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Wet Etching of InGaP and GaAs in HCl: H_3PO_4: H_2O_2

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We present the measured etch rates of lattice-matched InGaP and GaAs in HCl:H_3PO_4:H_2O_2 solutions with variable contents of H_3PO_4 and H_2O_2. The content of H_3PO_4 in the solution affected the etch rates markedly; in contrast, the content of H_2O_2 had only a weak influence. The ageing of the HCl:H_3PO_4:H_2O_2 (1:10:1) etchant did not alter the etch rate for InGaP, while that for GaAs decreased notably. For this solution we measured the temperature dependence of the etch rate. An increase in temperature from 20 to 44°C resulted in a growth in the etch rate by about a factor of three. Without the presence of H_2O_2 in the solution one can achieve highly selective etching of InGaP over GaAs. The etch rate for InGaP varied rapidly with the mole fraction of HCl in HCl:H_3PO_4 and HCl:H_2O solutions.

1. Introduction

InGaP, a wide band gap compound semiconductor, is currently attracting a great deal of attention. Occasionally, somewhat sceptical prognoses of its wider utilization appear,[1,2] yet many authors consider this material to be highly promising for manifold applications in electronic and optoelectronic devices, such as light-emitting diodes, heterobipolar transistors and lasers.[3–5]

The attractiveness of the InGaP/GaAs heterostructure derives from its energy band line-up, the valence band offset being markedly larger (ΔE_v = 0.24 – 0.40 eV) than the conduction band offset (ΔE_c = 0.03 – 0.22 eV). This is believed to be more favorable than

the energy band structure of the AlGaAs/GaAs heterosystem. In particular, there is intense interest in the use of InGaP emitters in heterojunction bipolar transistors, which may avoid the oxidation and deep level problems in AlGaAs.

One of the key technological operations used for device fabrication is wet chemical etching. In our previous paper[6] we presented a set of results on wet etching of InGaP and GaAs in $HCl:CH_3COOH:H_2O_2$ (the so-called KKI) solutions. Previously, these etchants were found to yield satisfactory effects.[7] Nevertheless, a serious drawback of these solutions is that they attack gold, which may bc subsequently redeposited on the slopes of MESA structures and on the etched surface itself. Therefore it is highly desirable to look for other etchants which might be more suitable for device fabrication.

2. Etch Rate Studies

In our studies, we used InGaP layers grown on semiinsulating, Cr-doped, (001)-oriented GaAs substrates by low-pressure metal organic chemical vapor deposition. AsH_3, PH_3, TMGa (trimethylgallium) and TMIn (trimethylindium) were used as the sources of As, P, Ga and In, respectively. Hydrogen was used as the carrying gas, the total pressure in the reactor being 5 kPa. The epitaxial layers were prepared at 560°C and the growth rate was 0.6 μm/hr. The thickness of the layers ranged from 0.36 to 0.70 μm. The nominal composition of the layers was $In_{0.485}Ga_{0.515}P$.

Before etching, the samples were cleaned in boiling acetone, trichloroethylene and methanol, and blown dry with nitrogen. Initially, a part of the sample was masked using a positive photoresist AZ 5214 (Hoechst). Then the sample was immersed in the etchant in a vertical position. During the etching process no agitation was applied. The etch times varied from 1 to 15 min depending on the thickness of the etched layer available. The amount of material removed was never allowed to exceed 95% of the total layer thickness. Etching was terminated by rinsing the sample in flowing distilled water for approximately 1 min, then the mask was dissolved in boiling acetone and, finally, the sample was blown dry with nitrogen.

The etch rates were evaluated by measuring the thickness of the step created between the etched and masked surfaces using a Talystep (Rank Taylor Hobson). The uncertainty in measuring the thickness is estimated to be less than 10 nm. Thickness measurements were repeated several times and we assessed the errors in etch rates to be of the order of 10%. The quality of the etched surface was examined using optical microscopy.

Figure 1 shows the etch rate of InGaP as a function of the volume content of H_3PO_4 in the solution 1 HCl:x H_3PO_4:1 H_2O_2. The etched surface remained smooth. In contrast, etching in solutions with higher contents of H_2O_2 resulted in markedly rough surfaces. The etch rates for GaAs were approximately the same as those for InGaP. Hence, the solution was suitable for nonselective MESA etching.

The ageing of the $HCl:H_3PO_4:H_2O_2$ (1:10:1) etchant did not affect the etch rate of InGaP, its magnitude being relatively low, while the etch rate of GaAs decreased notably with the time of ageing (see Fig. 2). For comparison, this figure also shows the etch rates for InGaP and GaAs in acetic acid-based solutions.

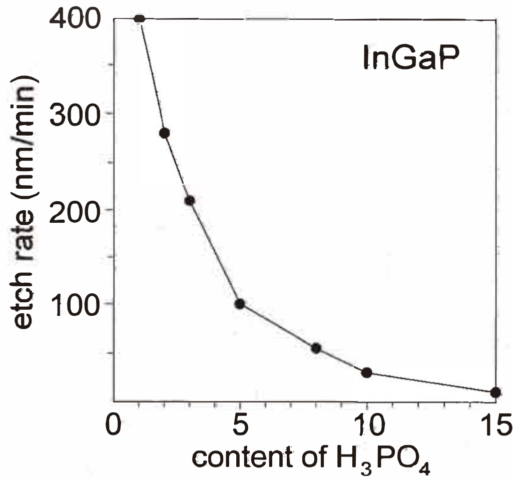

Fig. 1. The dependence of the etch rate of InGaP on the volume content of H_3PO_4, x, in the solution 1 HCl:x H_3PO_4:1 H_2O_2 at 20°C.

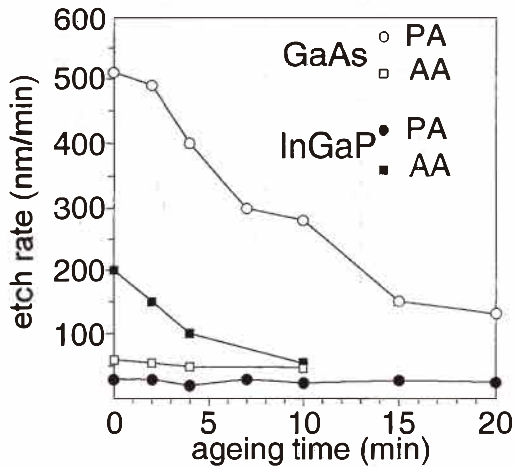

Fig. 2. The effect of etchant ageing upon the etch rate at 20°C. Etchant compositions: PA = 1 HCl:10 H_3PO_4:1 H_2O_2, and AA = 1 HCl:10 CH_3COOH:1 H_2O_2.

Figure 3 depicts the etch rate of InGaP with $HCl:H_3PO_4:H_2O_2$ (1:10:1) as a function of temperature. The increase in temperature from 20 to 44°C resulted in a rise in the etch rate by about a factor of three. Assuming thermal activation of etching with a rate proportional to exp $(-E_a/RT)$, where E_a is the activation energy, R is the universal gas constant and T is the absolute temperature of the etching solution, a least-square fit of the measured data yielded $E_a = 9.2$ kcal/mole (38.5 kJ/mole). This is a relatively high value, which is typical of etch processes whose rates are limited by the chemical reaction itself rather than by dissolution of the reacting products or diffusion of the reacted species towards the etched surface. Similarly, the smoothness of the etched surface, as observed using optical microscopy, suggests that the etching process has a reaction limited nature.

The $HCl:H_3PO_4:H_2O_2$ etchant is a nonaqueous solution of HCl and H_2O_2 in the H_3PO_4 solvent. H_2O_2, which is the oxidizing agent, plays a very important role. Hydrochloric acid alone, without H_2O_2, does not attack GaAs. However, it removes natural oxides from the GaAs surface. On the other hand, HCl has long been used as an etchant for InP. Hence, the etchant under investigation is a combination of the components used to etch GaAs and InP. As a result, by eliminating the oxidizing agent from the solution we obtained a highly selective etchant, efficiently etching InGaP while not attacking GaAs.

With an intention of attaining higher etching selectivity, we eliminated H_2O_2 in our subsequent experiments. Water was used to dilute the etchants so as to lower the etch rate.

Figure 4 shows the etch rate of InGaP *versus* the volume fraction of HCl in $HCl:H_3PO_4$ and $HCl:H_2O$ solutions at 20°C. Figure 5 displays the measured variations in the etch rates of InGaP as a function of the volume part, x, of HCl (open triangles) and H_2O (full squares) in $HCl:H_3PO_4:H_2O$ solutions at 20°C. The differences between the rates plotted in the two figures could be useful in situations in which selective and well-defined etching is required.

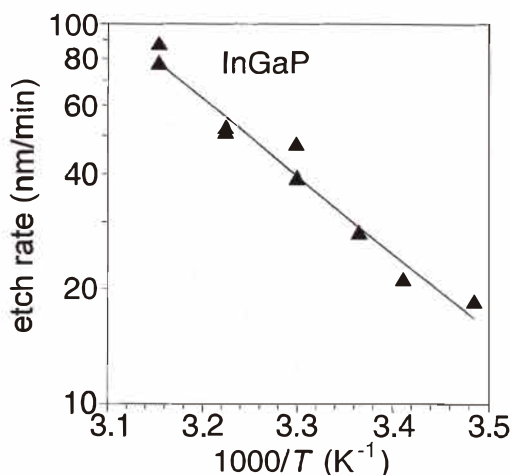

Fig. 3. Temperature dependence of the etch rate of InGaP in the solution 1 HCl:10 H_3PO_4:1 H_2O_2.

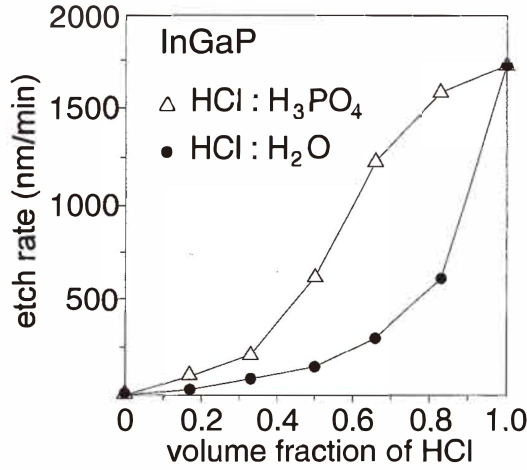

Fig. 4. The etch rate of InGaP vs. the volume fraction of HCl in $HCl:H_3PO_4$ and $HCl: H_2O$ solutions at 20°C. The volume fraction of HCl in the solution u HCl:v H_3PO_4 is given as $u/(u + v)$, u and v being respective volume parts.

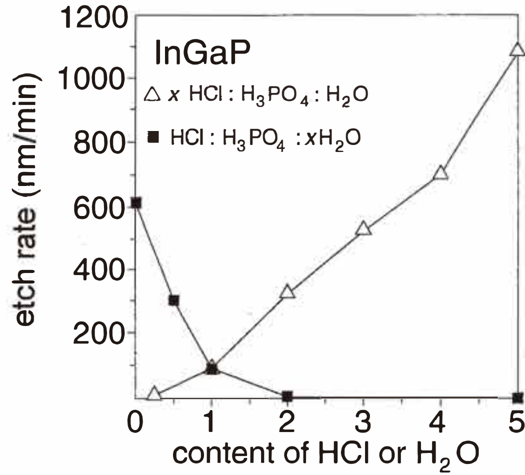

Fig. 5. The etch rate of InGaP in solutions with variable volume contents of HCl and H_2O in $HCl:H_3PO_4:H_2O$ solutions at 20°C.

3. Conclusion

We have succeeded in finding an etching solution based on HCl that may be used as an alternative to the commonly used KKI etchants. By varying the content of HCl in the solution, one can achieve both nonselective etching, useful for MESA formation, and strongly selective etching of InGaP over GaAs. An essential advantage of this solution is that it does not attack gold.

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