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Semiconductor Surface-Molecule Interactions

Wet Etching of InP by α-hydroxy Acids

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Controllable etching and surface passivation of InP semiconductors are desirable for removing damaged surfaces and obtaining good electronic properties. We have observed that organic acids (α-hydroxy acids: tartaric, lactic, citric, and malic), when used in conjunction with HCl to etch the (100) surface of InP results in smoother and defect-free surfaces, in comparison to etches based on inorganic acids alone. The chelating action of the organic acids aids in efficiently removing In from the surface, which leads to a very controllable etching. These chemical treatments have implications in controlling surface properties such as band bending and surface recombination velocity.
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A real (100) surface of a III-V semiconductor (InP) consists of both group III (In) and group V (P) ions. The surface is then charged and, under suitable conditions, molecules can bind to it. Organic compounds (*e.g.*, carboxylic acids) could chemisorb on the III-V semiconductors' surfaces (cf., the two-site adsorption of dicarboxylic acids on the (100) surface of GaAs[1]). There is then a mutual interaction of the electrons of the sp^2 orbitals of the III-V semiconductor's surface and the adsorbed molecules, which alters the surface properties of the semiconductor. These considerations allow us to use a wide variety of natural and synthetic organic molecules to manipulate surface properties. One such technologically important application is etching of InP-based semiconductors.

Semiconductor heterostructure growth on InP(100) has the advantage over GaAs, in that layers based on both AlInAs and InGaAs can be grown.[2] This flexibility has been used in the design of optoelectronic devices[3] such as lasers, heterojunction bipolar transistors (HBT) and field effect transistors (FET). Another avenue of extensive research is the *ex situ* regrowth of subsequent III-V semiconductor layers lattice matched to the underlying substrate/layer. In this way, desired functionality can be incorporated in a layer (creating buried channels, for instance[4]) prior to the growth of additional layers on the substrate. This regrowth technique[5] could replace the more elaborate ion implantation techniques in use today.

In order to grow semiconductor layers on the top of an InP processed layer/substrate, one would normally have to etch back a very small thickness of the InP to get rid of the damaged surface layers and surface impurities incorporated during processing. It is thus desirable to have an etching solution with a very low and controllable etch rate, which provides a smooth mirror-like finish to the surface. In this communication, it is proposed that an aqueous mixture of hydrochloric (HCl) and α-hydroxy acids (lactic, citric, malic, and tartaric acids) can be used to etch InP. We see that these acids bind strongly to the group III ions in the III-V semiconductor; their chelating nature binds the In atoms of the InP and renders the surface etching reaction more homogeneous. The preferential phosphorus depletion that results from HCl etching is thus circumvented. There is also the possibility for using these acids to passivate the surfaces and regulate the electronic properties, *e.g.*, the surface recombination velocity.[6]

Models for explaining the etching behavior of (100) surfaces in III-V compounds date back to the 1960s[7-9] and assume that the surface is polar, *i.e.*, terminates in In or P atoms. The P atoms would be more reactive than the In atoms, because of the unshared pair of electrons available for oxidation. This was the basis for the use of acidic and oxidizing reagents (HCl, HBr, H_3PO_4, H_2O_2, Br_2, Cl_2, MnO_4^-, $Cr_2O_7^{2-}$, etc.),[10] to break the covalent bonds (acids being electron acceptors in the Lewis sense) in III-V semiconductors. Another approach[11,12] postulates a mechanism where the etch rate of InP is determined by a synchronous exchange of bonds, where In-Cl and P-H bonds replace the original H-Cl and In-P bonds. In this model, the undissociated acid molecules are thought to control the rate of reaction. However, these models are simplistic because real semiconductor surfaces are very complex. A case in point is the recent observation of the (2×4) surface reconstruction on InP(100) by scanning tunneling microscopy (STM) studies, where the surface was found to be cation (In) rich and no P dangling bonds were seen.[13]

Etching reactions are classified as (i) surface reaction rate limited or (ii) diffusion controlled.[7] The former relies on the rate of reaction at the surface, whereas the latter hinges on how fast the reactant can be supplied to the surface, and can be improved by agitation. To produce a very small etch rate just sufficient for a few monolayers of InP to be removed, a slow reaction at the InP surface is needed and hence one should operate in the reaction-rate-limited regime. This implies that the chemistry and activation at the solid-liquid interface must be understood. Here, the proposed reaction mechanism is a modification of InP surface etching by HCl, caused by steric and oxidative effects of the organic acids.

There is an empirical rule in III-V semiconductor etching that slow etching faces consist of group III atoms,[14] since the group V (P) atoms are electron rich, and hence more reactive. The mottled surfaces (comprising of etch pits, steps, etc.) of InP etched with HCl, maybe due to the different reactivity of the In and P on the mixed (100) surface.[15] To etch smoothly, the indium atoms/ions must be removed as quickly as the P, and it is hypothesized that metal-removing (chelating) agents would be useful. The α-hydroxy acids are excellent chelating agents due to the presence of numerous lone electron pairs on the oxygen atoms of the —COOH and the —OH groups (Fig. 1). A plausible mechanism would then be as follows: (i) HCl breaks the covalent bonds of InP, and P would be oxidized;[11] (ii) subsequently the electron-rich α-hydroxy acids bind to the In ions (In^{3+}). The additional action of the α-hydroxy acids can aid in the simultaneous etching and removal of In and P, thereby yielding a smooth surface with no preferential features. The chelate reaction products are very soluble in water, and can be removed along with the acids by dipping the etched surface in water.

Another motivation for these studies was to understand the role of organic chemicals in etching semiconductors. These acids have been used as complexing agents, and catalyze a controllable rate of reaction by converting the etch products to products with greater solubility,[7,8] a particular example is the use of oxalic and tartaric acids and polyhydric alcohols for Ge.[7] There was also extensive use of tartaric acid mixed with other inorganic acids in etching III-V semiconductors such as InSb, GaSb, AlSb, InAs, and GaAs,[7] and the

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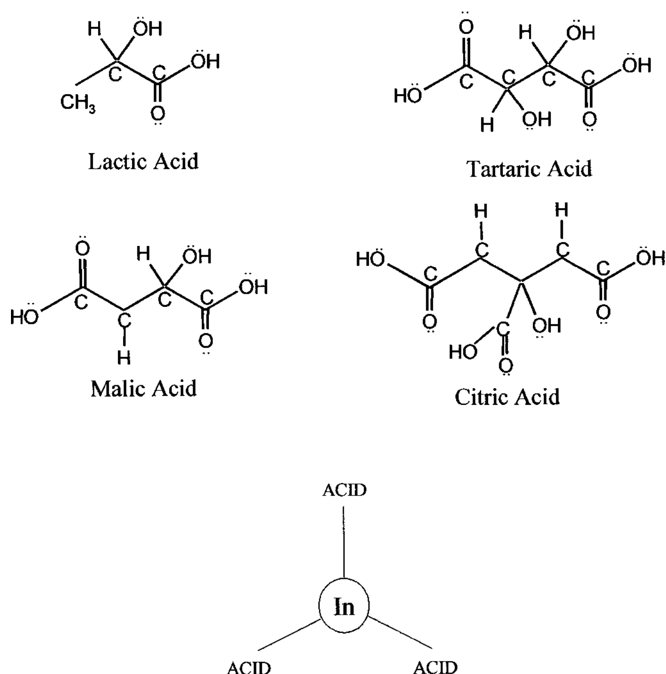


Figure 1. Different proportions of α-hydroxy acids (lactic/tartaric/citric/malic) were mixed with HCl for etching InP(100) surfaces. It is hypothesized that the presence of the lone pair of electrons on the oxygen atoms and the double bonds of the —COOH groups aid in chelating the indium atoms, and aid in a more homogeneous etching reaction.

use of stearic acid $[CH_3(CH_2)_{16}COOH]$ as an inhibitor on InSb.[9] InP however, has been little studied with respect to organic acid treatments.[16]

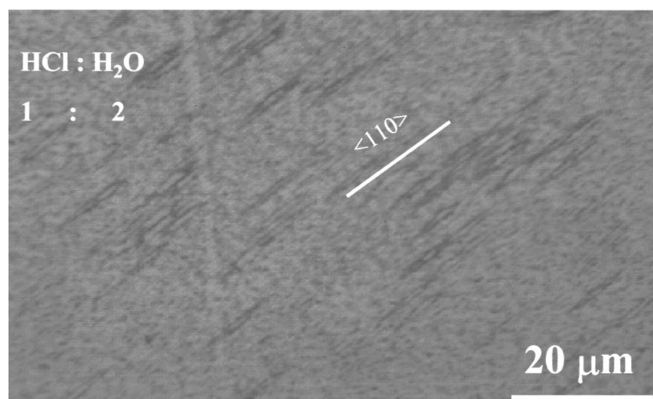
Experimental

The general strategy adopted was to carefully investigate the etching of the InP(100) surfaces with HCl in aqueous solution, with various proportions of the α-hydroxy acids. While fast etches of the InP are well documented, there is a much less work in obtaining very slow, controllable, and reproducible etches. It is shown in this study how the use of lactic, malic, citric, and tartaric acids can result in very slow and uniform etching of InP.

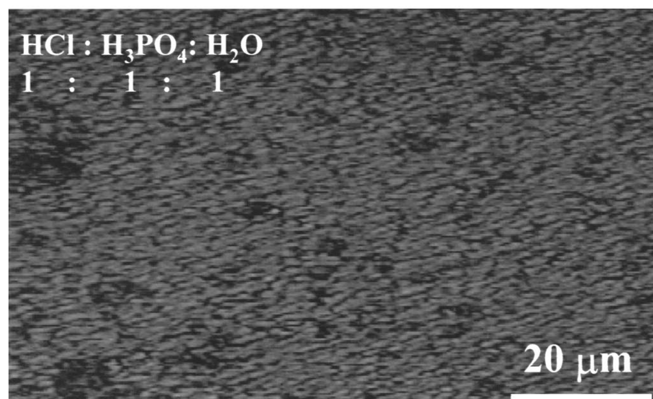
Semi-insulating InP(100) wafers and InGaAs/InP double heterostructure wafers were used in the etching experiments. The wafers were cut from single-crystal boules grown by a Czochralski (CZ) technique (supplied by American Xtal Inc.). The samples for the etching studies were ultrasonically cleaned in trichloroethylene (TCE), acetone, isopropanol, and deionized water for 3 min each, with a dry nitrogen blow dry in between each clean. Two kinds of etch masks were used: (*i*) photoresist (AZ5214) was spun on (4000 rpm, 30 s) to a thickness of ~1 μm and then photolithography was used to etch 10 μm lines, or *(ii)* as the photoresist is not completely immune to attack by HCl used, another set of samples was made by coating the samples with a Durabond® black wax. After the etching treatments, the wax was removed by immersing the samples in orange terpenes (OptiClear™). The α-hydroxy acids used in this study (obtained from Fisher Scientific, Inc.) were prepared to be 0.5 M, and reagent grade HCl (12.0 M) and H_3PO_4 (15.0 M) was used. The samples were cleaned again by a DI water rinse. The step height was determined by a stylus profilometer (Alphastep®), and the surfaces studied with an optical microscope (Nikon) and a Hitachi S-4700 scanning electron microscope (SEM).

Results and Discussion

HCl by itself violently attacks InP, with an etch rate $>$ 12 μm/min.[10,17] The use of HCl in an aqueous medium alone is



(a)

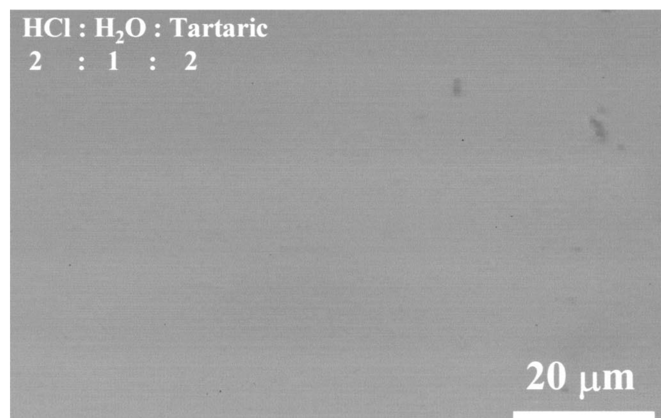


(b)

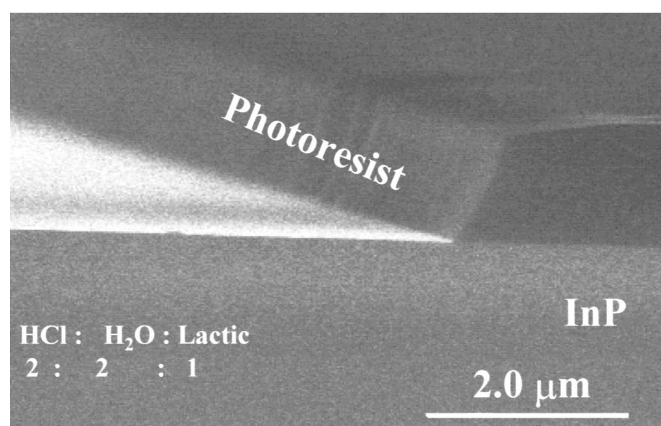
Figure 2. The effect of conventional etching treatments on the InP(100) surface: (a) when etched with an aqueous HCl mixture, a rough surface and elongated etch pits in the ⟨110⟩ direction are apparent. (b) With phosphoric acid added, the etch pits are more rounded in appearance, but the rough surface persists.

not suitable for slow controllable etches ($<$5 nm/min) as the surface is considerably roughened (Fig. 2a). Here the etching is selective, and leads to etch pits oriented at 45°, along the ⟨110⟩ direction. The etching mechanism basically involves the dissolution of In and P, and the etch pit surface could be either specie. In conventional etch treatments,[10] phosphoric acid (H_3PO_4) is added, presumably to slow down the preferential etching of phosphorus. However, this treatment results in a rounding of the etch pits, and does not improve the surface appearance (Fig. 2b). Stirring the solution results in smaller etch pits and a rough surface. However, the etch rate is not altered as HCl etching of InP is kinetically controlled.[11] Incidentally, H_3PO_4 alone (acidity constant pK_a ~2.12) was observed to have negligible etch rate in comparison to HCl (pK_a ~−3) on the etching of InP in 2 h.

When the α-hydroxy acids were incorporated into aqueous HCl, the most significant effect is that the surface becomes extremely smooth (±5 nm, the limit of the profilometer resolution), with no trace of etch pits (Fig. 3a and b). The etch rate was slower due to dilution, but also depends on the specific acid used (Fig. 4a). The dilution effect could possibly be ascribed to the increasing ionic dissociation of HCl, consequently less molecular HCl would be available[11] for the oxidation of the In-P bonds. Figure 4b offers a comparison with aqueous mixture of HCl, without organic acids; irrespective of the dilution the InP surface was always rough. It was also seen that stirring the HCl:H_2O:organic acid mixture did not change the etch rate, implying that the etching mechanism is still reaction-rate controlled.

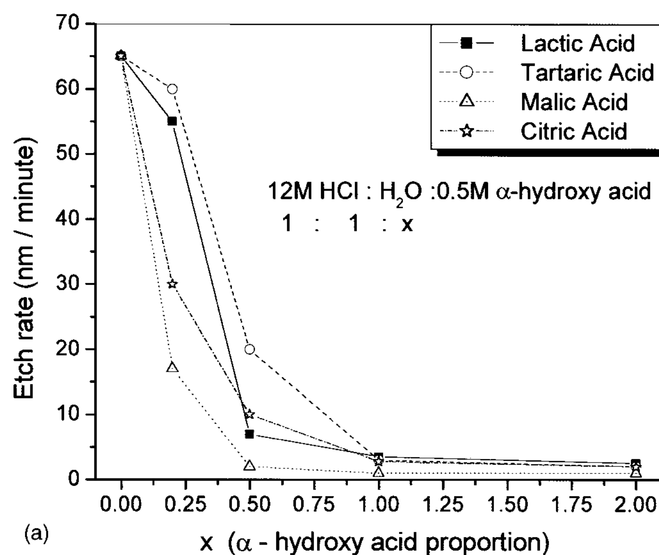


(a)



(b)

Figure 3. Etching InP with the α-hydroxy acids always results in controllable etches and smooth surfaces. (a) The (100) surface on etching with tartaric acid has a mirror-like finish and is defect-free. (b) A 70 nm shallow etch using lactic acid.



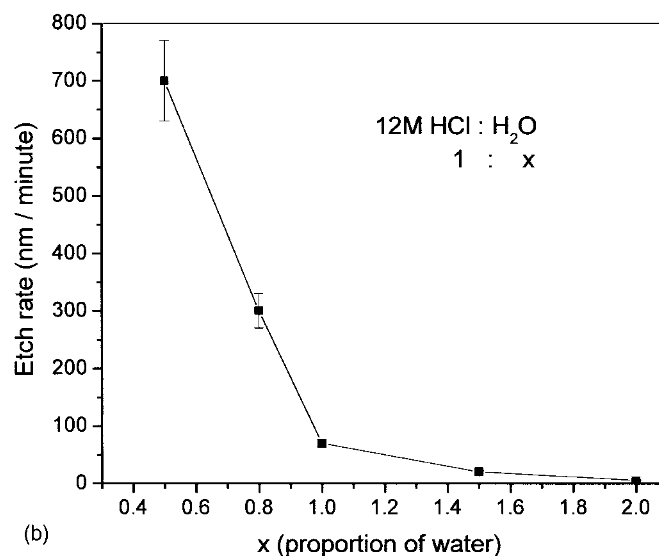


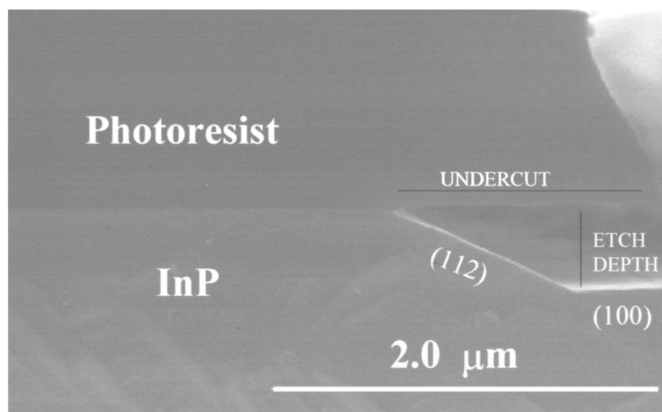
Figure 4. (a) The etch rate as a function of the α-hydroxy acid proportion. Controllable and reproducible etches of up to 5 nm/min can be obtained. Generally, the etch rate decreases with increasing amounts of organic acid due to a dilution effect. The efficiencies of the acids in binding the In atoms scales are tartaric > lactic > citric > malic. (b) A comparison of the etch rate for an aqueous HCl mixture ($HCl:H_2O::1:x$). The etch rate of reagent grade HCl alone is ~12 μm/min.[17] The InP surface was always rough, irrespective of the dilution.

The oxidative powers of all the α-hydroxy acids are similar ($pK_a \sim 2.9\text{-}3.4$) and are weaker than HCl by three orders of magnitude ($pK_a \sim -3$).[18] This would imply that the α-hydroxy acids themselves do not etch InP, and indeed immersion for 10 h had a negligible effect (± 20 nm). Instead, the differences in the etch rates are postulated to be due to the chelating tendencies of the acids. Examining the structures of the acids (Fig. 1), reveals the presence of lone electron pairs on the O atoms in the —COOH group and the —OH group, which indicates a bonding tendency.[19] The electrons at these sites bind the In atoms to form metal-acid complexes/chelates (Fig. 1). This aids in the removal of In and nonpreferential etching. The tendency of the acids to chelate the cation is proportional both to the number of electron pairs available for bonding, and their size (steric effects can inhibit efficient bonding). It can also determine the relative rates of etching.

We define a parameter, the etch anisotropy, to be the ratio of the undercut to etch depth. This is different for different crystal planes. From Fig. 5, the relative etch rates of the acids are tartaric < lactic < malic < citric. It is also seen that in all cases the undercut is greater than the etch depth on the (100) surface. This could be due to the greater reactivity of the (111) edge planes.

If it is assumed that the electrons in the π orbitals of the acids interact with In cations on the surface, then tartaric and lactic acid have one —COOH group on a side that binds to the surface, while citric and malic acids have two —COOH groups and bind more strongly (the electron withdrawing —OH group stabilizes the acids, and their number and position relative to the —COOH group is important). Tartaric and lactic acids are seen from this perspective as being the most benign.

From the above examples, it can be seen that organic molecules can be used as aids in etching reactions. The binding of organic molecules to the surface could saturate the surface dangling bonds and In-derived acceptor states. It can be hypothesized that this interaction of the α-hydroxy acid lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) energy levels with the semiconductor conduction/valence bands, and the consequent electron and hole transfer would influence surface properties such as surface recombination velocity (SRV) and band bending.[5,6] Recently, there was an application of the above concepts in the modification of the electronic properties of CdTe by benzoyl-substituted dicarboxylic acids.[20]



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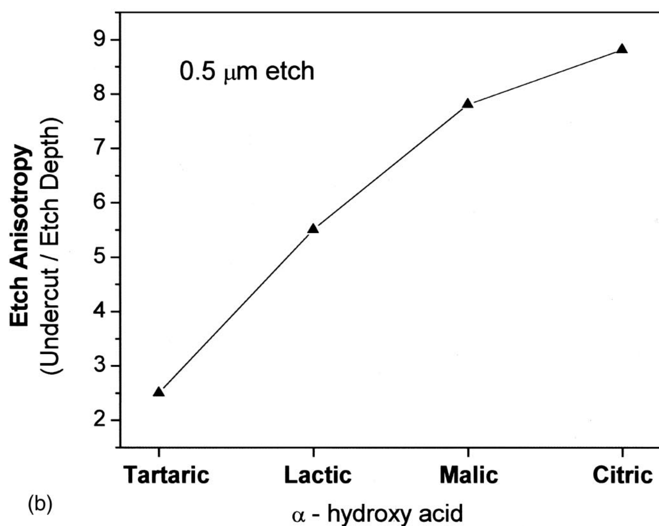

(b)

Figure 5. (a) The etch anisotropy (=undercut/etch depth) is proportional to the isotropic reactivity of the acid mixture. (b) Tartaric acid has the lowest etch anisotropy, while citric and malic acids react more strongly with the (112) planes.

Conclusions

It has been demonstrated that α-hydroxy acids can be used in conjunction with HCl for controllably etching InP(100) surfaces to a mirror-like finish, with a defect-free surface. The chemical etches presented here can be used to remove surface layers damaged due to radiation and device processing, and prepare for subsequent regrowth. In our model, the organic acids aid in the formation of In-hydroxy acid complexes (chelates) which results in the simultaneous removal of In and P, resulting in nonpreferential etches. The number and position of the —COOH and —OH groups determine the relative reaction rates, and from this perspective lactic acid and tartaric acids were the most benign while citric and malic acids more reactive. Tartaric and lactic acids had the lowest etch anisotropy with minimum undercut. It would be interesting to look at the effects of the α-hydroxy acids on different InP planes.[21]

Acknowledgments

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