

AlAs Etch-Stop Layers for InGaAlAs/InP Heterostructure Devices and Circuits

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Abstract—Wet chemical etching solutions have been developed that allow the selective etching of InP lattice-matched InGaAs and InAlAs compounds using thin pseudomorphic AlAs layers as etch stops. Several dicarboxylic acids were found that enable the etching of indium compounds. The best results have been obtained for etchants consisting of succinic acid, ammonia, and hydrogen peroxide. The etch rate of $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ is found to be over 1000 times the etch rate of AlAs, while the etch rate of $\text{In}_{0.52}\text{Al}_{0.48}\text{As}$ is over 500 times that of the AlAs. The dependences of the succinic acid based etch on pH and hydrogen peroxide concentration were also studied. Buffered HF can be used to remove the AlAs stop layer, while it does not etch InGaAlAs to any significant degree.

I. INTRODUCTION

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 show here that this limitation can be alleviated by the addition of either oxalic acid (ethanedioic acid) [5], malonic acid (propanedioic acid), or succinic acid (butanedioic acid), which readily form soluble complexes with indium [6]. In addition, it is found that the etching solutions thus obtained can be made selective, by regulating the pH, to etch $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ and $\text{In}_{0.53}\text{Al}_{0.48}\text{As}$ at much higher rates than those at which it etches AlAs. The selectivity is highest for the succinic acid solutions, and lowest for the oxalic acid solutions. The selectivity of the oxalic acid solutions can be improved through buffering with citric acid.

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These etchants have already found applications in the elimination of mesa-sidewall gate leakage current in HFET's [7] and for uniform and reliable control of etch depth in ridge laser structures [8]. Other devices that could be improved by use of these etchants to facilitate their fabrication are devices, like the resonant tunneling hot-electron transistor [9], where electrical contact to a layer, typically $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$, adjacent to an AlAs layer is needed (see [10] and references therein for a collection of devices that could benefit from the selective etch discussed here). These etches should also facilitate the fabrication of other novel devices, among them devices that need an electrical contact to the quantum well of a resonant tunneling diode, as in a resonant tunneling transistor [11], and several optical devices that make use of the intersubband transitions in a quantum well [12].

II. 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 $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ or $\text{In}_{0.52}\text{Al}_{0.48}\text{As}$ followed by a strained AlAs layer, and a top 100-nm layer of $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ or $\text{In}_{0.52}\text{Al}_{0.48}\text{As}$. Several test samples were grown, with the thicknesses of the strained AlAs layer ranging from 3 to 10 monolayers (m.l.). Prior to testing the etch rate in the etchant solutions, the samples were degreased and briefly etched in 10:1:1 $\text{H}_2\text{O}:\text{H}_3\text{PO}_4:\text{H}_2\text{O}_2$ 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. The breakthrough of the AlAs stop layer 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 four etchant solutions that have been studied: oxalic acid and ammonia (from here on abbreviated as OA), oxalic and citric acid and ammonia (OCA), malonic acid and ammonia (MA), and succinic acid and ammonia (SA). Table II gives a summary of the

TABLE I
CONCENTRATION AND pH OF THE ACID AMMONIA SOLUTIONS USED

Label	Acid Added per l H ₂ O	pH, by Adding Ammonia
OA	15 g oxalic · 2H ₂ O	6.3
OCA	25 g oxalic · 2H ₂ O, 100 g citric	6.3
MA	75 g malonic	6.1
SA	200 g succinic	4.2

TABLE II
In_{0.53}Ga_{0.47}As AND In_{0.52}Al_{0.48}As ETCH RATES AND SELECTIVITY OF THE FOUR ACID SOLUTIONS STUDIED

Acid:H ₂ O ₂ Ratio	In _{0.53} Ga _{0.47} As Etch Rate (nm/min)	In _{0.52} Al _{0.48} As Etch Rate (nm/min)	10-m.l. AlAs Break Time (min)	In _{0.53} Ga _{0.47} As to AlAs Selectivity	In _{0.52} Al _{0.48} As to AlAs Selectivity
OA 20:1	40	20	5	70	35
OCA 25:1	75	5	15	410	25
MA 25:1	100	6	6	220	13
SA 15:1	120	60	>25	>1000	>500

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 time required to break through the AlAs stop layer, and the thickness of the AlAs stop layer, which is taken to be 0.273 nm/m.l.

As an example, Fig. 1 shows the etch depth as a function of etch time for an In_{0.53}Ga_{0.47}As and an In_{0.52}Al_{0.48}As sample, both with a 10-m.l. AlAs stop layer, for an etching solution consisting of a mixture of 20 parts OA and 1 part peroxide (H₂O₂ 30%) regulated to a pH of 6.3 by adding ammonium hydroxide (NH₄OH). The pH of 6.3 was chosen as a compromise between lower InGaAs etch rates at higher pH, and lower selectivity at lower pH.

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. 2(a) and (b), respectively.

In another experiment, to demonstrate the high selectivity, different regions of the test sample containing an AlAs stop layer were exposed to the etching solution in such a fashion that different regions of the sample were exposed to the etchant for different lengths of time. This was achieved by successively covering part of the sample with black wax followed by exposure to the etchant and subsequent removal of the black wax. A series of photomicrographs, shown in Fig. 3, clearly shows the progression of the etch, and the resulting planarization of the surface when the AlAs stop layer is reached. The etchant used was a 15:1 SA:H₂O₂ mixture. Fig. 4 shows the etch pits that developed after 25-min overexposure to the etchant. The bottom of the etch pits are flat, indicating that the etchant does not etch the InP substrate.

Stop layers as thin as 5 and 3 m.l. were also tried with the 15:1 SA:H₂O₂ etchant. The etchant was found not to be selective for these thinner stop layers at a pH of 4.2.

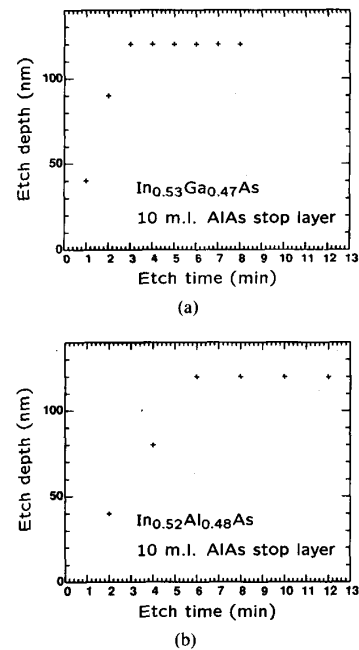


Fig. 1. Etch depth as a function of time for (a) an In_{0.53}Ga_{0.47}As sample and (b) an In_{0.52}Al_{0.48}As sample, both containing a 10-m.l. AlAs stop layer 120 nm below the top surface. The etchant used is oxalic acid and ammonia (OA) at a pH of 6.3 with peroxide as the oxidizing agent.

However, by increasing the pH the selectivity can be regained. A 5-m.l. AlAs stop layer is broken after 15 min at a pH of 6.0, and a 3-m.l. AlAs stop layer is broken after 2 min at a pH of 6.2.

For completeness, the 15:1 SA:H₂O₂ etchant (pH 4.2) was also tested on GaAs epilayers on GaAs substrates with AlAs stop layers. The GaAs etch rate is 180 nm/min, and the time to break through a 10-m.l. AlAs stop layer is more than 20 min. The GaAs to AlAs selectivity is therefore greater than 1000:1.

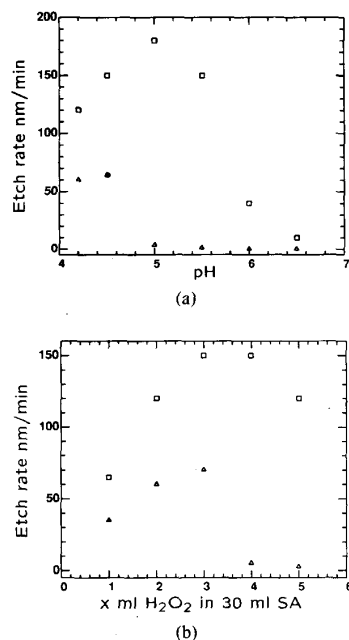


Fig. 2. $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ (\square) and $\text{In}_{0.52}\text{Al}_{0.48}\text{As}$ (\triangle) etch rate as a function of (a) pH and (b) added m.l. peroxide in 30-ml SA.

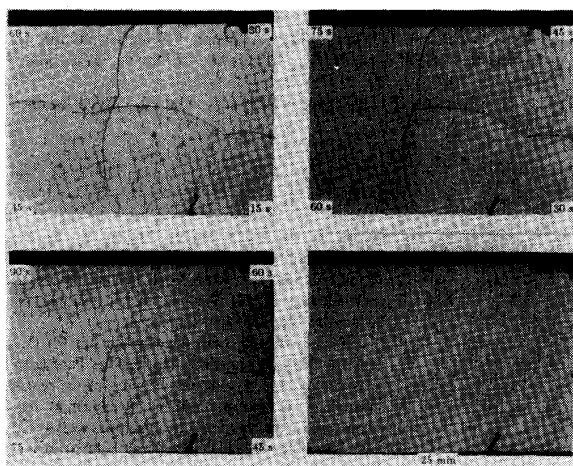


Fig. 3. Photomicrographs showing the evolution of etching with time on an $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ sample with a 10-m.l. AlAs stop layer. The sample was treated so as to obtain regions with different total etch time (see text). These regions can be seen planarizing as a result of the etchant selectivity. The inset numbers indicate the total etch time for each region. The selective etchant used is 15:1 SA: H_2O_2 .

All the etchants described thus far have also been used in device processing [5], [7], [8] and it was found that they do not noticeably affect standard positive photoresists and Cr/Au contacts.

Pseudomorphic AlAs layers can be selectively removed in buffered HF, i.e., 1:7 HF (49%): NH_4F (40%). HF alone can also be used for selective removal of AlAs [13], but it was found that this results in considerable lateral etching of the AlAs layer, and in the case of a resonant

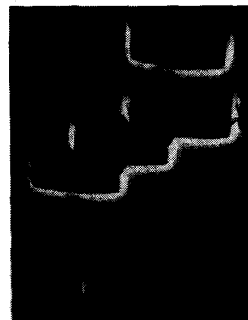


Fig. 4. SEM picture showing etch pits in an $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ sample with a 10-m.l. AlAs stop layer after 25-min overexposure to the etchant (15:1 SA: H_2O_2). The top surface seen is the AlAs stop layer, while the bottom of the etch pits is the InP substrate.

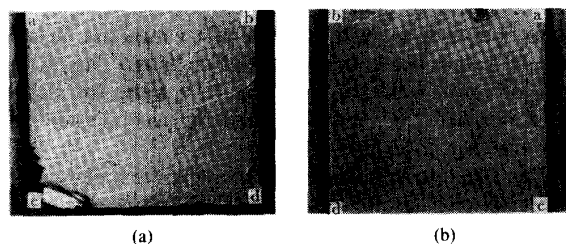


Fig. 5. Photomicrograph and SEM picture showing the successive removal of the AlAs barriers of a resonant tunneling diode. (a) The etch sequence is as follows: 1. The entire surface is selectively etched (SE) to the first barrier. 2. Regions "b" and "d" are exposed to 5 s HF followed by 15 s SE. 3. Regions "c" and "d" are exposed to 5 s HF followed by 15 s SE. 4. All regions are exposed to 2 min SE. The selective etch used in 15:1 SA: H_2O_2 . (b) Same as in (a) except for the HF which is replaced by buffered HF. At the end of this sequence region "a" still has the first AlAs barrier on top, regions "b" and "c" are etched down to the second AlAs barrier, and region "d" has etched beyond the second barrier into the $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ buffer layer. The HF (a) can be seen to have caused etch pits in regions "b", "c," and "d" due to local lift-off of both AlAs barriers upon first exposure to the HF. The buffered HF (b) removes only a single AlAs barrier as is desired.

tunneling structure resulted in the removal of both AlAs barriers, together with the quantum well. The buffered HF is a much more controllable etch and it has no measurable effect on adjacent InGaAlAs epilayers. These results are shown in Fig. 5, showing the successful removal of the first, and then the second barrier of a resonant tunneling-diode structure when buffered HF is used. When the same experiment is tried with HF alone, etch pits result in the

regions where only the first barrier is expected to be removed, indicating that the HF has lifted off the complete resonant tunneling structure upon exposure to the first barrier.

III. DISCUSSION

A clear improvement in $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ 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 $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ to AlAs selectivity improved dramatically, and the $\text{In}_{0.52}\text{Al}_{0.48}\text{As}$ 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. The pK_1 and pK_2 of oxalic acid are 1.23 and 4.19 while for malonic acid they are 2.83 and 5.69, and for succinic acid they are 4.16 and 5.61 [14].

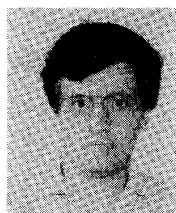
The succinic acid based etch, having the highest selectivity, is most useful for device fabrication, and is relatively insensitive to pH and peroxide concentration for etching $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$. However, for $\text{In}_{0.52}\text{Al}_{0.48}\text{As}$ the etch rate drops dramatically at a pH of 5 and higher, and a peroxide concentration of 30:3 $\text{SA}:\text{H}_2\text{O}_2$ and larger. Therefore, if $\text{In}_{0.52}\text{Al}_{0.48}\text{As}$ is to be etched, the pH and peroxide concentration must be kept low. On the other hand, by using an $\text{SA}:\text{H}_2\text{O}_2$ solution at high peroxide concentration and at a pH of about 5.5, $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ can be etched selectively over $\text{In}_{0.52}\text{Al}_{0.48}\text{As}$, with a selectivity better than 100:1.

IV. 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.

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