Selective etching of GaN over AlN using an inductively coupled plasma and an O₂/Cl₂/Ar chemistry

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An alternative method for achieving etching selectivity between GaN and AlN has been demonstrated. The etch rate of AlN was significantly decreased by the addition of a low concentration of O₂ to a Cl₂–Ar mixture in an inductively coupled plasma (ICP) etching system. The etch rate of GaN in the O₂-containing plasma was approximately 15% less than the plasma without the O₂ for the same parameters. The pressure and the ICP power were varied to achieve a maximum selectivity of 48 at a pressure of 10 mTorr, a direct current bias of −150 V, and an ICP power of 500 W. The etch rates of GaN and AlN at these parameters were 4800 and 100 Å/min, respectively. © 2000 American Vacuum Society. [S0734-2101(00)01503-7]

I. INTRODUCTION

The application of growth techniques which substantially reduce the density of dislocations, e.g., lateral epitaxial overgrowth¹ and pendeo-epitaxy,² should allow the potential to reduce the density of dislocations, e.g., lateral epitaxial growth techniques. However, for commercial purposes this rate should be increased.

II. EXPERIMENTAL PROCEDURE

The etch rate of GaN was measured using an inductively coupled plasma etching system. The plasma chemistry was a mixture of Cl₂ and Ar. While selectivity between GaN and AlN has been achieved using the mixtures ICl/Ar and BCl₃/Cl₂,⁴,⁵ with high resolution masking, highly anisotropic and smooth sidewalls can also be achieved. Other important properties of any plasma etching process are the degree of ion-induced damage (electrical and physical) and the selectivity of the etchants. Selectivity is important for applications such as the processing of high electron mobility transistors or any other heterojunction device where the etching must stop at a particular buried layer.

Selectivity in etching between GaN and AlN is the ratio of the etch rates of these two materials. Until recently the achievement of selectivity between GaN and AlN had minimal success in the nitride community. The ratios were either very low (≤10) or the GaN etch rates were low. Both should be moderately high for this property to be commercially useful. Vartuli et al.⁶ demonstrated a selectivity of 10 between GaN and AlN using an electron cyclotron resonance etching system, but the etch rates were not stated. Smith et al.⁷ achieved a selectivity of 38 between these two materials using inductively coupled plasma (ICP) etching and low direct current (dc) biases (<−50 V). The etch rate of GaN was approximately 2000 Å/min. This is the highest value reported while attaining high selectivity; however, for commercial purposes this rate should be increased.

The method employed by Smith et al.⁷ relies on the fact that the etching is initiated at a lower bias for the GaN than for the AlN. This was attributed to the higher bond strength of AlN. In the present research a different method for attaining selectivity between GaN and AlN has been used, namely, the introduction of a small concentration of O₂ into the ICP system with the Cl₂ and Ar. While selectivity between GaN and AlGaN currently has more practical applications, selectivity between GaN and AlN was chosen because it demonstrates the extreme case, which is more helpful in understanding the mechanism behind this selectivity.

The GaN and AlN samples used for this study were epitaxially grown on 6H-SiC-(0001) substrates via metalorganic vapor phase epitaxy using trimethylaluminum and triethylgallium as the Al and Ga sources, respectively, and NH₃ as the nitrogen source.⁸,⁹ An ≈100 nm monocristalline AlN buffer layer was deposited on the SiC substrates prior to the growth of the GaN. Preparation of the samples for etching employed the sequence of applying a Ni coating, patterning with photoresist, dipping into HNO₃ to remove the Ni, and into acetone to remove the photoresist. Just prior to placement into the etching system, the samples were sequentially dipped into acetone, methanol, and 10% HCl acid for 10 min each to degrease and remove the carbon contaminants. Samples were attached to a 7.6 cm diameter anodized aluminum transport plate using vacuum grease which was mounted onto the wafer chuck. A base pressure of ≤5 ×10⁻⁷ Torr was attained prior to etching. The etch rates were determined by measuring the step heights using a Dektek II profilometer. The GaN and AlN samples were etched concurrently to insure accurate selectivity values.

The etch rate was determined as a function of pressure and ICP power. The dc bias was held constant at −150 V. A
lower dc bias would have resulted in slow GaN etch rates, thus, defeating the purpose of this type of selectivity. Using higher biases would have increased the AlN etch rates too much, lowering the selectivity. The pressure was varied from 5 to 20 mTorr in steps of 5 mTorr. Once an optimum pressure for selectivity was determined, the ICP power was varied from 300 to 800 W. There were two similar chemistries used for these experiments, namely, a mixture of \( \text{O}_2 \) (2 sccm) and \( \text{Cl}_2 \) (18 sccm) with and without the addition of Ar (5 sccm). Though we previously determined that the addition of Ar did not significantly enhance the GaN etch rates in pure \( \text{Cl}_2 \), it was added to increase the plasma density that was significantly decreased by the addition of \( \text{O}_2 \). This was verified through the use of a Langmuir probe.

### III. RESULTS

Figure 1 shows a plot of the etch rates of GaN and AlN in the \( \text{Cl}_2-\text{O}_2 \) and \( \text{Cl}_2-\text{O}_2-\text{Ar} \) chemistries as a function of total pressure. At 5 mTorr, the etch rates were similar for both chemistries. At 10 mTorr, the GaN etch rate in the chemistry without the Ar decreased while the one with the Ar increased slightly. Beyond 10 mTorr, the GaN etch rates decreased considerably and in parallel for both chemistries. The AlN etch rates were eventually constant and similar throughout the entire pressure range for both chemistries. The AlN etch rates were extremely low (\( \leq 100 \text{ Å/min} \)) at 10 mTorr and beyond, which was the basis of the selectivity studies.

Figure 2 shows the selectivity as a function of pressure for both chemistries. The addition of Ar increased the plasma density from \( 7.963 \times 10^{19} \text{m}^{-3} \) to \( 1.050 \times 10^{17} \text{m}^{-3} \), which increased both the GaN etch rate and the selectivity, but not the AlN etch rate. Thus, the ion density was not the rate limiting factor for the AlN. A maximum selectivity of 48 was determined at 10 mTorr with a GaN etch rate of 4800 Å/min. Above 10 mTorr the selectivity dropped considerably due to the much lower GaN etch rates. At 20 mTorr for both chemistries no step in the AlN detected with the profilometer, but due to resolution constraints we assumed a step of 50 Å. An AlN etch rate of 0 Å/min at this pressure would be inconsequential, since the GaN etch rates were so low. As previously stated, the benefit of this type of selectivity is to achieve high selectivities over AlN at high GaN etch rates.

The GaN and AlN etch rates as well as selectivity as a function of ICP power are shown in Fig. 3. The dc bias and pressure were held constant at \(-150 \text{ V} \) and 10 mTorr, respectively, in the \( \text{Cl}_2-\text{O}_2-\text{Ar} \) mixture. Their values were chosen because they resulted in a selectivity of 48 for 500 W ICP power, as shown in Fig. 2. The selectivity sharply increased from 10 to 48 as the ICP power was increased from 300 to 500 W. Above 500 W the GaN etch rate did increase, but the AlN etch rate also increased, resulting in a decrease in the selectivity to 30.

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**Fig. 1.** Etch rates of GaN and AlN as a function of pressure.

**Fig. 2.** Selectivity of GaN over AlN as a function of pressure.

**Fig. 3.** Etch rates of GaN and AlN, and the selectivity of GaN over AlN as a function of ICP power.
IV. DISCUSSION

The underlying principle behind this selectivity is the passivation of the AlN layer through the formation of a stable oxide layer. Since \textit{in situ} surface analysis techniques were not available, the question remains as to what happened to the GaN surface that allowed it to continue to etch in the presence of oxygen. Possible scenarios are that (1) an oxide does not form on the GaN, (2) an oxide does form but it is continually sputtered off and does not prevent the reaction between the Ga and Cl, or (3) an oxide does form and it has an etch rate similar to that of the GaN. It is important to note the similarity of the GaN etch rates between the Cl$_2$/O$_2$/Ar and Cl$_2$/Ar chemistries; the former etched approximately 15% slower than the latter for the same settings.

It is expected that combining this technique with the one developed by Smith \textit{et al.}\textsuperscript{7} employing low dc biases would result in extremely high selectivities, but at lower GaN etch rates. This may be a viable solution if there is the necessity to stop at extremely thin layers (<50 Å) after etching through a GaN layer. Selectivities of 10 between GaN and Al$_{0.28}$Ga$_{0.72}$N were accomplished using the low dc bias method; thus, it is expected that higher selectivities will be attained by combining the two methods.

In summary, an alternative method for achieving ICP etching selectivity between GaN and AlN has been demonstrated. The addition of small concentrations of O$_2$ to a Cl$_2$–Ar chemistry passivates the AlN surface via the formation of aluminum oxide on the surface and significantly reduces the etch rate. The GaN etch rate was affected minimally by the addition of the O$_2$, thus, resulting in a high selectivity between the GaN and AlN. A maximum selectivity of 48 was achieved at a pressure of 10 mTorr, a dc bias of $-150$ V, and an ICP power of 500 W. The GaN etch rate at these parameters was 4800 Å/min; the AlN etch rate was 100 Å/min. This technique should also work for Al$_x$Ga$_{1-x}$N but at reduced selectivities due to the lower Al concentration at the surface.

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