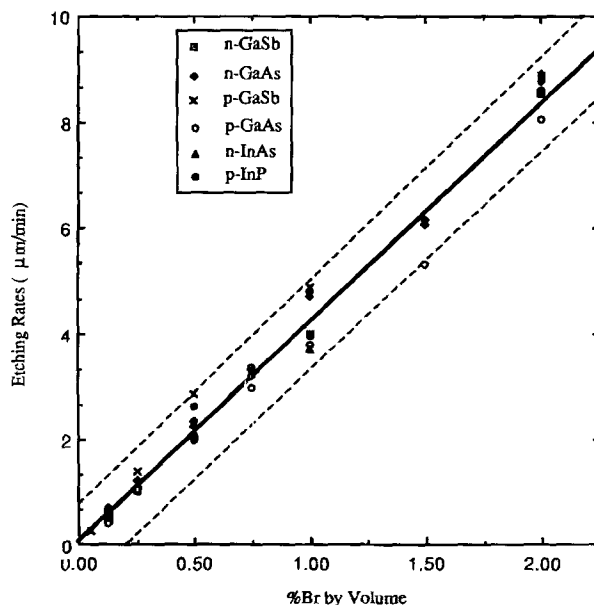
Fig. 6. Etching rates of {100} planes for the various semiconductors with Br$_2$ concentrations by volume.
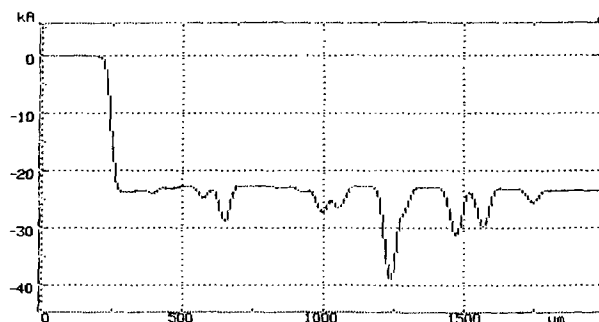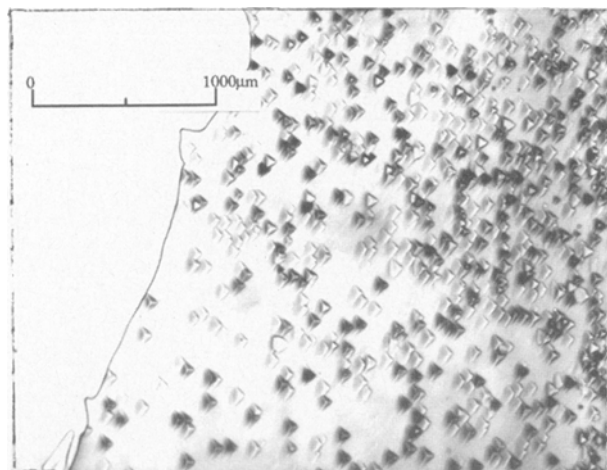
Fig. 7. (a, right) The micrograph of an etching step of the {111}A GaSb sample. **(b, left)** The surface profile of the etching step measured by Tencor Instrument Model 200. Note that at the mask edge (~300 μm) there is no enhanced etching dip (unlike Fig. 1 inset), and this indicates a surface-reaction-limited process. The dips shown in this figure correspond to etch pits.

the cleavage edges of [011] or [01$\bar{1}$] on the (100) plane. The cross sections of the etched grooves were examined for shape and dependence on groove width. When preferential etching of the {111}Ga plane was studied, the GaSb 1.5° off {111} samples displayed different etching morphology and etching rates. The etch pits gave evidence of the vicinal nature of the surface and therefore it was not convenient to use them to estimate pure {111} plane etching rate. Since V grooves of pure {111}A planes developed in the grooves along [01$\bar{1}$] on (100) wafers, it was possible to use these to estimate the etching rate of a pure {111}A plane by observing the rate of change of groove width as discussed later.

Results and Discussion

The etching rate of {100}GaSb.—The preliminary experiments showed (as expected) that there was no difference in the etching rates on both sides of a {100} wafer. Increasing the agitation of the solution increased the etching rates, so we decided to conduct our experiments with a moderate degree of agitation (as described in the previous section), since this gave the most reproducible results. Figures 1 and 2 show that the measured etching depths are in linear proportion to the etching time within the measurement error for n-type and p-type {100}GaSb. The slope of each curve can be calculated by linear regression and be put together
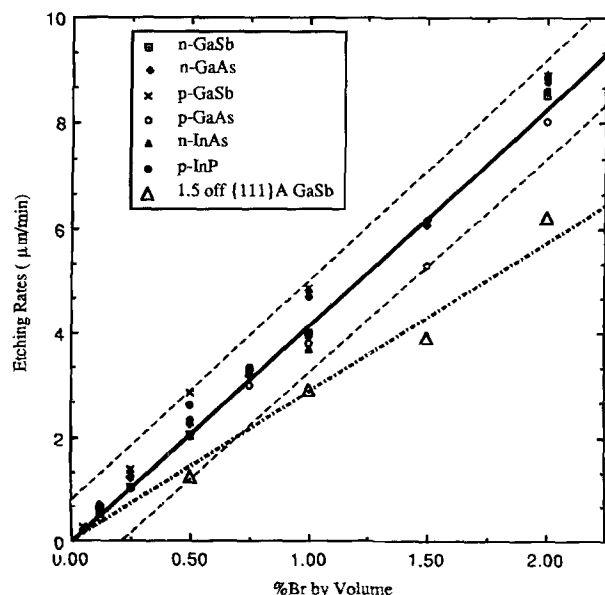
to show the variation of the etching rate with the Br_2 concentration as shown in Fig. 3. It indicates that the etching rates of {100}GaSb are almost linearly proportional to the Br_2 concentration up to 8% by weight and that there is no significant difference between n- and p-GaSb within experimental error.

The typical profile of an etching step in the vicinity of the mask edge is shown in the insert of Fig. 1. There is enhanced etching near the boundary between etched and unetched parts, and then a flat level appears. The etching depth in Fig. 1 and 2 is measured as the difference between the surface level of the unetched area and the flat level of the etched area. The enhanced etching phenomenon apparent at the mask edge is discussed in a companion paper.[7]

The activation energy of the etching process.—The linear dependence of the etching rates on time and concentration (Fig. 1, 2) does not allow us to conclude the characteristics of the etching process. However, the agitation effect and the etching profiles do indicate that the etching of {100}GaSb in the Br_2-methanol solution is diffusion controlled. In order to make a more reliable confirmation, it is worthwhile to determine the activation energy for the process by measuring the dissolution rate as a function of temperature.[8] A plot of etching rate as a function of temperature is shown in Fig. 4. Etching rates were determined between approximately 0 to 50°C with intervals of about 5°C. From the Arrhenius equation, the apparent activation energy was determined to be approximately 2.88 kcal/mol (0.125 eV) which is near the bottom of the activation energy range for diffusion-controlled etching processes.[9] The results of molecular dynamics analysis on hard-sphere assemblies and a substantial body of experimental data all show that the diffusion coefficient and the viscosity of the medium in which the diffusion process takes place bears some kind of inverse relationship to one another.[10] So the activation energy of the diffusion coefficient should be similar to that of the viscosity, but with the opposite sign. This was demonstrated in the etching of germanium and silicon in HNO_3-HF-CH_3COOH solutions by Bogenschütz et al.[11] The major content of the etching solution used in this work was methanol, and the activation energy for the viscosity of methanol is about 2.47 kcal/mol,[12] which almost matches the value of 2.88 kcal/mol observed for the etching process.

The comparison of etching rates.—If a dissolution process depends on the diffusion of the reactant to the surface, the reactant is consumed as soon as it reaches the surface. Under this regime, different materials would dissolve at the same rate in a given solution.[9] Since the etching process of {100}GaSb in Br_2-methanol solution is controlled by diffusion, it is interesting to compare the GaSb etching data with that for n-{100}GaAs presented by Tarui et al.,[4] which

Fig. 8. Comparison of the etching rates for {100} and 1.50 off {111}A planes of GaSb in Br_2-methanol solutions.
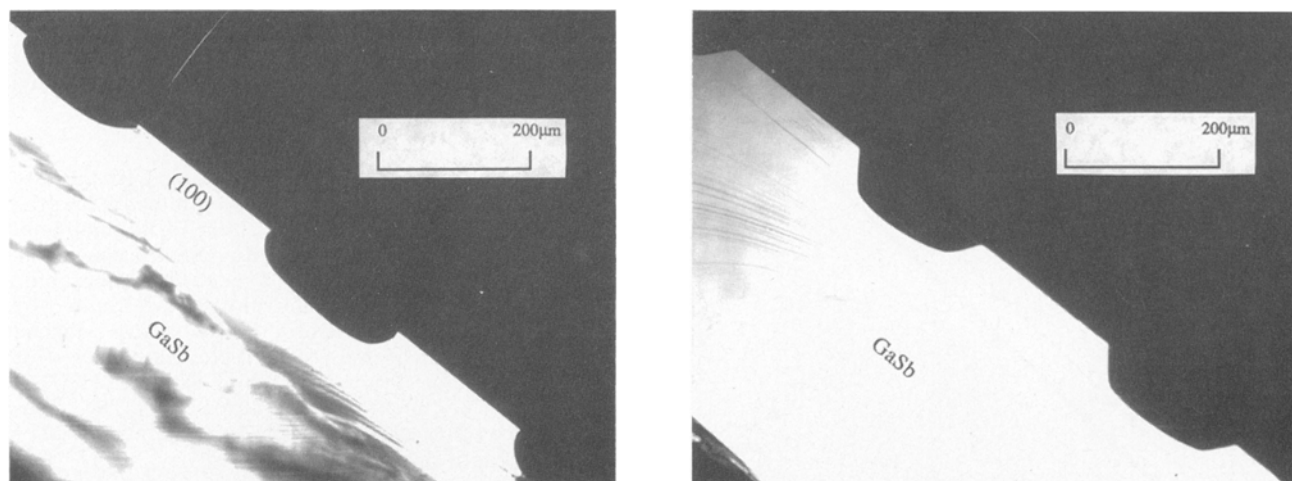
Fig. 9. (a, left) Micrograph of the (011) cross section cleaved from (100)GaSb wafer with grooves along [011] direction. (b, right) Micrograph of the (011) cross section cleaved from (100)GaSb wafer with grooves along [011] direction.

has been cited in many papers. Five of eight experimental points of n-{100}GaAs almost follow the same track as that for n-{100}GaSb. According to the diffusion-controlled model, the rate at which the species reaches the surface, and so the etching rate, can be determined using Fick's law

$$\frac{dn}{dt} = DA(C/h)$$

where A is the surface area of the sample, D the diffusion coefficient of the species in the liquid, C the concentration of species in the bulk of the liquid, and h the thickness of the stagnant layer adjacent to the sample surface. The etching rates should be linearly proportional to the concentrations of the reactant in the liquid for a diffusion-limited etching process. The three points of n-{100}GaAs deviating from the linear track could be caused by experimental error. Experiments involving n- and p-{100}GaAs, n-{100}InAs, and p-{100}InP, therefore, were also made in this study. All the data fall in a linear belt with a deviation of ±10% as shown in Fig. 6. It is worthwhile to point out that the etching rate of 4 μm/min (0.032 mg · cm^{-2} · s^{-1}) for n-{100}InP etched in 1% Br$_2$-methanol solution presented by Tuck and Baker[13] and the etching rate of 2 μm/min for n-{100}InP etched in 0.5% Br$_2$-methanol solution by Turley and Greene[14] also fall in the same belt.

From the fundamental considerations, if the etching rate is controlled by diffusion, it is necessary to consider not only the means whereby the species reach the surface, but also the means of removal of the reaction products.[13] This means that either the diffusion to the surface of the components effective in etching or the removal of reaction products determines the etching rate.[11] In the former case, different materials would be etched at the same rate in a given solution. It has been found, for example, that InSb, GaSb, and InAs dissolve at the same rates in sulfuric acid solution

containing Fe^{+++} ions.[9] But in the latter case, the etching rate would be affected by the material etched, although perhaps only as a minor effect. For instance it has been found from the chemical etching of Si and Ge in HNO$_3$-HF-CH$_3$COOH solution,[11] that the etching rates of Si and Ge are slightly different, but the dissolution process is definitely diffusion limited from the activation energy measurement. From careful experiments by etching different materials at the same run, we believe that the chemical etching of {100}GaSb, GaAs, InAs, and InP have minor difference not larger than ±10% as shown by Fig. 6.

The etching rate of {111}GaSb.—Like most III-V compounds, the GaSb has a zinc blende structure crystal belonging to the cubic noncentrosymmetric space group, which causes polarity on the crystal lattice along the <111> direction. The polarity of most III-V compounds along <111> directions leads to pronounced chemical etching differences between the nonequivalent sides of {111} wafers. Gatos and Lavine[9] reported that dislocation etch pits were observed on the {111}A plane of GaSb in a number of etching solutions, containing oxidizing agents such as HNO$_3$, H$_2$O$_2$, Fe^{+++}, MnO$_4^-$, Cr$_2$O$_7^-$, Ce^{++++}, and V(OH)$_4^+$, but pits were not observed on the {111}B plane of GaSb.

In this work, an undoped p-GaSb {111} wafer cut 1.5° off toward [211] with both sides polished was etched in various strength solutions of Br$_2$-methanol. The {111}A plane developed many triangular pits (shown in Fig. 7a), with the pits slightly distorted corresponding to the 1.5° angle cut. The profile of the etching step did not display enhanced etching near the boundary of the etching step (shown in Fig. 7b). The dips appearing on the profile of the etching area are in correspondence with the triangular features of Fig. 7a. The etched {111}B plane of GaSb retained a mirror surface. The etching rates measured for the {111}A GaSb are shown in Fig. 8. The etching rates of the {111}A plane are less than that of the {111}B plane which is almost the same as for the {100}GaSb plane. However, the etch ratio of {111}B to {111}A is not as large as might be expected, and this is related to the vicinal form of the {111}A plane.

Orientation effects on etching rates have been attributed to the surface densities of free bonds. For the III-V compound InSb, the relative rates of the low index surfaces were found to be as follows[9]

$$\{111\}Sb > \{100\} > \{110\} > \{111\}In$$

But for GaSb, the dissolution process of most crystal planes is diffusion controlled, so no difference of the etching rates between the {111}Sb and {100} planes was observed. Similar results were also observed in the case of InP etched by Br$_2$-methanol solutions.[13] Tarui *et al.*[4] measured the etch rates for different crystal planes of GaAs to be in the order
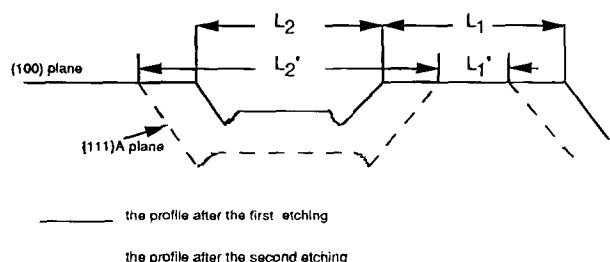

Fig. 10. Groove widening from L_2 to L_2' as a result of continued etching and development of the {111}A planes. The etching rate may be derived from $R_{\{111\}A} = [(L_1 - L_1') + (L_2 - L_2)]/[(2 \sin 54.7°)2t]$ where $R_{\{111\}A}$ is the etching rate of {111}A and t is the etching time.
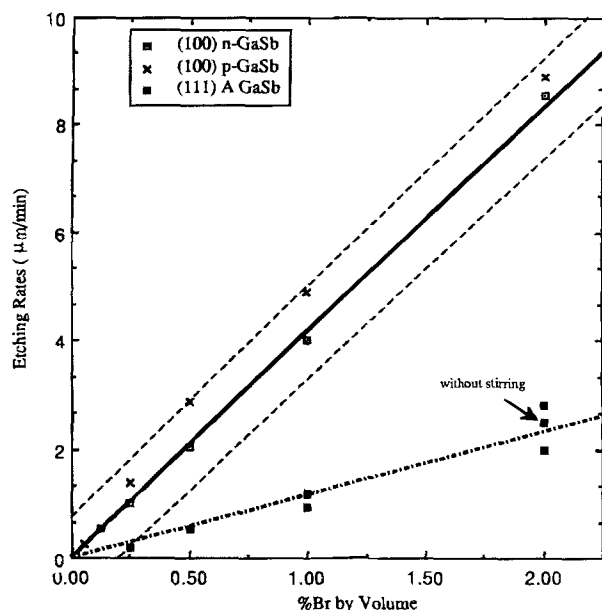
Fig. 11. Comparison of the etching rates for {100} and {111}A planes of GaSb in Br_2-methanol solutions.

pointed out that the obtuse angle wall would be smaller if the minimum etching rate is larger or the etching ratio of {111}B to {111}A smaller. This is consistent with the profile observed in Fig. 9b.

Conclusion

The measured etching data are comparable with the data presented for other III-V compounds and indicate that the etching process of III-V semiconductors in Br_2-methanol solutions is reproducible with careful preparation of the etching process. The reactions of most crystallographic planes of GaSb in Br_2-methanol solutions are limited by the diffusion of Br_2 or etching products, so smooth polished surfaces of GaSb can be prepared in this etchant, except for the {111}A plane of GaSb. The etching ratio of {111}B to {111}A for GaSb is smaller than that for GaAs. The steep-angled wall on the sides of a [011] groove on a {100} wafer may be of benefit in device fabrication.[16]

{110} > {111}As > {100} > {111}Ga

but this is contrary to the expectations based on the free-bond model. From diffusion-limited etching considerations, the etching rates for {110}, {111}As, and {100} of GaAs should be the same.

Since we were not sure of the role of the 1.5° cut, another method was devised to determine the etching rate of a pure {111}Ga plane from a {100} cut sample. The etching grooves along both cleavage edges on a {100} wafer were observed to have cross sections as shown in Fig. 9. For the (011) cross section, the sidewalls of the groove are composed of two sections making an obtuse angled plane with the portion of the wall nearest the upper surface, and a curved wall near the groove bottom. The upper section is inclined to the upper surface by an angle of about 110°, which corresponds to the crystallographic plane of $(\overline{1}22)$Ga.[15] For the $(01\overline{1})$ cross section, however, the sidewalls are sharply defined planar walls inclined with the upper surface by an angle of 55°, corresponding to the {111}Ga surfaces. From the shift of these lateral {111}Ga planes during further increase in the etching time, the etching rate of a {111}Ga plane can be measured as shown in Fig. 10. The etching rates measured in this way are presented in Fig. 11, and the etching ratio of {111}B to pure {111}A reaches a value of about 3.5. This is still less than an etch ratio of about 5 reported for GaAs.[4] Using a modified Wulff construction method, Shaw[16] has

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