

Citric Acid Etching of $\text{GaAs}_{1-x}\text{Sb}_x$, $\text{Al}_{0.5}\text{Ga}_{0.5}\text{Sb}$, and InAs for Heterostructure Device Fabrication

Gregory C. DeSalvo, Ron Kaspi, and Christopher A. Bozada

Wright Laboratory, Solid State Electronics Directorate, Research Division,
Wright-Patterson Air Force Base, Ohio 45433-7323

ABSTRACT

Citric acid/hydrogen peroxide ($\text{C}_6\text{H}_8\text{O}_7\cdot\text{H}_2\text{O}_2$) at volume ratios from 0.2:1 to 20:1 was found to provide selective etching between $\text{GaAs}_{1-x}\text{Sb}_x$ ($x = 0.15$ to 1.0), $\text{Al}_{0.5}\text{Ga}_{0.5}\text{Sb}$, InAs, and various III-V semiconductor materials for use in new GaAs and InP based heterostructure transistors and optoelectronic devices. By choosing different concentration volume ratios of citric acid to hydrogen peroxide ($\chi\text{C}_6\text{H}_8\text{O}_7\cdot 1\text{H}_2\text{O}_2$), highly selective as well as uniform (nonselective) etching regions were found to exist in these material systems. Etchant selectivities greater than 50 were found for most combinations of the III-V semiconductor materials under investigation, with selectivities of over 100 measured for GaAs/GaSb and InAs/GaSb material combinations, and with selectivities of over 3850 calculated for InAs/ $\text{Al}_{0.5}\text{Ga}_{0.5}\text{Sb}$ to 13,650 for GaAs/ $\text{Al}_{0.5}\text{Ga}_{0.5}\text{Sb}$. The highest overall etch rates were measured for InAs and the lowest etch rates were found for $\text{Al}_{0.5}\text{Ga}_{0.5}\text{Sb}$. The etch rate for the $\text{GaAs}_{1-x}\text{Sb}_x$ materials systematically decreased from the highest etch rate for the smallest Sb mole fraction examined of $\text{GaAs}_{0.85}\text{Sb}_{0.15}$ to the lowest etch rate for GaSb. The dramatic change in etch rate with citric acid/hydrogen peroxide volume ratio previously observed for the GaAs/AlGaAs material system was also observed for $\text{GaAs}_{0.85}\text{Sb}_{0.15}$, but this effect was not seen in higher Sb mole fraction alloys of $\text{GaAs}_{1-x}\text{Sb}_x$ examined. $\text{Al}_{0.5}\text{Ga}_{0.5}\text{Sb}$ and GaSb were found to have very low etch rates with this etchant system at all volume ratios, making both materials suitable as an etch stop layer for simplified processing in device fabrication. Finally, citric acid/hydrogen peroxide can be used to preferentially etch these materials through a photoresist mask, since it does not erode photoresist at any volume ratio.

Many new heterostructure electronic devices require the selective removal of one or more semiconductor material layers, in order to make electrical contact, isolate individual devices on a wafer, or remove excess substrate material. A selective etch which removes one semiconductor material faster than another allows easy and accurate fabrication and helps to prevent damage to devices due to over-etching. Earlier work has shown that citric acid/hydrogen peroxide ($\text{C}_6\text{H}_8\text{O}_7/\text{H}_2\text{O}_2$) provides highly selective etching of the pseudomorphic InGaAs, AlGaAs, and GaAs as well as the lattice matched InAlAs, InGaAs, and InP material systems for device fabrication of high electron mobility transistors (HEMT).¹⁻⁶ $\text{GaAs}_{1-x}\text{Sb}_x$, $\text{Al}_{0.5}\text{Ga}_{0.5}\text{Sb}$, and InAs are another family of semiconductor materials of interest for heterostructure field effect transistors (HFET),⁷⁻¹⁵ heterojunction bipolar transistors (HBT),¹⁶⁻¹⁸ and long wavelength infrared (LWIR) emitters and detectors.¹⁹⁻²² This work presents the results of our investigation to determine if the $\text{C}_6\text{H}_8\text{O}_7/\text{H}_2\text{O}_2$ system provides selective etching of these materials.

Experimental

The semiconductor materials for the etching experiments were grown on semi-insulating (100) oriented GaAs substrates using molecular beam epitaxy (MBE). The layers were unintentionally doped and had thicknesses ranging from 2.0 to 5.0 μm . Although these grown layers have varying degrees of lattice mismatch with GaAs, the layers were grown thick enough to have single-crystal, bulk material properties. Also, the thick layers provide enough material for accurate measurement of the etching step height for these experiments using mechanical profilometers. The group III (Al and Ga) and group V (As and Sb) mole fractions were established during MBE growth by *in situ* measurement of reflection high energy electron diffraction (RHEED) intensity oscillations as well as *in situ* measurement of desorption mass spectroscopy (DMS).²³ The mole fractions were then measured after growth using x-ray diffraction analysis.

All etching experiments were performed at room temperature using a two-part etch mixture. First, anhydrous citric acid ($\text{C}_6\text{H}_8\text{O}_7$) crystals were dissolved in deionized water (DI H_2O) at the ratio of 1 g $\text{C}_6\text{H}_8\text{O}_7$:1 ml DI H_2O . The reaction is endothermic and hinders quick dissolution, so the citric acid is mixed with deionized water at least one day in advance to ensure complete dissolution and room temperature stability. Approximately 15 min before conducting any material etching, the liquid citric acid/water mixture (con-

sidered as 1 part $\text{C}_6\text{H}_8\text{O}_7$ in this paper) was mixed with fresh 30% hydrogen peroxide at a given volume ratio (χ parts $\text{C}_6\text{H}_8\text{O}_7$ to 1 part H_2O_2 by volume). The 15 min delay is used to allow the etchant to return to room temperature, if any temperature change occurs due to mixing.

The use of monohydrate citric acid ($\text{C}_6\text{H}_8\text{O}_7\cdot\text{H}_2\text{O}$) instead of anhydrous citric acid ($\text{C}_6\text{H}_8\text{O}_7$) for the selective etchant has been reported elsewhere.²⁻⁴ This slight discrepancy will cause a change in the volume ratios reported using anhydrous citric acid and shift the etch rates. However, monohydrate citric acid can be substituted for anhydrous citric acid by modifying the ratio of $\text{C}_6\text{H}_8\text{O}_7\cdot\text{H}_2\text{O}$ added to DI H_2O to provide the same citric acid solution using anhydrous $\text{C}_6\text{H}_8\text{O}_7$. That is, to provide the same amount of $\text{C}_6\text{H}_8\text{O}_7$ from $\text{C}_6\text{H}_8\text{O}_7\cdot\text{H}_2\text{O}$ for the aqueous solution requires

$$1.00 \text{ g } \text{C}_6\text{H}_8\text{O}_7 \left(\frac{210.140 \text{ g/mol } \text{C}_6\text{H}_8\text{O}_7\cdot\text{H}_2\text{O}}{192.125 \text{ g/mol } \text{C}_6\text{H}_8\text{O}_7} \right) = 1.094 \text{ g } \text{C}_6\text{H}_8\text{O}_7\cdot\text{H}_2\text{O}$$

This extra 0.094 g is the H_2O present in the monohydrate crystals and needs to be subtracted from the 1 ml H_2O (=1 g H_2O) added to form the citric acid solution. Therefore, the original anhydrous citric acid solution of

$$1.000 \text{ g } \text{C}_6\text{H}_8\text{O}_7:1.000 \text{ ml } \text{H}_2\text{O}$$

can be made equally from monohydrate citric acid using

$$1.094 \text{ g } \text{C}_6\text{H}_8\text{O}_7\cdot\text{H}_2\text{O}:0.906 \text{ ml } \text{H}_2\text{O}$$

$$\text{or } 1.207 \text{ g } \text{C}_6\text{H}_8\text{O}_7\cdot\text{H}_2\text{O}:1.000 \text{ ml } \text{H}_2\text{O}$$

$$\text{or } 1.000 \text{ g } \text{C}_6\text{H}_8\text{O}_7\cdot\text{H}_2\text{O}:0.829 \text{ ml } \text{H}_2\text{O}$$

A comparison between measured etch rates for GaAs using both 1.00 g $\text{C}_6\text{H}_8\text{O}_7$:1.00 ml H_2O and 1.00 g $\text{C}_6\text{H}_8\text{O}_7\cdot\text{H}_2\text{O}$:0.829 ml H_2O solutions at equal citric acid solution/hydrogen peroxide volume ratios have produced the same etch rates to within 10%.

The amount of material removed during etching was determined by masking a portion of the semiconductor surface from the etchant and measuring the resulting step height formed. Previous research has shown that $\text{C}_6\text{H}_8\text{O}_7/\text{H}_2\text{O}_2$ does not erode photoresist patterns for volume ratios between 0.1 and 100,^{1,2,24} thus Shipley 1400-17^a photoresist

^a Certain commercial equipment, instruments, or materials are identified in this paper in order to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by Wright Laboratory or the United States Air Force, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

was used as the mask material. Masking was accomplished by applying photoresist over part of the semiconductor surface, followed by baking at 100°C for 5 min in air on a hot plate. The substrate was then cooled for 5 min to room temperature and etched for a set time without stirring. The etch time varied from 5 min to over 8 h depending on the material etch rate and layer thickness, although the amount of etched material was never allowed to exceed 80% of the total layer thickness. Etching was stopped by rinsing in flowing DI H₂O for at least 1 min. The photoresist mask was then removed in acetone, and the wafer was cleaned using methanol, isopropanol, and then blown dry with N₂ gas. The height of the newly etched step was immediately measured using either of two mechanical profilometers with a minimum resolution of at least 100 Å. Profilometer measurement accuracy was adjusted using several calibrated step height standards of 911, 8200, and 9400 Å, and 1.78 µm traceable to National Institute of Standards and Technology (NIST). The height of each step was measured several times at a minimum of eight different points across the wafer. Any variations in measurement for a single step height was assumed to be due to random measurement errors, allowing for the calculation of the mean etch rates and standard deviation for each concentration ratio using normal probability statistics.

Etching Mechanisms

The chemistry of the etching and the dominant etching mechanism must be established to determine how to calculate the etch rates.²⁵⁻²⁸ Chemical etching of previous GaAs and InP based semiconductor materials using citric acid/hydrogen peroxide has been shown to proceed by an oxidation-reduction reaction at the semiconductor surface by the hydrogen peroxide, with the dissolution of the oxide material by the acid.^{1,25-28} This same process was assumed for the III-V semiconductor materials examined here. This etching chemistry assumption was tested by measuring the etch rates of each semiconductor material using various concentration volume ratios of the two etchant components (C₆H₈O₇ and H₂O₂) as well as with each component alone.²⁶ Although all materials showed some etching at all volume ratios studied, no measurable etch depth was found for any material when soaked for 5 to 8 h in either citric acid or hydrogen peroxide alone. Therefore, the assumption that C₆H₈O₇/H₂O₂ etches these III-V semiconductor materials by oxidation-reduction of the semiconductor surface followed by dissolution of the oxide appears valid.

The chemical etching mechanism is normally limited either by a chemical reaction rate or a diffusion rate.²⁵⁻²⁸ If etching is reaction rate limited, then the material removal rate is a function of the chemical reaction rate between the etchant and the semiconductor (or semiconductor oxide). In diffusion-limited etching, the material removal rate depends on the transport of active etching components by diffusion to the material surface or of the reaction products away from the surface. Some general rules which are characteristic of each etching mechanism are useful in determining the dominant etching mechanism for these III-V semiconductor materials.²⁵⁻²⁹

Reaction-rate-limited etching.—

1. Etch rate (etch depth) is linearly proportional with the etching time.
2. Etch rate is unaffected by stirring or agitation of the liquid etchant.
3. Etch rate changes with temperature (usually etch rate $\propto e^{-1/T}$).
4. Slight changes in relative proportions of etchant components can result in large changes in etch rate.
5. Etchant gives faceted surface structure characteristic of the crystal material properties with flat bottomed openings.

Diffusion-limited etching.—

1. Etch rate (etch depth) is proportional to the square root of the etching time.

Table I

| Material | Slope (Å/min) | Correlation Coefficient | 400 rpm Stirring (Å/min) | Global Avg (Å/min) |
|---|---------------|-------------------------|--------------------------|--------------------|
| GaAs _{0.75} Sb _{0.25} | 38.72 | 0.9967 | 39.80 | 38.78 |
| GaAs _{0.67} Sb _{0.33} | 34.86 | 0.9938 | 37.10 | 36.17 |
| GaAs _{0.5} Sb _{0.5} | 21.30 | 0.9983 | 20.47 | 23.02 |
| GaSb | 9.76 | 0.9873 | 8.63 | 9.27 |
| InAs | 896.98 | 0.9996 | 851.40 | 905.04 |

† Etch times for GaAs_{0.75}Sb_{0.25} materials were 60, 93, 124, and 196 min, with 126 min at 400 rpm.

‡ Etch times for InAs were 5, 10, 15, and 30 min, with 15 min at 400 rpm stirring.

2. Etch rate increases with stirring or agitation of the liquid etchant.

3. Etch rate is relatively insensitive to temperature variations.

4. Etching is more isotropic with respect to crystal orientation.

Previous research using citric acid/hydrogen peroxide to etch GaAs and InP based materials has shown that etching is reaction rate limited.^{1,24} To determine if these new III-V semiconductors are also chemical reaction rate limited, several etching experiments were conducted to compare measured etch depths vs. etch times, effects of etching under agitation, and measurement of etched material profiles along known crystallographic orientations. A series of etches for each material were made at a fixed volume concentration ratio of 2C₆H₈O₇:1H₂O₂ over various periods of time. The etch depth (or the step height) was measured and each set of data (etch depths vs. etch times) was fit to a straight line using linear regression by the least squares criterion.³⁰ Curve fitting the data to the line

$$\text{Etch depth } (\text{\AA}) = A [\text{etch time (min)}] + B$$

yields the effective etch rate (Å/min) which is equal to the slope (A) of the line, and the correlation coefficient was calculated to quantify how well the calculated linear curve fit the experimental data. Also, a global average etch rate for each material was calculated assuming a linear etch rate

$$\text{Global average etch rate } (\text{\AA}/\text{min}) = \left[\sum_{i=1}^N \left(\frac{\text{Etch depth}}{\text{Etch time}} \right)_i \right] / N$$

The results of the curve fit data show a linear response of etch depth with respect to etch time and have correlation values nearly equal to unity.³⁰ A comparison of the global

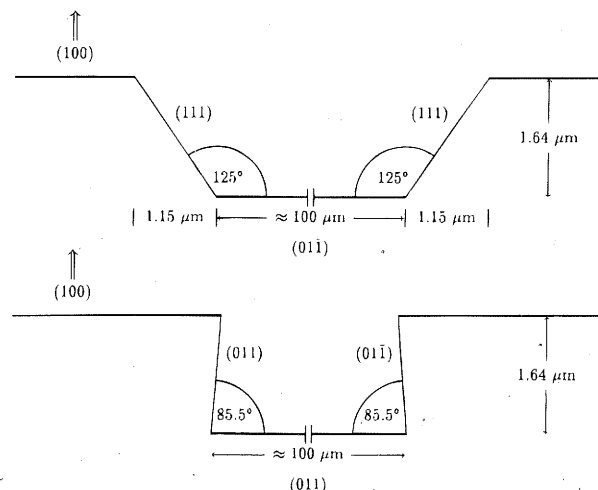


Fig. 1. Etching profiles of InAs cleaved along the $[01\bar{1}]$ and $[011]$ direction after etching with 2C₆H₈O₇:1H₂O₂. Drawings are to scale except for the break in the middle representing the 100 µm wide trench.

Fig. 2. Etching profiles of GaSb cleaved along the [011] and [011] direction after etching with $2C_6H_8O_7:1H_2O_2$. Drawings are to scale except for the break in the middle representing the 100 μm wide trench.

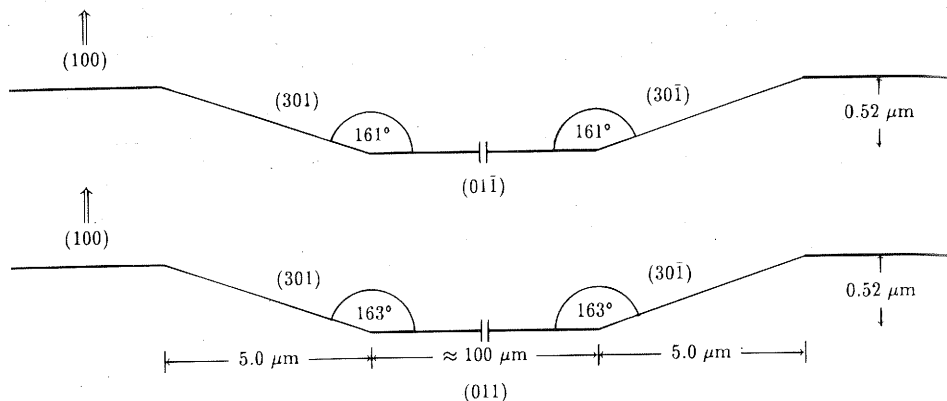
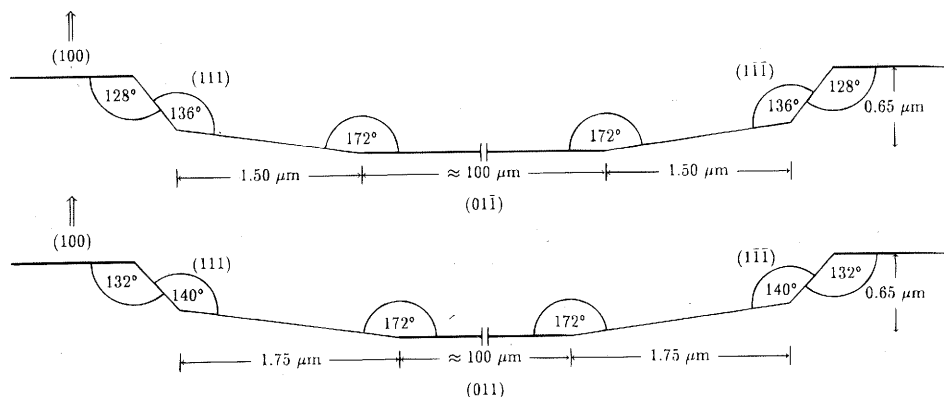


Fig. 3. Etching profiles of $GaAs_{0.54}Sb_{0.46}$ cleaved along the [011] and [011] direction after etching with $2C_6H_8O_7:1H_2O_2$. Drawings are to scale except for the break in the middle representing the 100 μm wide trench.



average etch rates with the slope from the linear curve fit given in Table I also shows very good agreement for each material, reinforcing the conclusion that the etch rate is linearly proportional to the etch time. Other etching experiments included etching these semiconductor materials while agitating the citric acid/hydrogen peroxide solution using a magnetic stirrer at 400 rpm. As shown in Table I, agitating the solution did not increase the measured etch rates of these materials when compared to not stirring for the same $C_6H_8O_7/H_2O_2$ volume ratio. Furthermore, etching InAs, GaSb, and $GaAs_{0.54}Sb_{0.46}$ at different crystal orientations to the (100) substrate reveal faceted (nonisotropic) edges as shown in Fig. 1, 2, and 3. Although the reaction-rate-limited process has not been proven for these semiconductor materials at higher citric acid/hydrogen peroxide volume ratios, earlier research has demonstrated that this etchant system is reaction rate limited for GaAs at volume ratios from 2.0 to 100.0, and for AlGaAs, InGaAs, and InAlAs based materials at volume ratios of 5.0 and 20.0.^{1,24} From these experimental results and drawing from previous research,^{1,24} it is concluded that the etching of these III-V semiconductor materials by citric acid/hydrogen peroxide appears to be reaction rate limited. Therefore, a constant rate of material removal can be assumed during etching, allowing the etch rates to be calculated using

$$\text{Etch rate } (\text{\AA}/\text{min}) = \frac{\text{Thickness of material removed } (\text{\AA})}{\text{Etch time (min)}}$$

Experimental Results and Conclusions

Table II shows the average etch rates of the $GaAs_{1-x}Sb_x$ material system, and Table III gives the average etch rates for InAs and $Al_{0.5}Ga_{0.5}Sb$ for citric acid/hydrogen peroxide volume ratios from 0.2 to 20. Table III also presents known etch rates of GaAs and InP from previous work¹ to facilitate the calculation of etchant selectivities for these materials. Finally, the etchant selectivity between specific semiconductor materials is given in Table IV and Table V. The selectivity is defined as³¹

$$\text{Selectivity} = \frac{\text{Etch rate of material 1 } (\text{\AA}/\text{min})}{\text{Etch rate of material 2 } (\text{\AA}/\text{min})}$$

The selectivities between given semiconductor materials are chosen based on heterostructure devices currently being investigated. The selectivities listed in Table III incorporating $GaAs_{1-x}Sb_x$ materials are used in HBTs,¹⁶⁻¹⁸ light emitting diodes (LED),²⁰ and other photoemitters,¹⁹ as well as selectivities for GaSb which are used in HFETs,⁷⁻¹² tandem solar cells,³² and negative differential resistance (NDR) tunnel diodes.^{33,34} Table IV lists calculated selectivities for $Al_{0.5}Ga_{0.5}Sb$ material used in HFETs,⁷⁻¹² NDR tunnel diodes^{35,36} and quantum well/wire structures,^{21,37,38} and finally $GaAs_{0.54}Sb_{0.46}$ selectivities with InP and other lattice matched semiconductors are given which are used in complementary HFET circuits.¹³

The sharp increase in etch rates using $C_6H_8O_7/H_2O_2$ that was initially observed in earlier work on GaAs and AlGaAs¹⁻³ was also seen in $GaAs_{0.85}Sb_{0.15}$ at volume ratios greater than 7.0 (cf. Table III), which was the lowest Sb mole fraction alloy of $GaAs_{1-x}Sb_x$ examined. $GaAs_{0.85}Sb_{0.15}$ also gives the highest etch rate (1523 $\text{\AA}/\text{min}$) measured in these experiments, which are approximately half of the maximum etch rate calculated earlier for GaAs (3140 $\text{\AA}/\text{min}$). At higher Sb mole fractions in the $GaAs_{1-x}Sb_x$ material system, this sharp change in etch rates is no longer observed for any volume ratios examined. In general, the $GaAs_{1-x}Sb_x$ material system has a progressively slower etch rate at all $C_6H_8O_7/H_2O_2$ volume ratios as the Sb mole fraction approaches unity, with GaSb giving the lowest etch rates for this semiconductor material system. On the other hand, InAs has relatively large etch rates between the volume ratios of 5 to 10, with a maximum etch rate of 900 $\text{\AA}/\text{min}$ between concentration ratios 2 and 5. These results are in good agreement with earlier work involving citric acid etching of $In_xGa_{1-x}As$,^{1,4,5} where the highest etch rates are seen for lower In mole fraction with 3140 $\text{\AA}/\text{min}$ for GaAs, decreasing to 2588 $\text{\AA}/\text{min}$ for $In_{0.2}Ga_{0.8}As$ and 1433 $\text{\AA}/\text{min}$ for $In_{0.5}Ga_{0.5}As$ and finally down to 895 $\text{\AA}/\text{min}$ for InAs at $2C_6H_8O_7:1H_2O_2$ volume ratio. The $Al_{0.5}Ga_{0.5}Sb$

Table II

| Etch Rates of Citric Acid/Hydrogen Peroxide at Room Temperature with No Stirring (Mean Etch Rate \pm Standard Deviation in [Å/min]) | | | | | | | |
|--|---|---|---|---|---|---|---------------|
| Volume Ratio | GaAs Substrate | | | | | | |
| $\frac{[C_6H_8O_7]}{[H_2O_2]}$ | GaAs _{0.85} Sb _{0.15} | GaAs _{0.76} Sb _{0.24} | GaAs _{0.62} Sb _{0.38} | GaAs _{0.54} Sb _{0.46} | GaAs _{0.28} Sb _{0.72} | GaAs _{0.05} Sb _{0.95} | GaSb |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0.2 | 39.3 \pm 0.8 | 45.7 \pm 0.5 | 39.2 \pm 0.8 | 27.6 \pm 0.4 | 22.7 \pm 0.2 | 8.8 \pm 0.5 | 8.1 \pm 0.2 |
| 0.5 | 40.8 \pm 0.5 | 38.8 \pm 0.9 | 37.5 \pm 1.0 | 30.2 \pm 0.2 | 18.0 \pm 0.7 | 8.4 \pm 0.3 | 7.1 \pm 0.3 |
| 1.0 | 47.4 \pm 2.1 | 38.8 \pm 0.7 | 38.2 \pm 1.2 | 26.8 \pm 0.5 | 21.2 \pm 2.6 | 13.0 \pm 0.4 | 6.5 \pm 0.2 |
| 2.0 | 49.6 \pm 1.5 | 38.8 \pm 1.3 | 36.2 \pm 0.8 | 23.4 \pm 0.6 | 23.0 \pm 0.9 | 9.3 \pm 0.3 | 9.3 \pm 0.3 |
| 5.0 | 52.3 \pm 2.0 | 47.3 \pm 3.5 | 40.2 \pm 3.4 | 25.8 \pm 2.2 | 21.6 \pm 0.7 | 9.6 \pm 0.5 | 9.1 \pm 0.3 |
| 10.0 | 1284.4 \pm 32.6 | 42.9 \pm 2.4 | 43.0 \pm 3.4 | 17.2 \pm 0.5 | 16.8 \pm 0.6 | 8.7 \pm 0.4 | 7.2 \pm 0.2 |
| 20.0 | 997.0 \pm 23.1 | 43.9 \pm 0.7 | 33.0 \pm 1.2 | 21.2 \pm 0.6 | 15.1 \pm 0.2 | 6.8 \pm 0.3 | 6.9 \pm 0.3 |
| ∞ | 0 | 0 | 0 | 0 | 0 | 0 | 0 |

Table III

| Etch Rates of Citric Acid/Hydrogen Peroxide at Room Temperature with No Stirring (Mean Etch Rate \pm Standard Deviation in [Å/min]) | | | | | |
|--|------------------|--|---|-------------------|------------------|
| Volume Ratio | GaAs Substrate | | | | InP Substrate |
| $\frac{[C_6H_8O_7]}{[H_2O_2]}$ | InAs | Al _{0.5} Ga _{0.5} Sb | GaAs _{0.85} Sb _{0.15} | GaAs [†] | InP [†] |
| 0 | 0 | 0 | 0 | 0 | 0 |
| 0.2 | 465.4 \pm 17.9 | 0.38 \pm 0.03 | 39.3 \pm 0.8 | 36 \pm 1 | 11 \pm 1 |
| 0.5 | 655.0 \pm 21.7 | 0.29 \pm 0.03 | 40.8 \pm 0.5 | 60 \pm 1 | 12 \pm 1 |
| 1.0 | 825.7 \pm 12.2 | 0.28 \pm 0.05 | 47.4 \pm 2.1 | 69 \pm 1 | 11 \pm 1 |
| 2.0 | 905.0 \pm 16.5 | 0.24 \pm 0.04 | 49.6 \pm 1.5 | 85 \pm 2 | 9 \pm 1 |
| 3.0 | — | — | — | 2169 \pm 84 | — |
| 4.0 | — | — | — | 2235 \pm 204 | — |
| 5.0 | 895.2 \pm 13.6 | 0.23 \pm 0.04 | 52.3 \pm 2.0 | 3140 \pm 295 | 5 \pm 1 |
| 6.0 | — | — | 78.6 \pm 6.9 | — | — |
| 7.0 | — | — | 1523.5 \pm 102.3 | 2882 \pm 67 | 3 \pm 0 |
| 8.0 | — | — | 1485.2 \pm 30.5 | — | — |
| 9.0 | — | — | 1391.0 \pm 10.1 | — | — |
| 10.0 | 726.6 \pm 7.3 | 0.34 \pm 0.05 | 1284.4 \pm 32.6 | 2513 \pm 151 | 4 \pm 1 |
| 20.0 | 472.8 \pm 4.6 | 0.32 \pm 0.02 | 997.0 \pm 23.1 | 762 \pm 31 | 2 \pm 0 |
| ∞ | 0 | 0 | 0 | 0 | 0 |

[†] GaAs and InP etch rate data from reference 1.

material gave the lowest etch rates ever measured using $C_6H_8O_7/H_2O_2$ etchant (0.23 to 0.38 Å/min), being more than one order of magnitude lower than InP (2 to 12 Å/min), both of which are basically impervious to citric acid/hydrogen peroxide. Since the etch rate decreases with increasing Sb mole fraction for $GaAs_{1-x}Sb_x$ and for increasing Al mole fraction in $Al_xGa_{1-x}As$, it seems reasonable to assume that $Al_{0.5}Ga_{0.5}Sb$ should provide a very low etch rate using $C_6H_8O_7/H_2O$. Following this reasoning, AlSb has the potential to provide even lower etch rates, but confirmation of the AlSb etch rate is very difficult because this material oxidizes readily when exposed to air as does AlAs. However, AlAs has also been shown by others to be an effective etch stop layer,³ which has been confirmed by GaAs/AlAs and InAs/AlAs etch stop experiments here at Wright Laboratory.

The selectivities of the various heterostructure III-V semiconductors given by Table IV and Table V show both selective and nonselective (uniform) etching useful in device fabrication for selective removal of one material over another, or to remove all the semiconductor layers (uniform etching) for device isolation. Regions of high selectivity over 50 are found for most of the material combinations selected, with large selectivities of over 100 found for GaSb and $Al_{0.5}Ga_{0.5}Sb$ semiconductor combinations. Finally, calculated selectivities of over 1000 are obtained using InAs/ $Al_{0.5}Ga_{0.5}Sb$ and GaAs/ $Al_{0.5}Ga_{0.5}Sb$, with the highest selectivity of 13,650 found for GaAs/ $Al_{0.5}Ga_{0.5}Sb$ at a $5C_6H_8O_7:1H_2O_2$ volume ratio. Figure 4 graphically compares calculated selectivities for several $GaAs_{1-x}Sb_x$ and $Al_{0.5}Ga_{0.5}Sb$ combinations with GaAs, and shows a trend where the etchant selectivity significantly increases for citric acid/hydrogen peroxide volume ratios above 2. This

Table IV

| Selectivity of Citric Acid/Hydrogen Peroxide Etchant | | | | | | |
|--|---|-------------------------------------|---|-------------------------------------|---------------------|---------------------|
| Volume Ratio | GaAs ₂ Sb _{1-x} and InAs Selectivity Ratios | | | | | |
| | $\frac{[C_6H_8O_7]}{[H_2O_2]}$ | $\frac{GaAs}{GaAs_{0.85}Sb_{0.15}}$ | $\frac{GaAs_{0.85}Sb_{0.15}}{Al_{0.3}Ga_{0.7}As^\dagger}$ | $\frac{GaAs}{GaAs_{0.75}Sb_{0.25}}$ | $\frac{GaAs}{GaSb}$ | $\frac{InAs}{GaAs}$ |
| 0.2 | | 0.9 | 1.5 | 0.8 | 4.4 | 12.9 |
| 0.5 | | 1.5 | 1.5 | 1.6 | 12.9 | 10.9 |
| 1.0 | | 1.5 | 1.8 | 1.8 | 10.6 | 12.0 |
| 2.0 | | 1.7 | 2.1 | 2.2 | 9.2 | 10.7 |
| 5.0 | | 60.0 | 1.9 | 66.4 | 345.8 | 0.3 |
| 10.0 | | 2.0 | 0.7 | 58.6 | 349.1 | 0.3 |
| 20.0 | | 0.8 | 1.1 | 17.4 | 111.1 | 0.6 |

† Al_{0.3}Ga_{0.7}As etch rate data from reference 1.

Table V

| Selectivity of Citric Acid/Hydrogen Peroxide Etchant | | | | | | |
|--|---|-----------------------------------|-----------------------------------|--|------------------------------------|---|
| Volume Ratio | Al _{0.5} Ga _{0.5} Sb Ratios | | | GaAs _{0.54} Sb _{0.46} Ratios | | |
| | $\frac{[C_6H_8O_7]}{[H_2O_2]}$ | $\frac{InAs}{Al_{0.5}Ga_{0.5}Sb}$ | $\frac{GaSb}{Al_{0.5}Ga_{0.5}Sb}$ | $\frac{GaAs}{Al_{0.5}Ga_{0.5}Sb}$ | $\frac{GaAs_{0.54}Sb_{0.46}}{InP}$ | $\frac{In_{0.52}Al_{0.48}As}{GaAs_{0.54}Sb_{0.46}}$ |
| 0.2 | | 1224.7 | 21.4 | 94.7 | 2.5 | 0.8 |
| 0.5 | | 2258.5 | 24.4 | 206.9 | 2.5 | 0.7 |
| 1.0 | | 2949.0 | 23.3 | 246.4 | 2.4 | 0.8 |
| 2.0 | | 3771.0 | 38.6 | 354.2 | 2.6 | 1.1 |
| 5.0 | | 3892.0 | 39.5 | 13652.2 | 5.2 | 1.7 |
| 10.0 | | 2137.1 | 21.2 | 7391.2 | 4.3 | 9.0 |
| 20.0 | | 1477.5 | 21.4 | 2381.3 | 10.6 | 9.6 |

is due to the dramatic change in GaAs etch rates observed at C₆H₈O₇:H₂O₂ concentration ratios greater than 2. The only exception to this occurs for the GaAs/GaAs_{0.85}Sb_{0.15} material combination, where the GaAs_{0.85}Sb_{0.15} etch rate itself significantly increases beyond 7C₆H₈O₇:1H₂O₂ (cf.

Table III), such that a window of high selectivity for this system only occurs between the volume ratios of 3 and 7. Finally, Fig. 5 compares the selectivities of several InAs, GaSb, and Al_{0.5}Ga_{0.5}Sb material combinations. Since these semiconductors did not exhibit large changes in etch rates over the citric acid/hydrogen peroxide volume ratios stud-

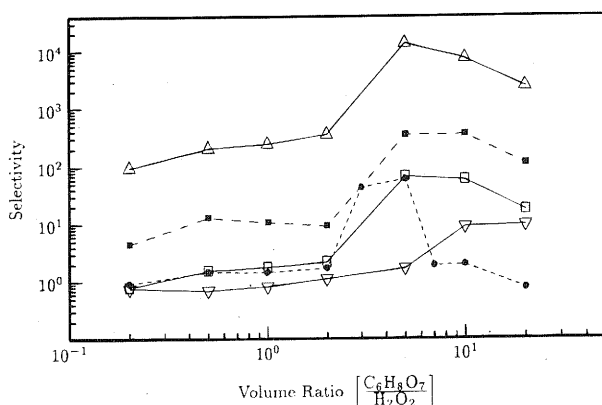


Fig. 4. Selectivity of citric acid/hydrogen peroxide on the material system combinations (Δ) GaAs/Al_{0.5}Ga_{0.5}Sb, (\blacksquare) GaAs/GaSb, (\square) GaAs/GaAs_{0.75}Sb_{0.25}, (\bullet) GaAs/GaAs_{0.85}Sb_{0.15}, and (∇) In_{0.52}Al_{0.48}As/GaAs_{0.54}Sb_{0.46} at room temperature.

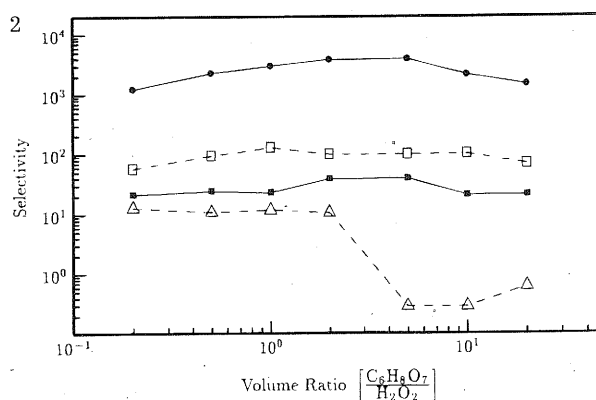


Fig. 5. Selectivity of citric acid/hydrogen peroxide on the material system combinations (\bullet) InAs/Al_{0.5}Ga_{0.5}Sb, (\square) InAs/GaSb, (\blacksquare) GaSb/Al_{0.5}Ga_{0.5}Sb, and (Δ) InAs/GaAs at room temperature.

ied, the calculated selectivities remain fairly constant at all concentration ratios.

In general, GaSb, InP, and especially $\text{Al}_{0.5}\text{Ga}_{0.5}\text{Sb}$ are virtually unetched by $\text{C}_6\text{H}_8\text{O}_7/\text{H}_2\text{O}_2$ at any volume ratio, making these semiconductors ideal etch stop layers for selective removal of heterostructure semiconductor materials for device fabrication. Since other work has shown that GaSb and $\text{Al}_{0.5}\text{Ga}_{0.5}\text{Sb}$ can be selectively etched over InAs using weak bases such as diluted NH_4OH ,³⁸ the appropriate use of NH_4OH and citric acid can provide complete selectivity in preferentially etching one of these three semiconductor materials over the other for controlled heterostructure device fabrication. Also, since citric acid/hydrogen peroxide does not attack photoresist, this etchant is useful in preferentially etching these semiconductor materials through a photoresist mask.

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