Dry etching of GaP with emphasis on selective etching over AlGaP


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(Received 12 June 2002; accepted 3 September 2002)

A technique to etch GaP by reactive ion etching was developed and the effects of different etching parameters were studied. Also, selective etching of GaP over AlGaP was examined and demonstrated. Etching is achieved by using SiCl4, which will react with GaP to form volatile compounds. Selective etching is accomplished when SiF4 is used in addition to SiCl4. The addition of the fluorine-based gas will result in a nonvolatile etch-inhibiting layer, AlF3, when aluminum is present on the sample surface. By adjusting etching parameters, a selectivity as high as 126 is demonstrated. The presence of the AlF3 etch-inhibiting layer is verified by Auger electron spectroscopy, and the removal of this layer by buffered oxide etch is demonstrated. In addition, a direct comparison of etch rates for GaP and GaAs was made, and etch rates were found to be similar.

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I. INTRODUCTION

Etching and selective etching are important aspects of semiconductor processing. Photonic devices such as vertical cavity surface emitting lasers, transport devices such as heterojunction bipolar transistors, and even microelectromechanical systems require the capability of etching and selective etching. Selective etching has been achieved with various materials heteroepitaxially grown on GaAs, InP, InAs, and GaN. Material systems. With regard to the GaP-based material systems, some groups have demonstrated the ability to wet etch both GaP and AlGaP and have reported etching selectivity of AlGaP over GaP. However, selective removal of GaP on AlGaP and dry etching of GaP have not been demonstrated.

Etching of the GaAs/AlGaAs material system has been achieved by dry etching using chlorine-based gases and selective etching has been performed using a mixture of chlorine- and fluorine-based gases. This etch chemistry has been used to demonstrate a selectivity of GaAs over AlGaAs as high as 500. Some gas choices are BC13 or SiCl4 for the chlorine source and SF6 or SiF4 for the fluorine source. In reactive ion etching (RIE), chlorine-based gases are effective etchants of both GaAs and AlGaAs due to the formation of volatile compounds. However, fluorine will react with aluminum and form a nonvolatile compound AlF3, which is not removed in standard chlorine plasmas. If the F:Cl ratio is high enough, a uniform AlF3 layer will form which will effectively stop the etching of the aluminum-based material altogether. Hence, etching selectivity is achieved. In this article, we report the selective etching of GaP on AlGaP by RIE using a mixture of SiF4 and SiCl4. We also show that GaP can be easily etched, having etch rates similar to those of GaAs under identical processing conditions.

II. EXPERIMENT

The AlGaP material used in these experiments was grown by metalorganic chemical vapor deposition. The first sample consisted of 5000 Å Al0.6Ga0.4P on a GaP substrate. An additional sample was grown in which 5000 Å of Al0.6Ga0.4P was buried beneath 1000 Å of GaP on a GaP substrate. The first sample was used to measure the etch rate of Al0.6Ga0.4P. The second sample was used to verify that a buried Al0.6Ga0.4P layer had the same etching behavior as the exposed layer does and to assure selectivity was not due to any native surface oxide. The GaP material used for the study was n-type substrate material and GaAs was semi-insulating substrate material. All samples utilized on-axis (100) substrates. Samples were cleaned by wet chemical processes. Then, standard photolithography was performed to create a photoresist mask consisting of 50 μm stripes separated by 50 μm. After etching, the photoresist was removed with a photoresist stripper and etch depths were measured using a surface profilometer.

Various process conditions were explored for this study. The F:Cl ratio was varied among pure fluorine, 9:1, and 4:1.
In varying the gas compositions, the SiCl$_4$ was kept at a constant flow rate of 2 sccm while SiF$_4$ was changed to 8 or 18 sccm. The rf power was varied between 30 and 60 W and the chamber pressure was varied between 20, 40, and 60 mTorr. Various conditions were tested to obtain the selectivity and calculate the etch rate for GaP. For comparison, GaAs was etched concurrently and the results were compared. In addition, to test the etching capability of SiF$_4$ on GaP, one sample was etched in a SiF$_4$ plasma with process conditions of 18 sccm SiF$_4$ flow, 40 mTorr chamber pressure, and 30 W power. Table I lists the different tests that were performed.

### III. RESULTS AND DISCUSSION

The etching of GaP using SiCl$_4$ and SiF$_4$ was studied under various conditions. As mentioned above one sample was etched using only SiF$_4$. No etching was seen indicating that fluorine does not contribute to the etching of these materials and is only useful in the reaction with aluminum for selective etching purposes. The results of changing process pressure and power on etch rates using a 9:1, SiF$_4$:SiCl$_4$ gas mixture can be seen in Fig. 1. Figure 1(a) shows the etch rates of GaP, GaAs, and Al$_{0.6}$Ga$_{0.4}$P with respect to pressure at a power of 30 W. Due to extremely slow etch rates for Al$_{0.6}$Ga$_{0.4}$P, those numbers are multiplied by 5 so they can be readily readable in Fig. 1(a). From the plot it can be seen that GaAs had a consistently faster etch rate, which was \sim 50% greater than that of GaP. It can also be seen that the etch rate gradually increased with pressure. GaP etch rates varied from 49 to 81 nm/min, while GaAs etch rates varied from 69 to 129 nm/min. Figure 1(b) shows the same process with 60 W of power. Under these conditions it can be seen that the etch rates of GaP and GaAs are much closer and are almost equal at the highest pressure condition, 135 nm/min compared to 142 nm/min for GaP and GaAs, respectively. It can also be seen that pressure has a much greater effect on etch rate at the higher power condition with the etch rate increasing more than 50%, from 84 to 135 nm/min for GaP, when the pressure is increased from 40 to 60 mTorr. In all cases it can be seen that the etch rate of Al$_{0.6}$Ga$_{0.4}$P is very slow, ranging from 0.6 to 2.8 nm/min. This slow etch rate makes high selectivity possible.

Selectivity was measured by comparing results of Al$_{0.6}$Ga$_{0.4}$P and GaP samples etched under identical conditions. Effects of process parameters are demonstrated in Fig. 2. With a F:Cl ratio of 9:1, the selectivity does not change greatly with a change in pressure when using the lower power setting of 30 W. However, when 60 W is used the selectivity is very dependent on pressure with a maximum value of 124 at a pressure of 60 mTorr. For pressure values of 20 and 40 mTorr, lower selectivity was noticed at the higher power condition due to a higher Al$_{0.6}$Ga$_{0.4}$P etch rate.
under these conditions. With a F:Cl ratio of 4:1, the results are analogous. It can be noted that the etch rate of Al$_{0.6}$Ga$_{0.4}$P was very similar for the two different ratios of F:Cl. However, for certain conditions the etching of GaP can be slightly faster with a lower F:Cl ratio due to less diluting of the etching gas. This is seen in Fig. 2 for the low-power etch in which the maximum selectivity rises from 81 to 107 when the F:Cl ratio lowers to 4:1. The maximum selectivity achieved at 60 W of power and a ratio of 4:1 was 126. This indicates that even with a lower amount of fluorine in the gas mixture, AlF$_3$ is still able to form without difficulty. More on the formation of AlF$_3$ will be discussed in the next section.

To verify that the selectivity has little to do with the native surface oxide on the Al$_{0.6}$Ga$_{0.4}$P layer, several etches were performed in which the Al$_{0.6}$Ga$_{0.4}$P layer was buried beneath 1000 Å of GaP. The etch properties of these samples were consistent with those samples with a single Al$_{0.6}$Ga$_{0.4}$P layer.

IV. FORMATION AND REMOVAL OF ETCH STOP LAYER

The mechanism for this GaP/AlGaP selective etch is in the formation of the AlF$_3$ etch-inhibiting layer on AlGaP. Under the plasma etching conditions, the presence of aluminum in the sample and fluorine in the plasma make possible the formation of AlF$_3$ that cannot be etched chemically by either SiF$_4$ or SiCl$_4$. Thus, an etch stop layer is formed that will prevent any further etching into AlGaP. The important factor in the formation of this etch stop layer is the presence of enough aluminum and fluorine to form the etch stop layer before the chlorine can etch away the aluminum present on the surface. Thus, higher amounts of aluminum and fluorine are necessary for the etch stop layer formation. In this work, an Al$_{0.6}$Ga$_{0.4}$P sample and a SiF$_4$/SiCl$_4$ plasma with a F:Cl ratio as low as 4:1, was found to contain a sufficient amount of aluminum and fluorine to form an etch stop layer before further etching could occur. The presence of this etch stop layer can clearly be seen in Fig. 3. Figure 3(a) shows Auger electron spectroscopy (AES) data of the Al$_{0.6}$Ga$_{0.4}$P sample following a typical etch. Aluminum, fluorine, oxygen, and carbon are the major elements detected with a very small gallium peak. This indicates very clearly the formation of an aluminum/fluorine-based layer on the surface. Meanwhile any trace of gallium on the surface that is not protected by the etch stop layer is etched away.

For device factors, the AlF$_3$ by-product etch stop layer may not be desirable. Therefore, it is important to ensure this etch stop layer can be removed from the sample to prevent any adverse electrical or optical effects of this layer. To remove the etch stop layer, a 2 s dip in BOE diluted (1:10) with DI water was used. The AES data for the sample after this process is shown in Fig. 3(b). It is seen that the fluorine originally present on the surface is completely removed after the dip in BOE, as is a large amount of aluminum. Also, the gallium and phosphorus peaks increase to be slightly higher than the aluminum peak. One negative effect of the BOE dip is that it will also etch AlGaP. Thus, the BOE surface treatment must be controlled.

V. CONCLUSION

This work demonstrated the capability to etch GaP using RIE techniques and to do so in a way that will not etch an AlGaP layer buried underneath. This selective etching was performed using a mixture of SiCl$_4$ and SiF$_4$, in which the SiCl$_4$ was the etching agent. The released chlorine ions react with aluminum, gallium, and phosphorous to etch the material. However, the SiF$_4$ reacts with aluminum to form nonvolatile AlF$_3$. This material is not etched in RIE by either gas and is thus only removed by sputtering. As a result, the etch rate becomes extremely slow and a high etch selectivity is achieved. It is important to be able to remove this etch stop layer for purposes of device fabrication, and this was found to be possible with a surface treatment using diluted BOE. Thus, the capability to selectively etch GaP over AlGaP has been demonstrated and the nonvolatile etch-inhibiting layer can be easily removed.

ACKNOWLEDGMENTS

The authors would like to thank the staff at the Materials Research Laboratory, and Nancy Finnegan for technical assistance. The AES was carried out in the Center for Microanalysis of Materials, University of Illinois, which is supported by the U.S. Department of Energy under Grant No. DEFG02-91-ER45439. This work is supported by DARPA under Grant No. DAAG55-98-1-0303.