In-situ Etching of β-Ga$_2$O$_3$ Using Tert-Butyl Chloride in an MOCVD System

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Abstract

β-Ga$_2$O$_3$ is an exciting ultra-wide bandgap semiconductor because of its potential in power electronic devices and other applications. One research area unexplored until now is the use of a tert-butyl chloride (TBCl) precursor to etch β-Ga$_2$O$_3$ *in-situ* in a metal-organic chemical vapor deposition (MOCVD) system. We report the successful etching of both heteroepitaxial and homoepitaxial β-Ga$_2$O$_3$ films. In this paper, we explore the effect of different parameters (TBCl flow, temperature, and pressure) on etch rate and the activation energy of etching. We also evaluate the impact of TBCl etching on homoepitaxial sample morphology via AFM. Further optimization of *in-situ* TBCl etching aimed at developing regrown ohmic contacts will push β-Ga$_2$O$_3$ device performance.

1. Introduction

The ultra-wide bandgap semiconductor β-Ga$_2$O$_3$ has garnered attention for its potential in power electronics, solar-blind UV photodetectors, and point-of-load voltage converters.[1] This potential is enabled by the ~4.9 eV bandgap in β-Ga$_2$O$_3$, leading to a higher breakdown voltage than other semiconductors.[1] Progress in β-Ga$_2$O$_3$ research has been spurred by the production of high-quality bulk crystalline substrates, allowing the growth of epitaxial films with precise thickness and doping across a range of n-type donor concentrations.[1] Metal-organic chemical vapor deposition (MOCVD) has emerged as a promising technique for producing high-mobility epitaxial β-Ga$_2$O$_3$. By adding an additional precursor, *in-situ* etching (ISE) of β-Ga$_2$O$_3$ can be achieved.

MOCVD ISE involves injecting a precursor into the growth chamber, which reacts with already-grown material to remove it. We report the first use of the precursor tert-butyl chloride (TBCl) to perform ISE of β-Ga$_2$O$_3$ in an MOCVD system. TBCl ISE of β-Ga$_2$O$_3$ may improve the performance of β-Ga$_2$O$_3$-based devices.

Over the summer I carried out a systematic study to elucidate the effect of various MOCVD parameters (TBCl flow, substrate temperature, and chamber pressure) on the etch rate and surface morphology of β-Ga$_2$O$_3$ films. We found that increasing TBCl molar flow causes an increase in the etch rate of heteroepitaxial films and that the etch rate and activation energy are dependent on temperature and pressure. We also found through AFM measurements of homoepitaxial β-Ga$_2$O$_3$ that etching induces roughening, but subsequent regrowth can recover some damage. Future work includes selective-area etching and regrowth towards improved ohmic contacts in β-Ga$_2$O$_3$-based devices.

2. Methods

Etching was performed with an Agnitron Agilis 100 MOCVD system. Both heteroepitaxial films, grown on c-plane sapphire, and homoepitaxial films, grown on Fe-doped (010) β-Ga$_2$O$_3$, were successfully etched. For heteroepitaxial films, etching was completed at chamber pressures of 15 and 30 Torr, temperatures between 700 and 1000 °C, and molar flows between 20.45 and 61.36 μmol/min. For homoepitaxial films, etching was completed at 30 Torr, 875 °C, and 61.36 μmol/min. A UV-vis optical reflectometry setup was used to measure the thickness of heteroepitaxial films. Atomic Force Microscopy (AFM) was used to evaluate surface morphology of homoepitaxial samples using an Asylum Research Cypher ES.

3. Results and Discussion

Etch parameters were explored extensively with heteroepitaxial β-Ga$_2$O$_3$ films grown on sapphire. We mapped the etch rate of heteroepitaxial films as a function of TBCl molar flow at several temperatures, shown in Figure 1. Holding pressure constant at 15 Torr, we found that etch rate increases linearly with TBCl molar flow between 20.45 and 61.36 μmol/min.
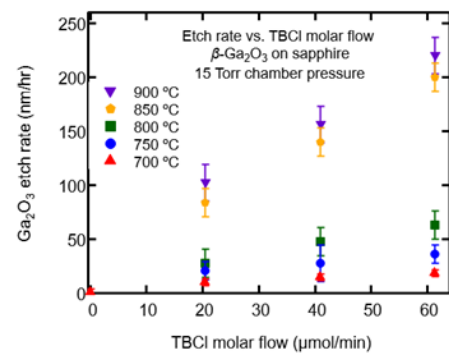

Figure 1: Etch rate of β-Ga$_2$O$_3$ as a function of TBCl molar flow. Five different temperatures are included in this plot, as indicated in the legend. At all temperatures, increasing the molar flow between 20.45 and 61.36 μmol/min results in a linear increase in etch rate.

Holding molar flow fixed and only increasing temperature also causes the etch rate to increase, a trend explored further in Figure 2. Between 700 and 850 °C, the etch rate at each molar flow increases by a greater amount at higher temperatures—i.e., the etch rate increase between 800 and 850 °C is greater than the etch rate increase between 700 and 750 °C. However, the etch rate increase between 850 and 900 °C is modest. As an explanation, we turn to Figure 2, which displays an Arrhenius plot of etch rate of heteroepitaxial films. Both 15 Torr (green) and 30 Torr (blue) are shown. From this plot, the activation energy of etching (and thus the change in etch rate in response to changing temperature) was found to be dependent on both temperature and pressure. This indicates that different steps of the etch process limit the etch rate and thus determine the activation energy between these two temperature regimes.
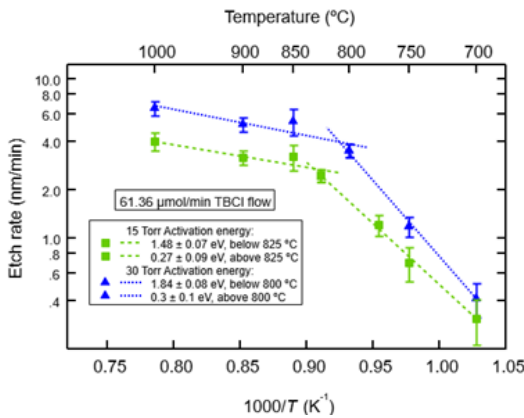

Figure 2: Activation energy of etching. This Arrhenius plot shows the etch rate of β-Ga_2O_3 on a logarithmic scale as a function of inverse temperature. The slope of the lines corresponds to the activation energy of etching, indicated in the legend. Both 15 and 30 Torr data are shown. As seen in the different slopes of the best fit lines in this plot, the activation energy of etching depends on both temperature and pressure.

To explain the different temperature regimes in Figure 2, we address the mechanism of β-Ga_2O_3 etching. We propose the following. First, TBCl dissociates into HCl and isobutene:

$$(CH_3)_3CCl(g) \rightarrow iso-C_4H_8(g) + HCl(g). \tag{1}$$
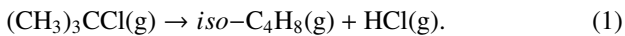
Next, HCl reacts with β-Ga_2O_3 to form $GaCl_3$ and H_2O:

$$Ga_2O_3(s) + 6HCl(g) \rightleftharpoons 2GaCl_3(g) + 3H_2O(g). \tag{2}$$

We propose that at low temperatures, reaction 1 limits the etch rate and determines the activation energy. A 1964 paper on the thermal dissociation of TBCl reports an activation energy of 2.01 eV for this reaction.[2] We observe a low-temperature activation energy of 1.48 eV at 15 Torr, and 1.84 eV at 30 Torr. Although these values differ from what has been reported in the literature, our work takes place at lower pressures. We observe that increasing pressure corresponds to increasing activation energy, and the work of Tsang takes place at higher pressures (85 Torr and above) and reports a higher activation energy than our results, thereby following the trend we observe.[2] The precedent of earlier literature suggests that reaction 1 determines the low-temperature etch activation energy. Given that

the high-temperature activation energy is significantly lower than at lower temperatures, we conclude that some etch-related process besides the thermal dissociation of TBCl limits the etch rate at high temperatures. One candidate is reaction 2.

We also evaluated the surface morphology of etched homoepitaxial surfaces via AFM to inform whether TBCl etching damages the β-Ga_2O_3 surface. We find that etching causes the β-Ga_2O_3 surface to roughen, but that most of this damage can be removed by regrowth of β-Ga_2O_3 on an etched surface. Figure 3 shows AFM of β-Ga_2O_3 surfaces with RMS roughness values reported.

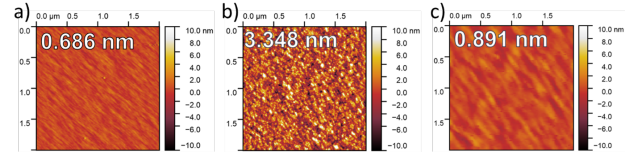
Figure 3: AFM of various surfaces. Panel a) shows an as-grown epitaxial layer of β-Ga_2O_3, panel b) shows β-Ga_2O_3 that was etched to a depth of approximately 50 nm, and panel c) shows a substrate that was etched to a similar depth, and approximately 200 nm of β-Ga_2O_3 was immediately grown on top. RMS roughness values are appended to each panel. The etched surface is roughest (panel b), while the etched-and-regrown surface (panel c) is nearly as smooth as the as-grown surface (panel a).

4. Conclusions

In this paper, the etching of β-Ga_2O_3 by TBCl in an MOCVD system was reported. The effect of susceptor temperature, chamber pressure, and TBCl molar flow on etch rate was explored for heteroepitaxial β-Ga_2O_3. The etch rate scaled linearly with TBCl flow across temperatures between 700 and 900 °C, and the activation energy of etching was found to depend on both temperature and pressure. Homoepitaxial β-Ga_2O_3 was etched and the resulting surface morphology was assessed. Although etching roughens the β-Ga_2O_3 surface, a smooth surface morphology can be recovered by regrowth of β-Ga_2O_3 on an etched surface. Future work includes finding a suitable material to mask β-Ga_2O_3 films. This will enable selective area etching and regrowth of β-Ga_2O_3 aimed at making high-quality ohmic contacts and improving β-Ga_2O_3 power electronics.

References

1. Tadjer, J. M.; Toward gallium oxide power electronics. Science 378, 724-725 (2022). 10.1126/science.add2713.

2. Tsang, W.; Thermal decomposition of some tert-butyl compounds at elevated temperatures. J. Chem. Phys. 40 (6), 1498-1505 (1964). doi.org/10.1063/1.1725353.