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Novel, Organic Acid-Based Etchants for InGaAlAs/InP Heterostructure Devices with AlAs Etch-Stop Layers

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ABSTRACT

Several organic acids have been identified that enable the etching of indium compounds, while maintaining selectivity with respect to AlAs, and these acids have been used to develop InGaAlAs etching solutions that allow the selective etching of InP lattice-matched InGaAlAs heterostructures using thin pseudomorphic AlAs layers as etch stops. Of the organic acids tested, the nonaromatic, polycarboxylic acids have been found to be most effective, and some of the best results have been obtained for etchants consisting of succinic acid, ammonia, and hydrogen peroxide. It is found that the etch rate of $In_{0.53}Ga_{0.47}As$ with this solution can be as much as 1000 times the etch rate of AlAs, while the etch rate of $In_{0.52}Al_{0.48}As$ can be as much as 500 times that of the AlAs.

Selective wet etchants for various III-V compounds have been known for quite some time and have found applications in the fabrication of numerous heterostructure devices[1-3]. More specifically, the (hydrogen) peroxide-ammonia system for etching GaAs preferentially over AlGaAs is well known[1,2]. A similar etchant that etches the InP-substrate-based quaternary InGaAlAs preferentially over a thin strained AlAs etch stop layer could prove equally useful, but has heretofore not been available. It is well known, for example, that the peroxide-ammonia system does not form any soluble complexes with indium, and thus cannot be used for etching InGaAlAs compounds[4]. We have shown[5,6] that this limitation can be alleviated by the addition of organic acids, some of which readily form soluble complexes with indium[7]. In addition, it is found that the etching solutions thus obtained can be made selective, by regulating their pH, to etch $In_{0.53}Ga_{0.47}As$ and $In_{0.52}Al_{0.48}As$ at much higher rates than those at which they etch AlAs.

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Table I. Concentration and pH of the acid ammonia solutions used. Acids marked with an asterisk must have ammonia added to dissolve all the acid, upon which the given pH is reached. The acids which are not marked with an asterisk are very soluble in water and can therefore also be tested at lower pH. pK_a values of the acids used are also indicated (Ref. 12).

Label	Acid added per 1 H_2O	pH, by adding ammonia	pK_1	pK_2
OA	15 g oxalic · 2 H_2O	6.3	1.27	4.27
OCA	25 g oxalic · 2H_2O, 100 g citric	6.3		
MA	75 g malonic	6.1	2.83	5.70
SA	200 g succinic*	4.2	4.21	5.64
GA	200 g adipic*	4.3	4.31	5.41
AA	200 g methylsuccinic*	5.2	4.42	5.41
MSA	250 g methylsuccinic*	3.8	4.13	5.64
DSA	100 g 2,2 dimethyl-succinic* (*rac*)	4.0	3.93	6.20
FA	50 g fumaric*	4.2	3.10	4.60
MEA	200 g maleic	4.0	1.83	6.07
CA	200 g citric (pK_4 = 6.40)	4.0	3.13	4.76
PTA	200 g 1, 2 3 propane tricarboxylic (pK_4 = 6.38)	1.75	3.67	4.87
BTA	200 g 1,2,3,4 butane tetracarboxylic (pK_3 = 6.38, pK_4 = 7.16)	1.85	3.43	4.58
AcA	130 ml acetic	4.75	4.76	

The results presented here extend this concept to a much wider range of organic acids than has previously been reported[6].

The following acids were found useful for the etching of indium containing compounds: oxalic (ethanedioic)[5], malonic (propanedioic)[6], succinic (butanedioic)[6], glutaric (pentanedioic), adipic (hexanedioic), methylsuccinic, 2,2-dimethylsuccinic, fumaric (*trans*-butenedioic), maleic (*cis*-butenedioic), citric (2-hydroxy-1,2,3-propane tricarboxylic), tricarballylic (1,2,3-propane tricarboxylic), 1,2,3,4-butane tetracarboxylic, acetic, L-malic (L-2-hydroxy butanedioic), tartaric (2,3-dihydroxy butanedioic). Acids that were also tested but that did not result in etching or had impractically low etch rates are: pimelic (heptanedioic), terephthalic (1,3-benzene dicarboxylic), isophthalic (1,4-benzene dicarboxylic), and L-glutamic (2-aminopentanedioic).

These etchants have already found applications in the elimination of mesa-sidewall gate leakage current in HFETs[8] and for uniform and reliable control of etch depth in ridge laser structures[9]. Other devices that could be improved by use of these etchants to facilitate their fabrication are devices, like the resonant tunneling hot electron transistor[10], where electrical contact to a layer, typically $In_{0.53}Ga_{0.47}As$, adjacent to an AlAs layer is needed (see Ref. 11 and references therein for a collection of devices of this type that could benefit from the selective etch discussed here).

Procedures and Results

Test samples for the etchants were grown by molecular beam epitaxy (MBE) and typically consisted of a buffer layer of 400 nm of $In_{0.53}Ga_{0.47}As$ or $In_{0.52}Al_{0.48}As$ followed by a strained 10 monolayer (m.l.) thick AlAs layer, and a top 100 nm layer of $In_{0.53}Ga_{0.47}As$ or $In_{0.52}Al_{0.48}As$. Several test samples were also grown in which the thicknesses of the strained AlAs layer was varied down to 3 m.l. Prior to testing the etch rate of the etchant solutions, the samples were degreased and briefly etched in 10:1:1 H_2O:H_3PO_4:H_2O_2 to obtain reproducible surface conditions. The samples were then partially covered with black wax to enable the measurement of step profiles. The etch rate was determined by measuring the etch depth as a function of immersion time into the etchant solution. The selectivity of the etchant was determined by measuring the time required for the etchant solution to break through the AlAs stop layer. The breakthrough of the AlAs stop layer was observed by inspection of the surface by optical microscopy, and resulted in a discolored surface for the low selectivity (less than 100:1) etchants, due to surface roughening as a consequence of local masking; and resulted in local etch pits for the highly selective (greater than 400:1) etchants.

Table I describes the etchant solutions that have been studied. They typically consist of an aqueous solution of an organic acid to which ammonia is added to regulate the pH. Not listed in Table I are etchants with L-malic and tartaric acid which were also tested but were not selective with respect to AlAs. Table II gives a summary of the etch rates and selectivity obtained with these solutions when peroxide is added as the oxidizing agent. The etch rate of the AlAs, required to calculate the etch rate selectivity, is obtained from the same required to break through the AlAs stop layer, and the thickness of the AlAs stop layer, which is taken to be 0.273 nm per monolayer.

It should be noted that the selectivities listed in Table II are based on the time required to break through a 10 m.l. AlAs stop layer. However, this break through time was only monitored for a maximum of 25 min. Consequently the selectivities listed for the etchants with low etch rates may only be lower bounds; the actual selectivity may be somewhat higher. For such high selectivity etchants, the time required to break through a 5 m.l. AlAs stop layer would be a better measure of selectivity relative to the other etchants.

The etch rate dependence of $In_{0.53}Ga_{0.47}As$ and $In_{0.52}Al_{0.48}As$ on pH and peroxide concentration for the succinic acid based etchant has been studied in more detail. The results are shown in Fig. 1a and b, respectively[6]. After 25 min of exposure to the etchant, the AlAs stop layer was still mostly intact, with the exception of a few square-shaped etch pits, mostly occurring at the edges of the sample[6]. The square shape of the etch pits is most likely due to stress relief cracking of the strained AlAs layer along the

Table II. $In_{0.53}Ga_{0.47}As$ and $In_{0.52}Al_{0.48}As$ etch rates and selectivity of the acid solutions studied.

Acid:H_2O_2 ratio (pH)	InGaAs etch rate (nm/min)	InAlAs etch rate (nm/min)	10 m.l. AlAs break time (min)	5 m.l. AlAs break time (min)	InGaAs to AlAs selectivity	InAlAs to AlAs selectivity	InGaAs to InAlAs selectivity
OA 20:1	40	20	5	2	70	35	2
OCA 25:1	75	5	15	—	410	25	15
MA 25:1	100	6	6	—	220	13	17
SA 25:1	76	40	>25	—	>700	>365	2
GA 25:1	56	11	>25	3	>500	>100	5
AA 25:1	30	0.4	>25	1.5	>640	>8	75
MSA 25:1	40	0.5	>25	3	>360	>4	80
DSA 25:1	25	<0.2	>25	15	>270	>4	>125
FA 25:1	50	6.5	20	2	370	45	8
MEA 25:1	65	13	10	0	240	45	5
CA(2) 25:1	55	30	5	0	100	55	2
CA(4) 25:1	70	5	>25	2	>640	>45	14
PTA(1.75) 25:1	50	20	12	2	220	85	2.5
PTA(4) 25:1	50	1	>25	3	>150	>9	50
BTA(1.85) 25:1	50	3.6	17	3	310	22	14
BTA(4) 25:1	50	<0.5	>25	10	>450	>4	>100
AcA 25:1	150	60	2	0	110	44	2.5
SA 15:1	120	60	>25	0.25	>1100	>550	2

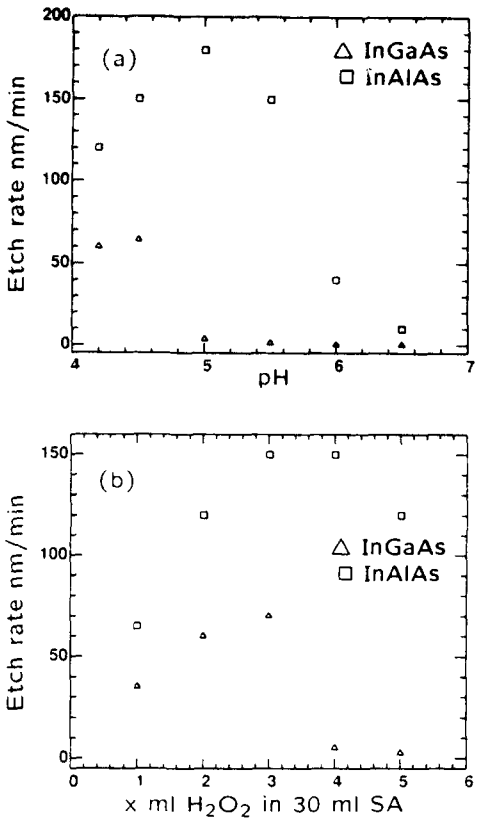

Fig. 1. $In_{0.53}Ga_{0.47}As$ (□) and $In_{0.52}Al_{0.48}As$ (△) etch rate as a function of (a) pH and (b) added m.l. peroxide in 30 ml SA.

<110> and <1$\bar{1}$0> directions as a result of undercutting of the AlAs layer at an initial breakthrough point.

All the etchants described thus far have also been used in device processing[5,8,9]. It is found that they do not noticeably affect standard positive photoresists, nor do they attack Cr/Au contact metallization patterns and can thus be used in self-aligned structures.

Discussion

A clear improvement in $In_{0.53}Ga_{0.47}As$ to AlAs selectivity can be seen in going from oxalic to malonic to succinic acid. The mechanism for this improvement is not well understood. However, it should be noted that for the oxalic acid-based etchant, the $In_{0.53}Ga_{0.47}As$ to AlAs selectivity improved dramatically, and the $In_{0.52}Al_{0.48}As$ etch rate dropped, by buffering through the addition of citric acid. Since these etchants are typically used in the pH 4 to pH 7 range in order to obtain selective behavior, the improvement in selectivity with the use of malonic and succinic acid seems due in part to the fact that they are better buffered as such, as their pK_1 values are closer to the pH values used in the selective etchants. Table I also gives the pK values of the acids used[12].

The succinic acid-based etch, having the highest selectivity, is most useful for device fabrication, and is relatively insensitive to pH and peroxide concentration for etching $In_{0.53}Ga_{0.47}As$. However, for $In_{0.52}Al_{0.48}As$ the etch rate drops dramatically at a pH of 5 and higher, and a peroxide concentration of 30:3 SA:H_2O_2 and larger. Therefore, if $In_{0.52}Al_{0.48}As$ is to be etched, the pH and peroxide concentration must be kept low. On the other hand, by using an SA:H_2O_2 solution at high peroxide concentration and at a pH of about 5.5, $In_{0.53}Ga_{0.47}As$ can be etched selectively over $In_{0.52}Al_{0.48}As$, with a selectivity better than 50:1. The best selectivity of $In_{0.53}Ga_{0.47}As$ to $In_{0.52}Al_{0.48}As$ etching rates has been obtained with dimethylsuccinic acid, *i.e.*, better than 125:1 as shown in Table I.

In an effort to understand some of the reaction mechanisms, a calculation was performed of the concentrations

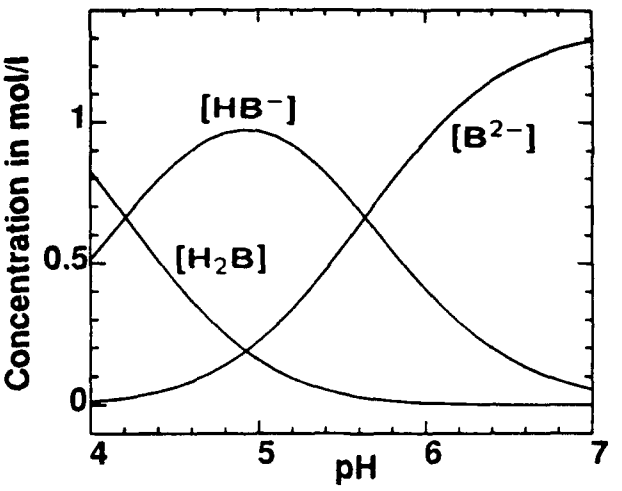

Fig. 2. Calculated concentration profiles as a function of pH for the succinic acid based etchant. H_2B represents succinic acid.

[H_2B], [HB^-], [B^{2-}] as a function of pH, where H_2B represents succinic acid. The result is shown in Fig. 2, which can be compared with Fig. 1 which showed the $In_{0.53}Ga_{0.47}As$ and $In_{0.52}Al_{0.48}As$ etch rates as a function of pH. The similarity between the $In_{0.53}Ga_{0.47}As$ etch rate and the [HB^-] profile implies that the etch-rate limiting reaction step is likely to be a reaction with the HB^- ion. Note that this means that the maximum etch rate is obtained at pH = (pK_1 + pK_2)/2 for which the HB^- ion concentration reaches a maximum. For the $In_{0.52}Al_{0.48}As$ etch rate, however, no such similarity occurs. The sudden drop in the etch rate of the $In_{0.52}Al_{0.48}As$ for higher peroxide concentrations, suggests that the etching of the Al compound material becomes inhibited due to passivation by Al oxidation products as a result of the higher Al oxidation rates. The sudden drop in $In_{0.52}Al_{0.48}As$ etch rate with increasing pH can then be explained to be due to the lower solubility of Al oxidation products with increasing pH. (The solubility of aluminum oxidation products decreases up to a pH of ≈5, after which the solubility rises again[12].)

It should be stressed that the other acids tested do not necessarily follow exactly the same pattern in etch rate as a function of pH. For example, the $In_{0.53}Ga_{0.47}As$ and $In_{0.52}Al_{0.48}As$ etch rate in maleic acid ((pK_1 + pK_2)/2 ≈ 4) peak at a pH of 3 and 2, respectively, indicating that a reaction with HB^- is not the rate limiting step in this etch. Other observations that can be made follow.

1. Succinic acid is the only acid of those tested that can be made to etch $In_{0.52}Al_{0.48}As$ and maintain high selectivity to AlAs. The pH must be less than 4.5 to achieve this, and the etchant cannot stop on very thin (5 m.l.) AlAs stop layers under these conditions.

2. Variations to succinic acid, like the addition of a methyl group or the introduction of a double bond, result in a significantly lower $In_{0.52}Al_{0.48}As$ etch rate.

3. Acids with a small pK_1 (oxalic, malonic, maleic) have lower selectivity.

4. The tri- and tetracarboxylic acids tested have good selectivity, even at very low pH. The monocarboxylic acid tested (acetic) has low selectivity.

5. Addition of an hydroxyl group results in lower, or loss of, selectivity (citric, L-malic, tartaric).

Conclusion

A technique for the selective etching of InGaAlAs compounds with the use of a strained AlAs layer as an etch stop has been described. Applications for these etchants can be found in the fabrication of a variety of novel, high-performance heterostructure devices, in particular, applications toward devices that include resonant tunneling diodes that have strained AlAs tunnel barriers seem promising. For purposes of a better understanding of the reaction mechan-

isms, a systematic study of the etch rate dependence on pH, and acid and peroxide concentration is needed. It was shown that for the succinic acid the likely $In_{0.53}Ga_{0.47}As$ etch-rate limiting step is a reaction with the once dissociated succinic acid molecule, whereas for $In_{0.52}Al_{0.48}As$, Al oxidation products can limit or prevent the etching. However, a more general picture of why certain acids are capable of etching, *e.g.*, $In_{0.53}Ga_{0.47}As$ and not $In_{0.52}Al_{0.48}As$ is lacking.

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