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WET CHEMICAL ETCHING SURVEY OF III-NITRIDES

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ABSTRACT

Wet chemical etching of GaN, InN, AlN, InAlN and InGaN was investigated in various acid and base solutions at temperatures up to 75°C. Only KOH-based solutions were found to etch AlN and InAlN. No etchants were found for the other nitrides, emphasizing their extreme lack of chemical reactivity. The native oxide on most of the nitrides could be removed in potassium tetraborate at 75°C, or HCl/H_2O at 25°C.

INTRODUCTION

Considerable progress has recently been made in the areas of growth, dry etching and implant isolation and doping of the III-V nitrides and their ternary alloys. This has resulted in nitride-based blue/UV light emitting diodes, lasers and electronic devices[1-9]. There has been less success in developing wet etch solutions for these materials due to their excellent chemical stability. High etch rates have been achieved in dry etch chemistries[10-19], but damage may be introduced by ion bombardment, and controlled undercutting is difficult to attain. In addition, since dry etching has a physical component to the etch, selectivities between different materials are generally reduced.

Amorphous AlN has been reported to etch in 100°C HF/H_2O[20-22], HF/HNO_3[23] and NaOH[24], and polycrystalline AlN in hot (≤ 85°C) H_3PO_4 at rates less than 500 $Å\cdot min^{-1}$[25,26]. Mileham et al.[27] reported the etching of AlN defective single crystals in KOH based solutions at etch temperatures ranging from 23-80°C. They reported decreased etch rates with increasing crystal quality, as the reactions occurred favorably at grain boundaries and defect sites. InN in aqueous KOH solutions was reported to etch at a few hundred $Å\cdot min^{-1}$ at 60°C[28]. The properties and etching characteristics of the nitrides are a function of post-growth or post-deposition annealing, with the etch rates decreasing for higher annealing temperature[29,30].

In this paper, we report a survey of wet etching of GaN, InN, AlN, InAlN and InGaN in various solutions as a function of etch temperature, and film composition.

EXPERIMENTAL

The GaN, AlN, InN, $In_{0.36}Al_{0.64}N$ and $In_{0.5}Ga_{0.5}N$ samples were grown by Metal Organic Molecular Beam Epitaxy (MOMBE) on semi-insulating (100) GaAs substrates or p-type (1 $\Omega\cdot cm$) Si substrates in an Intevac Gen II system as described previously[31-33]. The group-III sources were triethylgallium, trimethylamine alane and trimethylindium, respectively, and the atomic nitrogen was derived from an ECR Wavemat source operating at 200 W forward power. The layers were single crystal with a high density of stacking faults and microtwins. Some of the

AlN was reactively sputter deposited on a Si substrate to a thickness of ~1200Å using a N_2 discharge and a pure Al target. This type of AlN film was shown to be an effective annealing cap for GaN at a temperature of 1100°C[34].

For wet etching studies, all samples were masked with Apiezon wax patterns. Etch temperatures were varied between 20 and 80°C. Etch depths were obtained by Dektak stylus profilometry after the removal of the mask, with an approximate 5% error. Scanning electron microscopy(SEM) was used to examine the undercutting on the etched samples. ESCA measurements were made to determine the residue after etch of sputter deposited AlN etched in KOH and phosphoric acid.

RESULTS AND DISCUSSION

A variety of wet etch solutions were tried on the III-nitrides, as shown in Table 1.

Table 1. Compilation of etching results in acid and base solutions, performed at room temperature (25°C) unless otherwise noted.

	GaN	InN	AlN	InAlN	InGaN
Citric Acid (75°C)	0	0	0	0	0
Succinic Acid (75°C)	0	0	0	0	0
Oxalic Acid (75°C)	0	lifts off	lifts off	lifts off	lifts off
Nitric Acid (75°C)	0	lifts off	0	lifts off	lifts off
Phosphoric Acid (75°C)	0	0	oxide removed	oxide removed	0
Hydrochloric Acid (75°C)	0	0	0	0	0
Hydrofloric Acid	0	lifts off	0	0	lifts off
Hydroiodic Acid	0	0	0	0	0
Sulfuric Acid (75°C)	0	lifts off	0	0	0
Hydrogen Peroxide	0	0	0	0	0
Potassium Iodide	0	0	0	0	0
2% Bromine-Methanol	0	0	0	0	0
n-Methyl-2-Pyrrolidone	0	0	0	0	0
Sodium Hydroxide	0	lifts off	lifts off	lifts off	lifts off
Potassium Hydroxide	0	lifts off	22650 Å/min	0	0
AZ400K photoresist developer (75°C)	0	lifts off	~60-10000 Å/min	composition dependent	0
Hydroiodic Acid/hydrogen peroxide	0	0	0	0	0
Hydrochloric Acid/hydrogen peroxide	0	0	0	0	0
Potassium Triphosphate (75°C)	0	0	0	0	0
Nitric Acid/ Potassium Triphosphate (75°C)	0	lifts off	0	0	0
Hydrochloric Acid/Potassium Triphosphate (75°C)	0	0	0	0	0
Boric Acid (75°C)	0	0	0	0	0
Nitric/Boric Acid (75°C)	0	lifts off	0	0	lifts off
Nitric/Boric/Hydrogen Peroxide	0	lifts off	0	0	removes oxide
$HCl/H_2O_2/HNO_3$	0	lifts off	0	lifts off	lifts off
Potassium Tetraborate (75°C)	0	oxide removal	oxide removal	oxide removal	oxide removal
Sodium Tetraborate (75°C)	0	0	0	0	0
Sodium Tetraborate/Hydrogen Peroxide	0	0	0	0	0
Potassium Triphosphate (75°C)	0	0	0	0	0
Potassium Triphosphate /Hydrogen Peroxide	0	0	0	0	0

Ratios were 1:1 for the mixtures. Lift-off indicates that there was a delamination of the epitaxial film rather than etching. This is due to the etch solution attacking the interface between the two

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materials that is defective and is usually a mixture of interdiffused material phases. There is a high density of stacking faults and dislocations in this region due to the lattice mismatch. AZ400K, a KOH based solution, was found to etch AlN and InAlN. This solution was found to have no etch on $Al_xGa_{1-x}N$ (x = 0.2 and 0.31).

As found previously[27,35-38] only KOH or AZ400K are found to actually etch any of the nitrides, and no etch was found for GaN, InN or AlGaN at solutions temperatures up to 75°C. Recently, Minsky and Hu[39] reported that laser-enhanced (He-Cd) etch rates of GaN up to a few hundred Å·min^{-1} in 1HCl:2H_2O or a few thousand angstroms per minute in 45% KOH:H_2O(1:3) were obtained by photoenhancement of oxidation and reduction rates occurring in an electrochemical cell. Similarly, broad-area photochemical etching of GaN has been reported using a Hg-lamp source[40].

We found that the native oxide on the nitride could be removed in potassium tetraborate at 75°C or in HCl/H_2O at 25°C. For AlN, this oxide could also be removed in H_3PO_4 at 75°C. Figure 1 shows optical micrographs of AlN surfaces after immersion in HNO_3 at 75°C(left), HCl/H_2O at 25°C (center) or succinic acid at 25°C(right). The removal of the native oxide by the

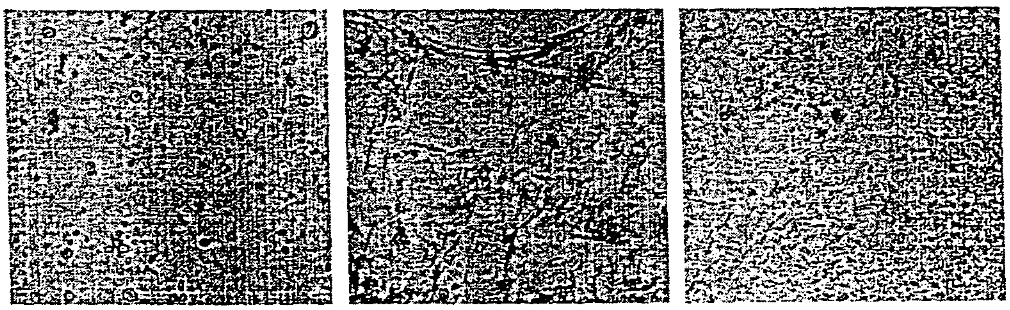

Figure 1. Optical microscopy images of AlN (X400 magnification) surfaces after immersion in HNO_3 at 75°C(left), HCl/H_2O at 25°C(center) or succinic acid at 25°C(right).

HCl/H_2O produces a more textured surface appearance. Figure 2 shows AFM scans of AlN before and after immersion in AZ400K or H_3PO_4. The removal of the native oxide by the latter

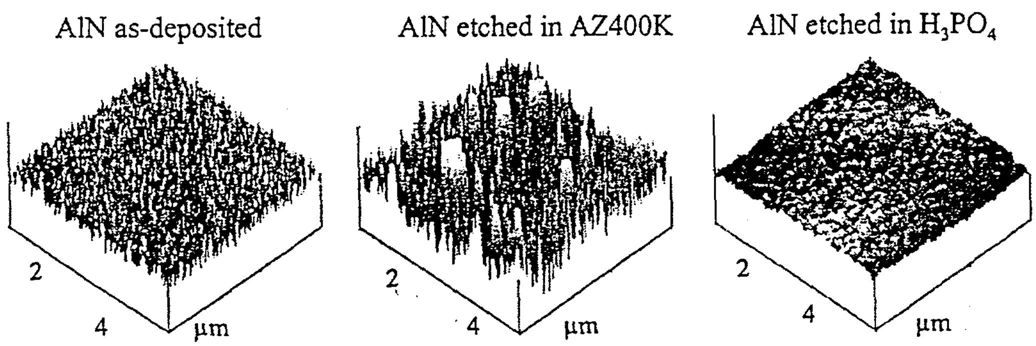

Figure 2. AFM tapping mode measurements of sputter deposited AlN, as-deposited(left), after 10 sec etch in 80°C AZ400K(center) and after a 10 sec etch in 80°C H_3PO_4(right).

the latter solution again changes the surface morphology, while the surface etched by AZ400K has evidence of micromasking.

Figure 3 shows ESCA spectra of these same three samples; the native oxide grows back in ~30mins. on the H_3PO_4 sample(bottom). The surfaces remain reasonably clean in both etching and oxide removal situations.

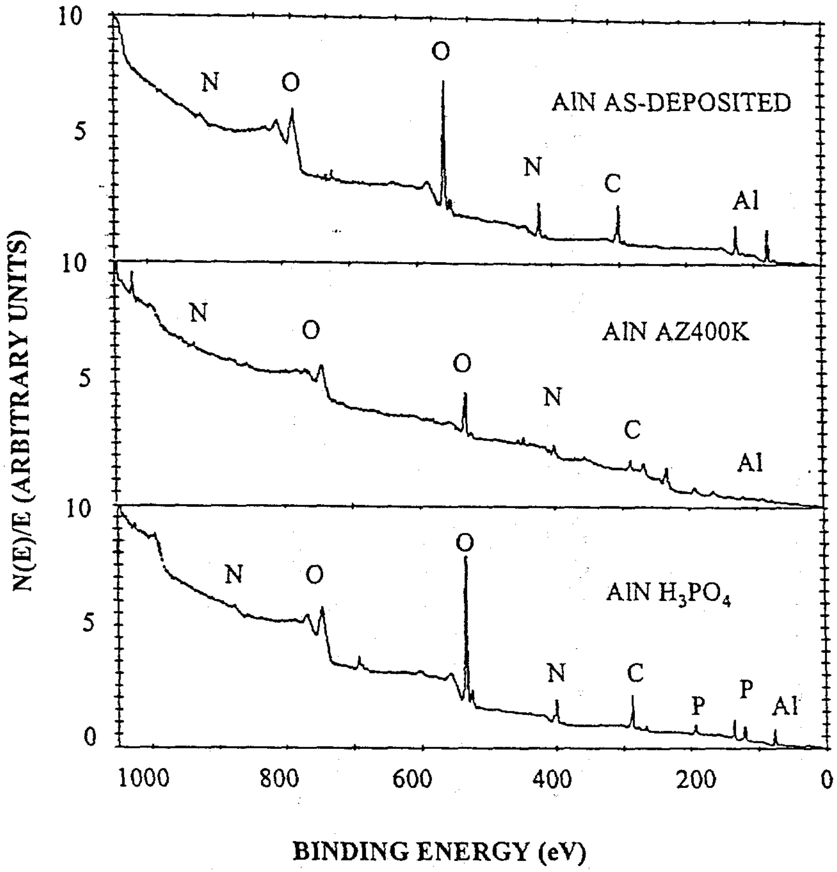

Figure 3. ESCA surface scans of sputter deposited AlN, as-deposited(top), after 10 sec etch in 80°C AZ400K(middle) and after a 10 sec etch in 80°C H_3PO_4(bottom).

SUMMARY

We have performed a survey of many different etching solutions for III-nitrides. At temperatures up to ~75°C, only KOH and related solutions are found to etch AlN and InAlN, while no wet etch solutions were found for GaN, InN, AlGaN and InGaN.

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