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PLASMA CHEMISTRIES FOR DRY ETCHING
GaN, AlN, InGaN and InAlN

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ABSTRACT

Etch rates up to 7,000Å/min. for GaN are obtained in $Cl_2/H_2/Ar$ or BCl_3/Ar ECR discharges at 1-3mTorr and moderate dc biases. Typical rates with HI/H_2 are about a factor of three lower under the same conditions, while CH_4/H_2 produces maximum rates of only ~2000Å/min. The role of additives such as SF_6, N_2, H_2 or Ar to the basic chlorine, bromine, iodine or methane-hydrogen plasma chemistries are discussed. Their effect can be either chemical (in forming volatile products with N) or physical (in breaking bonds or enhancing desorption of the etch products). The nitrides differ from conventional III-V's in that bond-breaking to allow formation of the etch products is a critical factor. Threshold ion energies for the onset of etching of GaN, InGaN and InAlN are ≥75eV.

INTRODUCTION

Dry etching proceeds by formation of etch products that are either spontaneously removed because of their gaseous nature, or can be ejected from the surface by ion-assisted processes such as sputtering. For III-V materials one can form chlorides, iodides, bromides, metalorganic or hydride species, and thus the basic etch chemistries are based on Cl_2, I_2, Br_2 or CH_4/H_2.[1] A table of the boiling points of various etch products is shown in Table 1.[2] From this data, one would expect to be able to rapidly etch GaN and related alloys in Cl_2 chemistries (with ion assistance for In containing alloys), I_2 chemistries, Br_2 chemistries (with ion assistance again to remove $InBr_3$) or CH_4/H_2, i.e. the normal plasma mixtures used for conventional III-V's such as GaAs.

However many different groups have reported low etch rates for GaN and the other III-N materials, with typical values of ≤1,000$Å\cdot min^{-1}$ under reactive ion etching conditions.[3-5] In higher ion density discharges, McLane et al. [6,7] and Shul et al.[8,9] have reported much faster rates, typically 3-5,000 $Å\cdot min^{-1}$ at moderate dc biases. The rates tend to peak around 1-3mTorr, and the fastest GaN etch rate obtained has been ~0.9$\mu m\cdot min^{-1}$ by the Sandia group using $Cl_2/H_2/Ar$ at high microwave (1000W) and rf (450W) powers.[10]

In this paper we show how different plasma chemistries, and in particular the ion current incident on the sample, can produce vast differences in GaN etch rates.

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Table 1: Boiling Points of III-V Etch Products

Species	Boiling Point (°C)	Species	Boiling Point (°C)
$GaCl_3$	201	NCl_3	< 71
$GaBr_3$	279	NI_3	explodes
GaI_3	sub 345	NF_3	-129
$(CH_3)Ga$	55.7	NH_3	-33
		N_2	-196
$InCl_3$	600	$(CH_3)_3N$	2.9
$InBr_3$	> 600		
InI_3	210	PCl_3	76
$(CH_3)_3In$	134	PBr_5	106
		PH_3	-88
$AlCl_3$	183		
$AlBr_3$	263	$AsCl_3$	130
AlI_3	191	$AsBr_3$	221
$(CH_3)_3Al$	126	AsH_3	-55
		AsF_3	-63

EXPERIMENTAL

The etching was performed in either Plasma-Therm SLR 770 load-locked ECR systems, which are capable of operation in either an RIE mode (where only the lower electrode is rf powered) or in the ECR mode (where the microwave source and the lower electrode are both powered), or in a magnetron system where high ion densities are achieved through magnetic confinement of the discharge. Many different plasma chemistries have been employed, indicating HI/H_2, HBr/H_2, CH_4/H_2, Cl_2/H_2 and BCl_3, generally with additions of Ar to enhance the ion bombardment component. In some case N_2 or SF_6 was added to investigate the role of the additive gas.

The samples were generally grown by Metal Organic Molecular Beam Epitaxy (MO-MBE)[11], although other material grown by Metal Organic Chemical Vapor Deposition (MOCVD) was used in some instances. Under optimized growth conditions for the two techniques, the MOMBE material generally etches slightly (~10-15%) faster. This is probably an indication that its much lower growth temperatures (≤900°C for GaN) leaves more weak or defective bonds available for attack by the reactive neutrals in the plasma.

RESULTS AND DISCUSSION

We generally found that Cl_2-based discharges produced the fastest rates for GaN, with CH_4/H_2 having the slowest rates. The other plasma chemistries (BCl_3, HI and HBr) produced rates that were intermediate between these extremes.[12,13] As discussed previously it is necessary to add either H_2 or SF_6 to the Cl_2/Ar mixture in order to achieve the maximum etch rates, best morphology and to retain the stoichiometry of the near-surface.[14,15] .

Figure 1 shows GaN and AlN etch rates in a 1.5mTorr, 0 or 1000W (ECR) plasma of $10Cl_2/5Ar$, as a function of rf power applied to the sample chuck. The rates are about a factor of 3 higher for the microwave-enhanced discharges and, are always higher for GaN relative to AlN. Since Table 1 shows that the volatility of the etch products are actually slightly higher for AlN, the rate-limiting step is the initial breaking of the group III-nitrogen bonds that must precede etch product formation. Further support for this idea comes from the fact that there is very little temperature dependence to the etch rates up to 300°C. If the rate-limiting step was etch product desorption then one would expect an exponential dependence of rate on sample temperature.

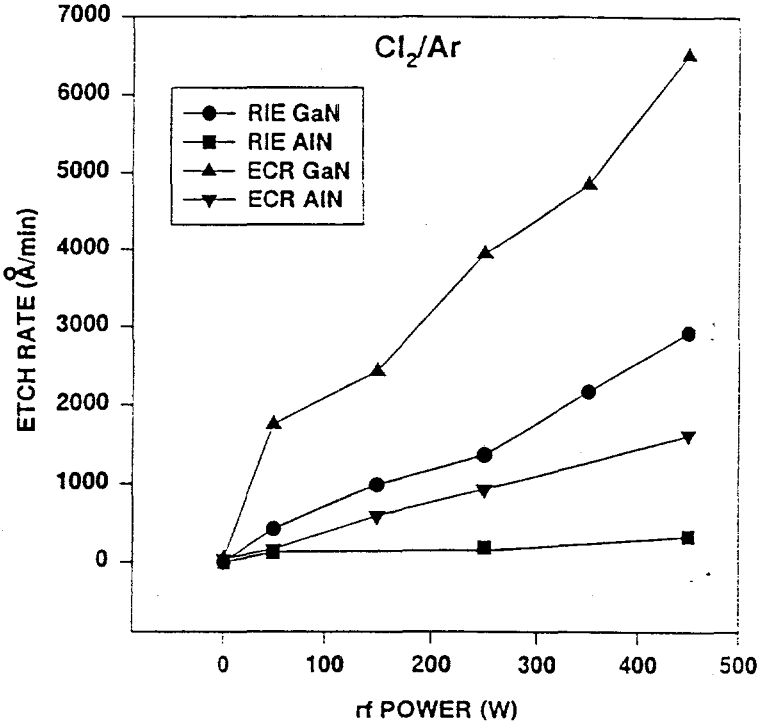

Figure 1. Etch rates of GaN and AlN in 10Cl$_2$/5Ar, 1.5mTorr RIE or ECR discharges.

Figure 2 shows similar data for RIE and ECR etching of InN and InGaN. Note that the rates under RIE conditions are extremely low which is most likely due to the involatile $InCl_3$ etch product. Under ECR conditions there is more efficient sputter desorption and consequently much higher rates. Note that the rates are lower for InGaN, which again is consistent with the idea that bond-breaking is the critical step in these etch processes, since the average volatilities of the etch products for InGaN are actually lower than for pure InN.

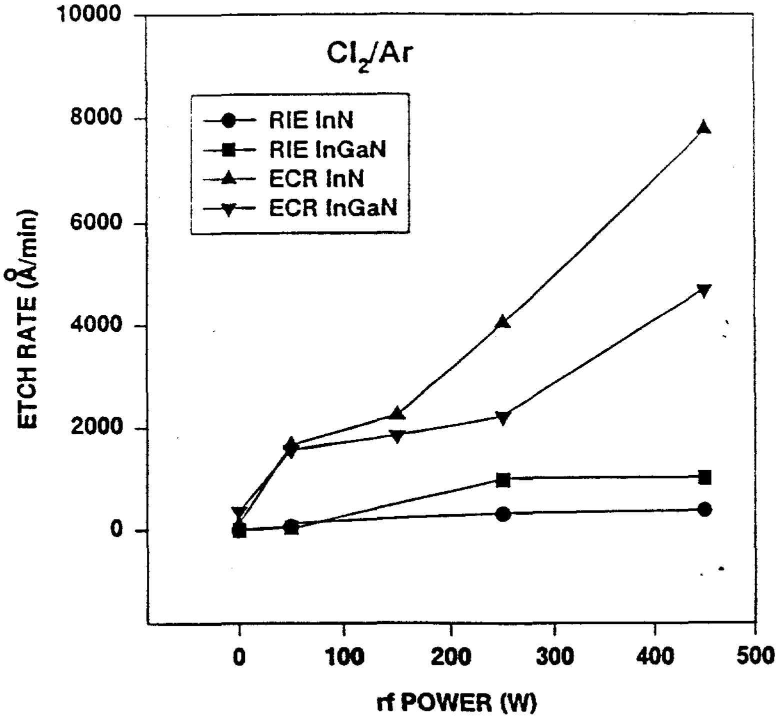

Figure 2. Etch rates of InGaN and InN in 10Cl$_2$/5Ar, 1.5mTorr RIE or ECR discharges.

The dependence on rf power of GaN and AlN etch rates in $5CH_4/15H_2/10Ar$ discharges at 1.5mTorr is shown in Figure 3. The first thing to notice is that the rates are much lower for GaN compared to the Cl_2/Ar data. Secondly, the rates for AlN are similar for the two chemistries, suggesting again that bond-breaking is the main impediment to the achievement of faster rates. Once again ECR conditions produce much higher etch rates compared to RIE.

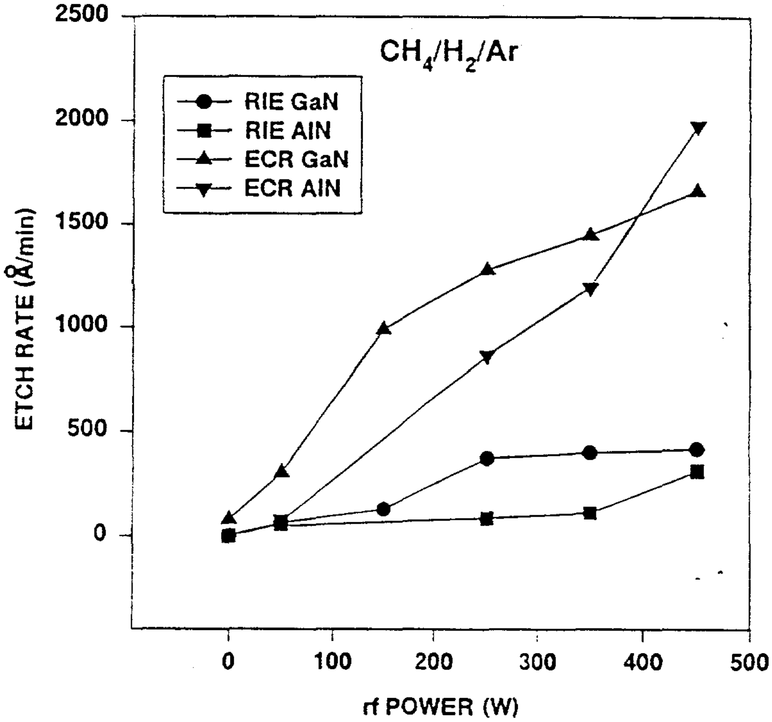

Figure 3. Etch rates of GaN and AlN in $5CH_4/15H_2/10Ar$. 1.5mTorr RIE or ECR discharges.

The most dramatic difference between ECR and RIE conditions was observed for $CH_4/H_2/Ar$ etching of InN and InGaN (Figure 4). The rates are negligible for both materials until very high rf powers in the RIE discharges, so that at moderate dc voltages one would be able to use InGaN or InN as an etch stop layer when removing GaN in $CH_4/H_2/Ar$. A similar result could be observed with AlN (Figure 3). Note also that the rates under ECR conditions are fairly similar to those obtained for InN and InGaN with Cl_2/Ar.

SUMMARY

The III-nitrides have slower etch rates than the more conventional compound semiconductors such as GaAs, GaP and GaSb. We have observed similar trends with the ternary compounds InGaP, AlInP and AlGaP. The average bond strength for AlGaP is higher than for the other two materials, and consequently it displays much lower etch rates in Cl_2-based plasma chemistries, even though the volatilities of the products are actually higher on average than for the InGaP and AlInP. We believe a similar explanation applies to the nitrides, because their etch products are volatile. The rate limiting step appears to be actually the initial bond-breaking which must precede etch product formation. Since the nitrides have high bond strengths, a high ion current is needed to enhance bond breaking and thus magnetically-enhanced discharges produce much higher rates than RIE conditions.

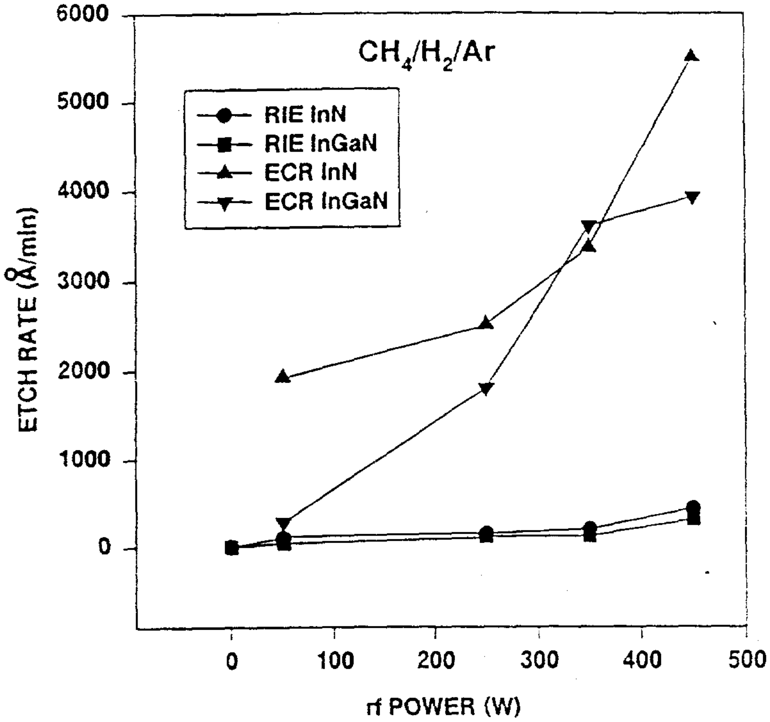

Figure 4. Etch rates of InGaN and InN in $5CH_4/15H_2/10Ar$ 1.5mTorr RIE or ECR discharges.

Acknowledgments

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