

# Photoelectrochemical Etching of GaSb

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## ABSTRACT

The photoelectrochemical behavior of GaSb has been investigated in aqueous NaOH, NaCl, and HCl solutions. Despite the relatively narrow bandgap, the photo-oxidation and dissolution process dominated the behavior of n-GaSb at potentials positive of the flatband potential ( $V_{FB}$ ). At high pH and sufficient solution agitation, the etch rate was proportional to light intensity. At potentials 0.5 V positive of  $V_{FB}$ , a tunneling oxidation current developed resulting in an etch process that was independent of the light intensity. XPS analysis of the etched surface suggested that an increase in the dissolution rate of antimony oxides took place at high pH and solution agitation. The formation of an antimony oxide film resulted in surface passivation. Because of the relatively negative flatband potential of n-GaSb, oxygen was reduced at the same potential that n-GaSb was photo-oxidized. Thus, at the flatband potential, an open-circuit photoetch rate of 1  $\mu\text{m}/\text{min}$  was observed in an air-saturated solution.

Compared to silicon, gallium antimonide is a relatively narrow bandgap semiconductor ( $E_{gap} = 0.72 \text{ eV}$ ) of interest for infrared detectors, and quantum-well devices because of the large bandedge discontinuity that can be achieved with lattice matched semiconductors.<sup>1-3</sup> However, the use of GaSb requires the development of processing, etching, and polishing techniques. The chemical processing of GaSb is particularly difficult because of its reactivity, small bandgap, and limited solubility of the reaction products. Photoelectrochemical (PEC) processing of semiconductors can be used to develop unique processes such as photoselective etching and dopant sensitive etching.<sup>4</sup> In PEC processing, a semiconductor is immersed in an electrolyte and is reverse biased forming a space charge region at the solution-semiconductor interface. The semiconductor is illuminated with light of energy greater than that of the bandgap, creating electron-hole pairs. The photogenerated minority carriers within the space-charge region migrate to the semiconductor-solution interface where they can participate in electrochemical reactions such as etching. If the reaction rate is limited by the supply of photogenerated holes at the surface, the rate of the PEC process can be directly proportional to the light intensity.

Little work has been done on the electrochemistry of GaSb. In 1980, Elliot and Regnault developed a surface-finishing procedure for n-GaSb.<sup>5</sup> The semiconductor was mounted on a rotating disk electrode, immersed in an aqueous solution of 0.2M ethylene diamine tetra-acetic acid disodium salt and ammonium hydroxide, and intensely illuminated under an applied potential of 50 V. Under these conditions, an etch rate of 4  $\mu\text{m}/\text{min}$  was achieved. Their observations indicate that the surface appearance is a function of solution pH. In 1986, Menezes and Miller, studied the electro-dissolution and passivation phenomena of several III-V semiconductors.<sup>6</sup> They assumed that the narrow bandgap results in a negligible photoreponse and obtained cyclic voltammograms of n-GaSb in the dark. They observed anodic dissolution with two current peaks, partial passivation, and reactivation on the reverse scan. The peaks were attributed to the formation of films in which antimony and gallium compounds were formed. They compared the passivation behavior to that of metals forming solubility-limited surface precipitates. In 1986, Buglass *et al.* developed a controllable wet etchant for GaSb.<sup>7</sup> Etch rates were 0.1 to 2  $\mu\text{m}/\text{min}$  with a smooth surface free from etch pits and surface films. However, the etch rate was strongly dependent on solution agitation and not photoactivation. In this study the electrochemistry of GaSb in aqueous solutions was investigated as a function of doping, light intensity, solution pH, and agitation. The etching process was investigated as a function of potential. The reaction surfaces were analyzed using x-ray photoelectron spectroscopy (XPS). Based on the observations a reaction mechanism was developed.

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## Experimental

The (100) GaSb samples were obtained from MCP Electronic Materials Ltd. (Fairfield, CT). The n-GaSb samples were doped with Te resulting in a carrier concentration of  $4.3 \times 10^{17} \text{ cm}^{-3}$  at 300 K, a mobility of  $3000 \text{ cm}^2/\text{V s}$  and a resistivity of  $0.0045 \Omega \cdot \text{cm}$ . The p-GaSb crystals had a carrier concentration of  $1.4 \times 10^{17} \text{ cm}^{-3}$  at 300 K, a mobility of  $600 \text{ cm}^2/\text{V s}$ , and a resistivity of  $0.072 \Omega \cdot \text{cm}$ . Ohmic contacts were made to the semiconductors by coating the back of the samples with a gallium indium alloy, forming a tunnel diode. The semiconductors were mounted to glass slides using epoxy to insulate the edges, back, and electrical contacts from the electrolyte solution. Solution agitation in the  $150 \text{ cm}^3$  cell was accomplished using a standard stirring/hot plate on the high speed setting and a 1 in. Teflon stirring bar. Reagent-grade chemicals and deionized water were used as well as a  $100 \text{ mW}/\text{cm}^2$  tungsten lamp and a 15 mW HeNe laser.

The electrochemical measurements were made using a Princeton Applied Research PARC 273 (Princeton, NJ) potentiostat. A saturated calomel electrode (SCE) was used as the reference, and a platinum wire was used as the counterelectrode. The electrochemical cell was a  $250 \text{ cm}^3$  Pyrex cell with an optical window and gas purge port. The solution was agitated with a Teflon stirring bar.

**XPS analysis.**—A Surface Science (Mountain View, CA) SSX-100 x-ray photoelectron spectrometer was used to analyze the GaSb surfaces. The SSX-100 was equipped with a K- $\alpha$  aluminum x-ray source and a crystalline x-ray monochromator. The operating pressure was  $2 \times 10^{-9}$  Torr. Depth profiles were collected by sputtering the GaSb samples with 4 keV argon ions at a pressure of  $3.7 \times 10^{-7}$  Torr. The sputter rate was calibrated using silicon dioxide where the sputter rate was 14  $\text{\AA}/\text{min}$ .

Kitamura *et al.* previously investigated oxidized GaSb surfaces with XPS.<sup>8</sup> The binding energy and full width at half maximum data were confirmed using XPS spectra for elemental antimony (99.999%) and gallium antimonide (99.999%), and is summarized in Table I. The sensitivity factors for Ga and Sb were obtained by measuring the in-

Table I. Binding energies and (full width half maximums) in electronvolts.

Compound	Ga 3d	Sb 4d	Sb 3d	O1s
Ga	183 (1.3)			
GaSb	19.0 (1.4)	32.1 (1.4) 33.3 (1.2)	528.1 (1.5) 537.4 (1.6)	
Ga <sub>2</sub> O <sub>3</sub>	20.6 (1.9)			
Sb		32.1 (1.2) 33.2 (1.3)	528.2 (1.4) 537.6 (1.5)	
Sb <sub>2</sub> O <sub>3</sub>		34.8 (1.9)	530.3 (1.6) 420.2 (1.8)	
Sb <sub>2</sub> O <sub>5</sub>		35.8 (2.1)	532.1 (1.6) 541.8 (1.8)	
O <sub>2</sub>				531.5 (1.8)

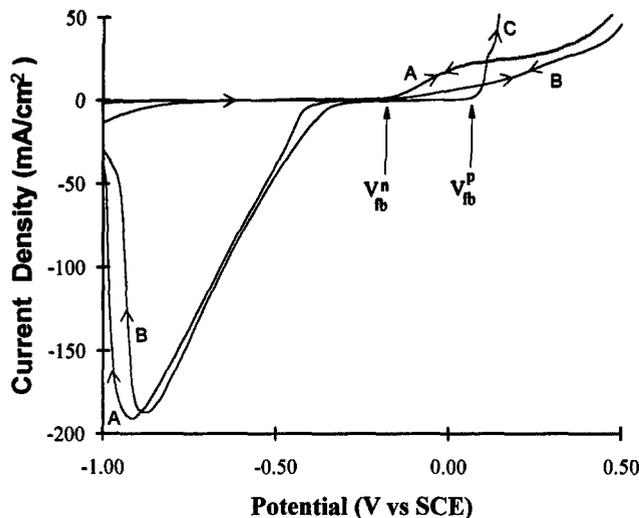


Fig. 1. Current-potential curves for (A) n-GaSb illuminated, (B) n-GaSb in the dark, and (C) p-GaSb in the dark in an agitated 1M NaOH solution: scan rate = 0.85 V/s.

tensity of stoichiometric GaSb. The relative sensitivity factors for Ga 3d and Sb 4d were determined to be 1:2.5. This is in good agreement with the corresponding photoelectron cross sections, 1.19:2.98.<sup>9,10</sup>

### Results and Discussion

The photoelectrochemical behavior of n-GaSb and p-GaSb was investigated in 1M solutions of NaOH, unbuffered NaCl, and HCl, Fig. 1-3, respectively. In each of the three figures curve A is n-GaSb under illumination, curve B is n-GaSb in darkness, and curve C is p-GaSb in darkness. The sweep rate was 0.85 V/s and the surface was uniformly illuminated with a tungsten halogen white light source. The three solutions show *i*-*V* behavior characteristic of a semiconductor-liquid junction. The energy position of the conduction band, valence band, and flatband potential ( $V_{FB}$ ) were estimated from the onset of the oxidation current for p-GaSb and the photo-oxidation current for n-GaSb. The initial potential for the voltage sweeps for n-GaSb in Fig. 1-3, was negative of  $V_{FB}$  and the sweep direction was toward positive potentials. The onset of the photo-oxidation, Fig. 1-3 curve A, was observed at -1.1, -0.5, and -0.3 V vs. SCE in NaOH, NaCl, and HCl, respectively, which is approximately  $V_{FB}$ . At potentials positive of  $V_{FB}$ , a Schottky barrier is formed within the n-GaSb and photogenerated holes migrate to the semiconductor solution interface where they can participate in faradaic processes. The photoanodic current observed in Fig. 1-3 for

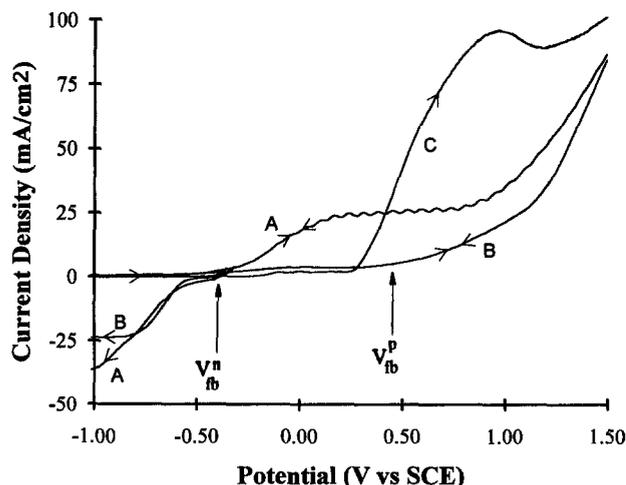


Fig. 2. Current-potential curves for (A) n-GaSb illuminated, (B) n-GaSb in the dark, and (C) p-GaSb in the dark in an agitated 1M NaCl solution: scan rate = 0.85 V/s.

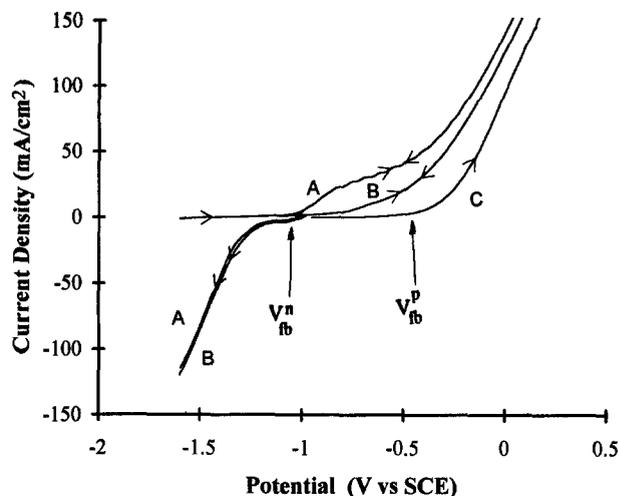
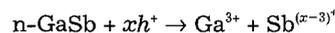


Fig. 3. Current-potential curves for (A) n-GaSb illuminated, (B) n-GaSb in the dark, and (C) p-GaSb in the dark in an agitated 1M HCl solution: scan rate = 0.85 V/s.

n-GaSb is due to the oxidative dissolution of n-GaSb, where the expected value of  $x$  is 6, based on final valence of 3+ for both Ga and Sb



A photoanodic plateau was observed in each solution at potentials just positive of  $V_{FB}$ . The illumination intensity was 60 mW/cm<sup>2</sup> resulting in a saturation current of 30, 25, and 30 mA/cm<sup>2</sup> in agitated solutions of NaOH, NaCl, and HCl, respectively. In the potential region between  $V_{FB}$  and ( $V_{FB} + 0.5$  V), negligible dark currents were observed with n-GaSb and p-GaSb because of the depletion region formed within the semiconductors. The photo-oxidation plateau with negligible dark current is in contrast to previous observations where a negligible photoresponse was attributed to the narrow bandgap of GaSb.<sup>6</sup>

At potentials positive of the anodic current plateau for n-GaSb, an anodic dark current, Fig. 1-3 curve B, was observed beginning at approximately -0.8, 0.0, and 0.2 V for NaOH, NaCl, and HCl, respectively. The dark current increased with potential and also resulted in the anodic dissolution of the GaSb. The onset potential for the increase in the dark current for n-GaSb corresponds to band-bending conditions approximately equal to the energy gap of the semiconductor. At this potential, the energy of the Fermi level in the bulk is approximately equal to the valence band edge at the semiconductor-solution interface. Under these band-bending conditions, electrons can be injected into the conduction band from tunneling, resulting in the dissolution of the lattice without the assistance of light. At 0.5 V vs. SCE in 1M NaOH,  $6 \pm 1$  ( $2\sigma$  value) electrons flowed in the external circuit for each molecule of GaSb etched. This result is in accordance with the expected value of 6 based on a final oxidation state of 3+ for both gallium and antimony.

The voltammogram for p-GaSb, Fig. 1-3 curve C, shows a dramatic increase in the anodic current on the positive-going scan when the potential approached  $V_{FB}$ ; -0.5, 0.2, and 0.1 V vs. SCE in NaOH, NaCl, and HCl, respectively. At potentials negative of  $V_{FB}$ , for p-GaSb a depletion region exists within the semiconductor where the concentration of holes at the semiconductor solution interface is small. Thus, the values for  $V_{FB}$  for p-GaSb corroborate the  $V_{FB}$  values for n-GaSb based on the onset potential of the photo-oxidation current. The potential region between the onset of the photoanodic current for n-GaSb and that of the dark oxidation current for p-GaSb is where a depletion region exists for both semiconductors.

On the negative-going sweep following the initial positive-going scan, the anodic current for n-GaSb retraces the *i*-*V* behavior of the forward sweep for potentials positive of  $V_{FB}$ . At potentials negative of  $V_{FB}$ , a cathodic current was

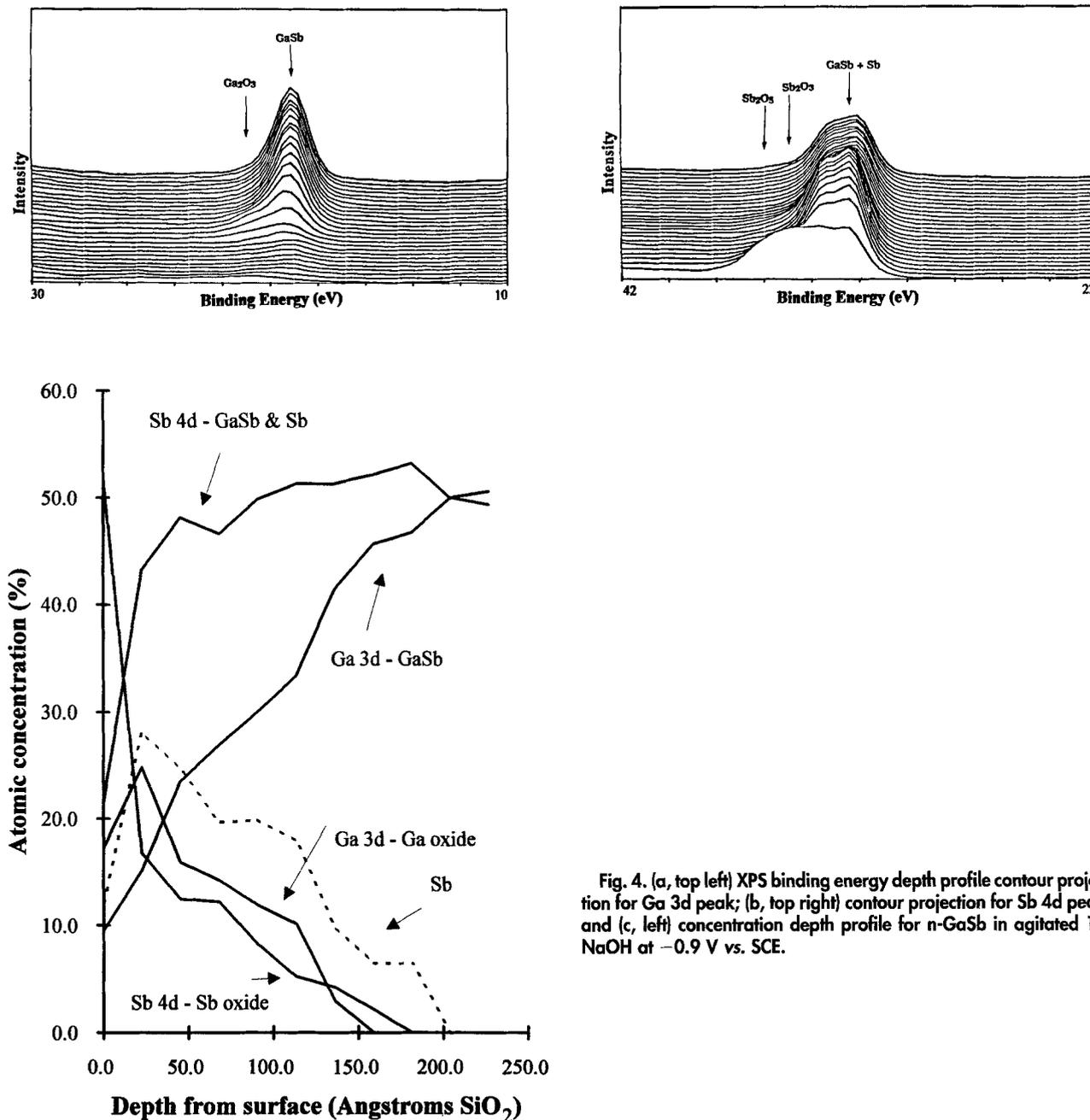


Fig. 4. (a, top left) XPS binding energy depth profile contour projection for Ga 3d peak; (b, top right) contour projection for Sb 4d peak; and (c, left) concentration depth profile for n-GaSb in agitated 1M NaOH at  $-0.9$  V vs. SCE.

observed due to the reduction of the oxidation products produced on the positive-going scan. The cathodic peak current was a function of scan rate, pH, solution agitation, illumination intensity during the positive-going scan, and switching potential. The faster the scan rate or higher the illumination intensity, the larger the peak current because a greater quantity of oxidation products were present. Agitation helped remove the oxidation products and decreased the cathodic peak. The onset potential for the reduction supports the flatband position of n-GaSb.

The photoetching of n-GaSb was studied in the potential range  $(V_{FB} + 0.5) > V > (V_{FB})$ , where high photocurrent to dark current ratios can be obtained. In an agitated 1M NaOH solution, the magnitude of the photocurrent was independent of scan rate for values investigated between 0.0085 and 8.5 V/s. The oxidation current was directly proportional to white-light intensity over the range from 0 to 60 mW/cm<sup>2</sup>, the maximum lamp intensity. Within these conditions, the current was directly proportional to the hole concentration at the semiconductor solution interface. The resulting etched surface was rough, mat gray, and appeared faceted. When the n-GaSb was illuminated with a 15 mW HeNe laser and poised at  $-0.9$  V, the observed current was 4 mA. The shape of the etched hole had a

slightly distorted Gaussian profile similar to the intensity distribution of the laser. The dark current was about 1% of the total current.

When the n-GaSb was irradiated with a 1.6 mW/cm<sup>2</sup>, 500 nm light, and biased at  $-0.9$  V,  $4 \pm 1$  ( $2\sigma$  value) electrons flowed in the external circuit for each molecule of GaSb etched. This value was lower than the expected value between 6 and 8 based on the oxidation states of gallium (3+) and antimony (3+ or 5+), and indicated that a chemical oxidation process accounted for part of the oxidation process, or that a reduction process occurred in parallel with the oxidation.

XPS was used to investigate the thickness and composition of the reaction products on the surface of n-GaSb. The n-GaSb was etched at  $-0.9$  V in NaOH under white-light illumination and solution agitation. While an effort was made to stop the process before the surface became roughened, the surface was visibly altered which tends to decrease the resolution of the XPS depth profile.

Figure 4a and b present contour projections of intensity as a function of binding energy for successive sputter cycles of the Ga 3d and Sb 4d spectra, respectively. The Ga 3d peaks at 19.0 and 20.6 eV correspond to the binding ener-

gies of Ga associated with GaSb and  $\text{Ga}_2\text{O}_3$ , respectively. At the surface, only a small amount of these two species were detected. As the number of sputter cycles increased, the concentration of Ga associated with GaSb increased.

In the Sb 4d spectra, peaks at 34.5 and 35.8 eV are associated with the binding energies of Sb in the form of  $\text{Sb}_2\text{O}_3$  and  $\text{Sb}_2\text{O}_5$ , respectively. These peaks decreased in magnitude from the surface toward the bulk. In the Sb 4d spectra, a doublet peak, GaSb + Sb, was present with peaks assigned at 32.1 and 33.2 eV. This doublet corresponds to both the binding energies of Sb associated with GaSb (32.1 and 33.3 eV) and elemental antimony (32.1 and 33.2 eV). As seen in Fig. 4b, the binding energy peaks associated with antimony oxides were greatest at the surface and decreased with sputtering into the bulk. The GaSb + Sb peak increased with depth.

Using the intensity *vs.* binding energy data, and corrections discussed in the Experimental section, the data can be expressed as concentration *vs.* film depth, as shown in Fig. 4c. The film was approximately 100 to 200 Å. This value was approximate because some surface roughening resulted from the etching process which decreased the sharpness of the depth profile. The film was a mixture of antimony and gallium oxides. Elemental Sb also appeared to be present based on the difference between the GaSb concentration as determined from the Ga 3d peak, and the GaSb + Sb concentration as measured by the Sb 4d doublet.

The presence of elemental antimony is not unique for this system. Kitamura<sup>11</sup> electrochemically oxidized undoped GaSb producing a thick oxide film. The samples were prepared at voltages between 30 and 100 V in an aqueous solution containing tartaric acid and propylene glycol adjusted to pH 5.5 with  $\text{NH}_4\text{OH}$ . The films produced under these conditions were homogeneous mixtures of antimony oxide and gallium oxide. However, elemental antimony was detected at the oxide-semiconductor interface.

For comparison, the composition of the film on n-GaSb oxidized in the dark at 0.5 V *vs.* SCE in an agitated NaOH solution was similar to that under illumination at -0.9 V. The n-GaSb was etched at 80 mA/cm<sup>2</sup> for 10 min. The thickness of the surface film was approximately 200 Å. The film consisted primarily of  $\text{Sb}_2\text{O}_3$  and  $\text{Sb}_2\text{O}_5$  as well as gallium oxides. The difference between the samples was the absence of elemental antimony at the more positive potential. This result shows that the insoluble reaction products at -0.9 V under illumination were essentially the same as those produced by thermally generated holes at 0.5 V. This result is expected because both are valence-band processes.

In the absence of forced convection in NaOH, the dissolution of the Sb products was slowed and caused a partial passivation of the electrode surface. Figure 5 shows the

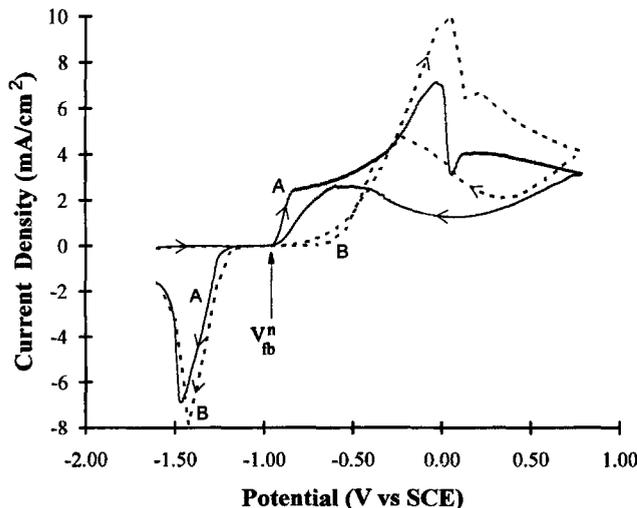


Fig. 5. Current-potential curves for (A) n-GaSb illuminated, (B dashed) n-GaSb in the dark, in a quiescent 1M NaOH; scan rate = 0.085 V/s.

cyclic voltammogram (0.085 V/s) for n-GaSb in a quiescent NaOH solution, curve A and B under illumination and in darkness, respectively. The photocurrent in the potential region from -1.6 to -0.6 V was 3 mA/cm<sup>2</sup> compared to 30 mA/cm<sup>2</sup> with agitation. At more positive potentials, a peak in the current was observed followed by partial passivation. On the reverse sweep, the oxidation current increased as the surface was reactivated.

This unusual behavior has been observed previously and is due most likely to the formation of a different mixture of oxides at very positive potentials.<sup>6</sup> The potential of the valence band edge shifts to more positive values when the electrode is biased far positive of  $V_{FB}$ . This change in the potential of the holes at the semiconductor solution interface can change the oxidation products. The passivation behavior was seen also in an agitated solution if the scan rate was less than 0.5 V/s. The magnitude of the current in the agitated solution was 10 times that in an unstirred solution. The reduction of the oxidation products produced on the forward scan was observed in the quiescent solution on the reverse scan at potentials negative of  $V_{FB}$ . The surface of the n-GaSb sample etched in an unagitated solution at a potential of 0.5 V *vs.* SCE was rough and dark in appearance. Based on XPS measurements, the oxide film was approximately 2500 Å thick, 10 times that associated with an agitated solution. The film consisted primarily of  $\text{Sb}_2\text{O}_5$ . There was some evidence of  $\text{Sb}_2\text{O}_3$  near the oxide semiconductor interface. Neither Ga nor its oxide was found.

The oxidation-dissolution process was a function of solution pH. The voltammogram in 1M HCl was not reproducible on subsequent scans. For example, if a fresh n-GaSb electrode was scanned from -1 to 0.4 V at a scan rate of 0.05 V/s in a stirred 1M HCl solution, a photocurrent of 30 mA/cm<sup>2</sup> was observed. The photocurrent after four subsequent scans was less than 10 mA/cm<sup>2</sup>. When the experiment was repeated with 0.25M tartaric acid added to the 1M HCl solution, the photocurrent did not decrease on subsequent voltage sweeps. Tartaric acid complexes Sb and has been included in the wet cleaning of GaSb.<sup>12</sup> The tartaric acid complexes the oxidized Sb thereby assisting its removal from the surface and eliminating the formation of a partially passivating film.

A thick oxide film (10,000 Å) consisting of  $\text{Sb}_2\text{O}_3$  and  $\text{Sb}_2\text{O}_5$  was found by XPS on n-GaSb poised at 0.0 V in an agitated 1M HCl under illumination for 10 min. These data show that the gallium is readily dissolved from the surface while the oxidation products of antimony are not. Previous studies on the oxidation and dissolution of elemental Sb have shown that the dissolution rate increased with pH, temperature, and solution agitation.<sup>13-16</sup> Partial passivation was also observed and attributed to the formation of  $\text{Sb}_2\text{O}_3$  on the surface.

The flatband potential of n-GaSb is sufficiently negative so that oxygen can be reduced on the GaSb surface at the same potential that n-GaSb is photo-oxidized. The open-circuit potential of n-GaSb under illumination in an aerated solution was -1.15, -0.60, and -0.30 V *vs.* SCE in NaOH, NaCl, and HCl. The n-GaSb was illuminated with a 15 mW HeNe laser at open-circuit conditions under several solution conditions. The etch rates were measured and are

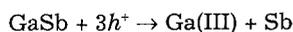
Table II.

Electrolyte	Purge gas	Solution agitation	Etch rate ( $\mu\text{m}/\text{h}$ )
1M NaOH	Air	Yes	60 $\pm$ 15
	Nitrogen	Yes	3 $\pm$ 1
	Oxygen	Yes	70 $\pm$ 15
	Air	No	10 $\pm$ 3
	Nitrogen	No	<1
	1M HCl	Air	Yes
Nitrogen		Yes	1 $\pm$ 1
Oxygen		Yes	60 $\pm$ 15
Air		No	8 $\pm$ 3
Nitrogen		No	<1

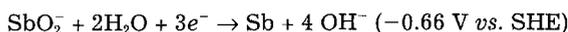
presented in Table II. The etch rates were equivalent in NaOH and HCl. Solution agitation increased the etch rate five times that of a quiescent solution. Purging the solution with nitrogen decreased the etch rate by 50 times compared to an aerated solution because, without oxygen serving as the oxidizing agent, the cathodic current at  $-1.1$  V in NaOH or  $-0.3$  V in HCl was nearly zero. Purging the solution with pure oxygen did not increase the etch rate over that of air.

The chemical composition of the n-GaSb surface etched by white light at  $-1.1$  V vs. SCE, the open-circuit potential, in 1M NaOH was characterized using XPS. The depth resolution of the profile was better than those previously discussed because the surface was smooth. A concentration depth profile, Fig. 6, was calculated based on the intensity data of the Sb 4d and Ga 3d spectra. The striking feature of the film composition was the presence of elemental antimony, which also was observed when the n-GaSb was etched at  $-0.9$  V. Gallium oxides, while detected, were a minor constituent of the film.

Thus, the anodic oxidation near  $V_{FB}$  for n-GaSb leads to the formation of Sb



The stability of Sb at  $-1.1$  V in NaOH can be understood in terms of its redox potential



The Sb in contact with dissolved oxygen can be oxidized as part of the reaction mechanism.

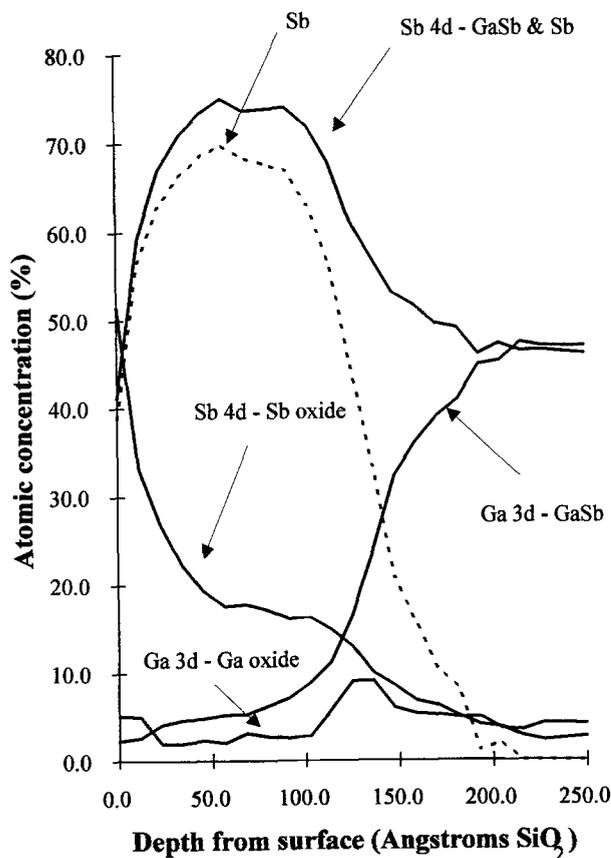


Fig. 6. Concentration depth profile for n-GaSb in agitated 1M NaOH at  $-1.1$  V vs. SCE (open circuit).

## Conclusion

Although GaSb has a bandgap of only 0.72 eV at room temperature, n-GaSb can be photoetched in aqueous solutions of NaOH, NaCl, and HCl. The flatband potential for n-GaSb, was  $-1.1$ ,  $-0.5$ , and  $-0.3$  V vs. SCE in 1M aqueous solutions of NaOH, unbuffered NaCl, and HCl, respectively.

In an agitated 1M NaOH solution, the photocurrent and etch rate were proportional to light intensity up to at least 60 mW/cm<sup>2</sup>. The oxidation process was associated with the flow of 4 electrons in the external circuit per molecule of GaSb dissolved, with the chemical oxidation of products. The etched surface was mat gray and appeared faceted. At lower pH and insufficient agitation, the surface passivated due to the buildup of antimony oxides on the surface.

At potentials approximately 500 mV positive of the flatband potential for n-GaSb, the oxidation and etching process was independent of light and proceeded through tunneling. The etched surface is mat gray and appears faceted. Six electrons per molecule were measured in the external circuit. XPS analysis showed only oxides at positive potentials, whereas elemental Sb was found at potentials negative of the redox potential for Sb.

In the presence of dissolved oxygen, a photoinduced etching process was observed at open circuit. Under uniform illumination the surface was smooth. Using a 15 mW HeNe laser etch rate up to 1  $\mu\text{m}/\text{min}$  were measured. Elemental antimony was identified on the etched surface by XPS. Based on these observations the mechanism for photodissolution involved the photo-oxidation of the semiconductor in forming a soluble oxidized gallium species and elemental Sb. The elemental antimony then oxidized by dissolved oxygen.

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