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### Comparison of AlGaAs Oxidation in MBE and MOCVD Grown Samples\*

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#### ABSTRACT

Simultaneous wet-thermal oxidation of MBE and MOCVD grown  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  layers ( $x = 0.1$  to  $1.0$ ) showed that the epitaxial growth method does not influence the oxidation rate. Nearly identical oxidation depths were measured for samples grown by both techniques. It was found, however, that the oxidation rate is very sensitive to non-uniformities in the Al concentration in the  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  layers, and that maintaining consistent and uniform Al concentrations is critical to achieving reproducible oxidation rates. The study also showed that the oxidation rate was not affected by the V/III ratio during growth nor by impurities at concentrations less than or equal to 10 ppm.

#### INTRODUCTION

Native oxides formed by wet-thermal oxidation of  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  are playing increasingly important roles in optoelectronic devices such as vertical cavity surface emitting lasers (VCSELs) [1, 2, 3]. They are also being considered for the gate material in field effect transistors (FET) [4]. In spite of the growing importance of these native oxides, there are several issues that complicate their use, including mechanical stability and fabrication reproducibility.

The multi-layers for VCSEL devices are fabricated by molecular beam epitaxy (MBE) [5, 6] or metal organic chemical vapor deposition (MOCVD) [7, 8]. The MBE-grown AlGaAs layers are sometimes pseudo or digital alloys, rather than the random alloys grown by MOCVD. Specifically, the MBE layers are made up of very thin (0.5 to 6 nm) alternating layers of AlAs and AlGaAs or GaAs rather than a single true AlGaAs. Other differences between these growth techniques are that MBE uses solid sources for growth under ultra high vacuum, while MOCVD uses organic precursors at pressures close to ambient. The purpose of this study is to investigate how these two growth methods and different growth systems affect the wet-thermal oxidation of AlGaAs. The effects of V/III ratio during growth and impurity concentrations on the oxidation rate are also reported.

#### EXPERIMENTAL PROCEDURES

Three labs provided four specimens for the study. One wafer was fabricated by MBE and the others were grown by MOCVD. In addition to the already mentioned differences between these two growth techniques, the MBE sample was grown at a lower temperature, 600°C, and at a slower rate, GaAs-0.18/AlAs-0.3/AlGaAs-0.52 nm/sec. The MOCVD samples were grown at 720°C, with MOCVD1 grown at 1.5 nm/sec, MOCVD2 at 0.6 nm/sec, MOCVD3 at 1.0 and 1.5 nm/sec. Three of the wafers had nominally identical structures with different AlGaAs layers ranging in composition from 90 % Al ( $\text{Al}_{90}\text{Ga}_{10}\text{As}$ ) to 100 % (AlAs), in increments of 2 %. The fourth sample, MOCVD3, had three sets of

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layers grown with V/III ratios of 90, 130 and 260. This sample had only 94, 96, 98 and 100 % AlGaAs layers.

Samples cleaved from the wafers were photolithographically patterned and wet-chemically etched, with  $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2:\text{H}_2\text{O}$  (6:1:40), to form 11 parallel grooves along [011] exposing the AlGaAs layers for oxidation. Simultaneous wet-thermal oxidation of a set of samples was carried out at 460 °C for either 10 or 20 min. Nitrogen was used as the carrier gas (2.5L/min) bubbling through a water bath maintained at 75 °C. After oxidation the samples were cleaved and the oxide depths measured with scanning electron microscopy (SEM). Some difficult measurements were verified with field emission SEM (FESEM) imaging. The largest variation of oxidation depth for different grooves in a single sample was 5 %. Secondary ion mass spectroscopy (SIMS) analysis of unoxidized samples was used to obtain concentrations of potential impurities, as well as to compare relative Al and Ga concentrations.

## RESULTS AND DISCUSSION

### Oxidation Results

Figure 1 is an SEM image of the cleaved edge of an oxidized sample. The arrows point to the oxidized/unoxidized interface in the AlGaAs layers. The measured oxidation rates for samples MBE1, MOCVD1 and MOCVD2 are plotted in figure 2. MBE1 and

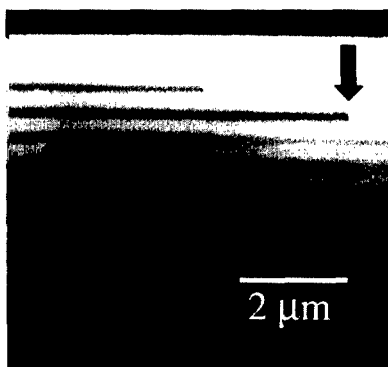


Figure 1. Oxidation front indicated by arrows in SEM image. Charging at the top surface made measurement near the surface difficult.

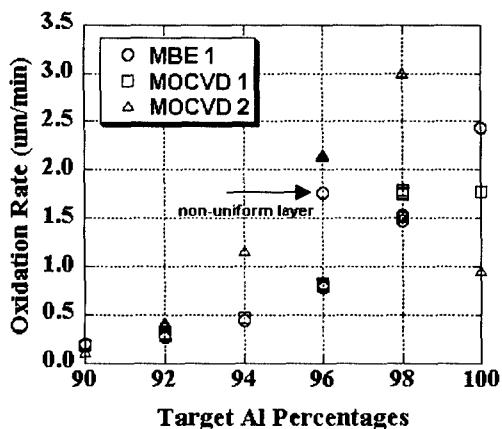


Figure 2. Oxidation rate for wafers grown by MBE and MOCVD. 20 min oxidation at 460°C with flow rate of 2.5L/min. Lower Al composition layers had very similar oxidation rates.

MOCVD1 had similar oxidation rates from 90 to 98 % Al, and the rate increased exponentially with Al composition, up to 98 %. The oxidation rates for 90 to 98 % Al layers in MOCVD2 were much higher than both the MBE1 and MOCVD1 rates, except for the AlAs layer.

Oxidation rates found for 90 to 98 % Al layers in MBE1 and MOCVD1 are in the same range as data reported previously [7,9]. The small differences in oxidation rates are probably due to the differences in oxidation process parameters such as oxidation time, oxidation temperature, bubbler temperature, gas flow rate and AlGaAs layer thickness.

Unlike those of the lower-Al-content layers, the oxidation rates of the 100 % Al layers vary widely and are quite different from those reported by other labs. The oxidation rate of the AlAs layer was highest in sample MBE1, but it is low relative to an extrapolated exponential fit to the data for lower Al concentrations. In MOCVD1 the oxidation rate was the same for the 98 and 100 % Al layers. Most unexpectedly, the oxidation rate of the AlAs layer in MOCVD 2 was lower than the rates for the 98, 96 and 94 % Al layers. These results do not agree with previous studies where the oxidation rate increased exponentially with Al composition from 90 to 100 % Al [7, 10]. While differences in the oxidation process may account for some of this variation, it is difficult to understand these results.

In order to eliminate potential sources of variation, the samples of each set were processed, etched and wet-thermally oxidized simultaneously. The oxide depths were very reproducible, with mean variations of less than 2 % for multiple samples from the same wafer. The observed variations, therefore, are unlikely to have been caused by the sample processing. The most probable cause of the variations is in the materials themselves and this likely results from the growth process. To investigate this, the V/III ratio, impurities and Al/Ga concentrations have been studied.

#### V/III Ratio Study

V/III ratio affects defect formation in epitaxial material, and diffusion in AlGaAs can be influenced by defect concentration [11, 12]. Therefore, V/III ratio could affect the wet oxidation rate since the oxidation process is a combination of diffusion and surface reactions.

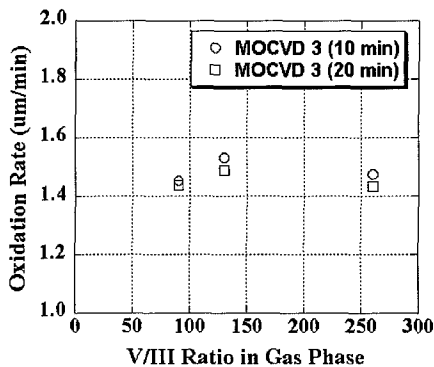


Figure 3. Dependence of oxidation rate on V/III ratio for  $\text{Al}_{0.98}\text{Ga}_{0.02}\text{As}$ , 460°C, 2.5 L/min, for 10 min and 20 min. No obvious correlation is evident exists between V/III ratio and oxidation rate.

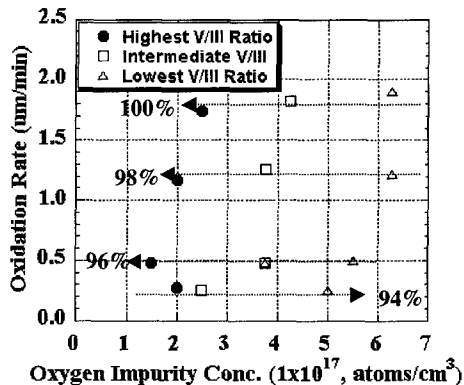


Figure 4. Oxygen impurity concentration did not affect the oxidation rate when impurity levels were less than or equal to 10 ppm. Arrows indicate the same Al% for different V/III ratios.

Wafer MOCVD3 was grown with three different V/III ratios to study the effect of V/III ratio on the oxidation rate. Figure 3 shows that the oxidation rate does not depend on the V/III ratio.

#### Impurity Analysis

Impurities may be incorporated in the wafers from background levels in the growth chamber or from the source materials. Oxygen and hydrogen are known to affect the oxidation process [13, 14], so their presence in the wafer as impurities may affect the oxidation rate. Low V/III ratios during growth are known to increase impurity concentrations in AlGaAs layers[15]. SIMS analysis was used to obtain the concentrations of O, H, C and Si in the un-oxidized wafers. The analysis confirmed that the impurity concentrations decreased with increasing V/III ratio (see Figure 4) and showed that, for all of the samples, the impurity concentrations were less than or equal to 10 ppm. Figure 4 shows that the oxygen impurity did not affect the oxidation rate. The rate was independent of the other impurities studied as well.

#### Al and Ga Concentrations

SIMS analysis was also used to examine the Al and Ga concentrations in the un-oxidized wafers. Depth profiles for MBE1 and MOCVD1 are shown in Figure 5. Both of these samples had uniform Al concentrations within each AlGaAs layer and the peak Al concentration matched the designed concentration. However, there was a spike in Al concentration in one of the 96 % AlGaAs layers in MBE1. That layer had a faster oxidation rate than the other 96 % layers in MBE1 (see Figure 2). From the SIMS analysis, the measured peak Al concentration for this particular "96 %" layer was actually 97.5 %, which is consistent with the faster oxidation rate measured for that layer.

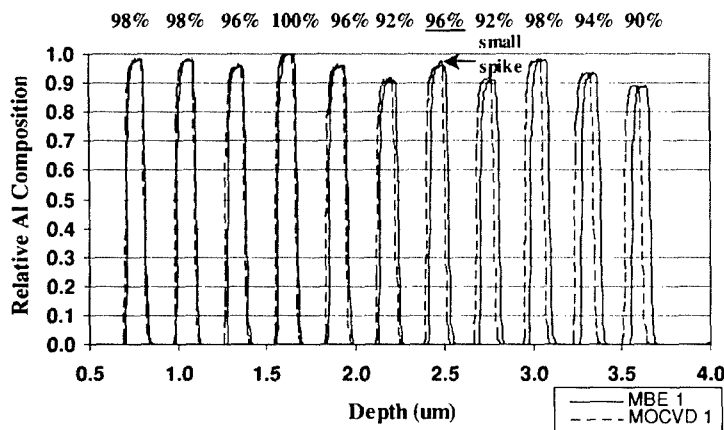


Figure 5 SIMS analysis showing uniform layer structure and Al concentration, in all but one 96 % layer in MBE1.

Non-uniformity in Al concentration was observed in almost all of the AlGaAs layers in MOCVD2 (see Figure 6). Most of the layers had a thin region with an Al content considerably higher than that of the rest of the layer and higher than the designed Al

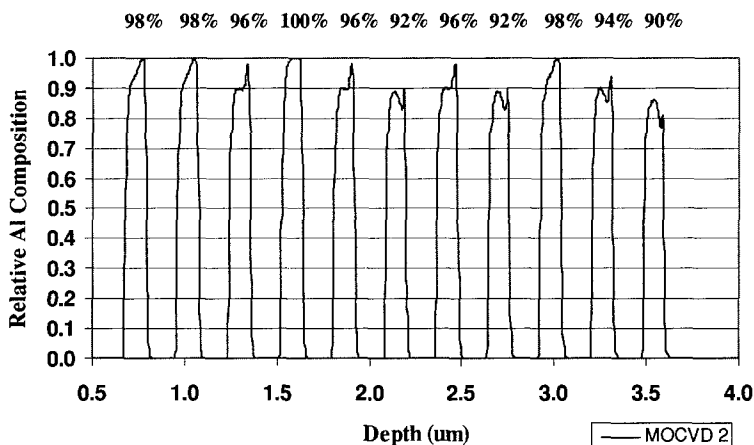


Figure 6. SIMS analysis showing MOCVD 2 has non-uniformity in Al concentration in AlGaAs layers.

concentration. This probably resulted from mass flow controller overshoot at the initiation of the layer growth. The oxidation rates for MOCVD2 were approximately twice as fast as the rates for MBE1 and MOCVD1 (see Figure 2). As shown in Figure 7, this rapid oxidation occurred in the thin region with high Al content. Oxidation rates reported in this paper were measured with reference to the section of the oxidation front that propagated the farthest.

Figure 8 is a plot of the oxidation rates as a function of the peak Al compositions

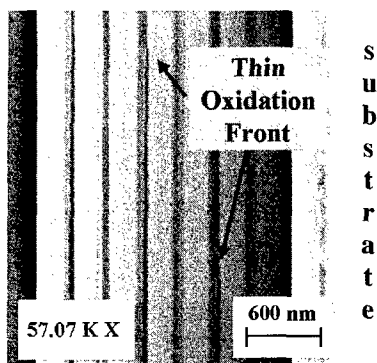


Figure 7. FESEM of MOCVD 2 showing propagation of the oxidation front through the sub-layer having elevated Al concentration.

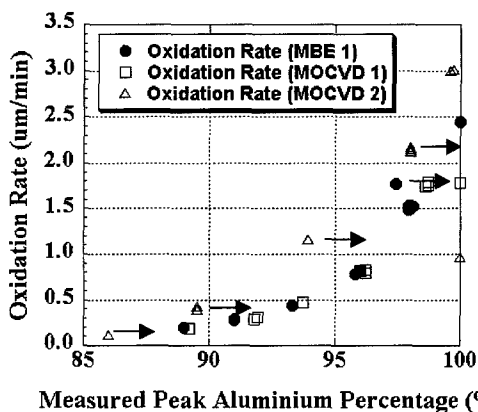


Figure 8. Oxidation rate (20 min oxidation) for all three samples are in better agreement when plotted against the peak Al concentration as measured by SIMS. Arrows indicate actual Al concentrations higher than measured by SIMS, see text.

determined from the SIMS analysis. The actual peak Al concentrations for MOCVD2 and the non-uniform 96 % Al layer in MBE1 are expected to be higher than the data measured by SIMS, as indicated with arrows. This is because intermixing and surface roughness created by sputtering during SIMS will both decrease the maximum Al concentration measured in the thin, high Al content regions. However, the extent of this effect is not certain. This new information about the actual layer compositions shows that the oxidation rates of the 90 to 98 % Al layers for all three samples are in reasonable agreement, considering the non-uniformities in MOCVD2. The cause of the variation in the rates for AIAs has yet to be found; however, experiments are underway to investigate this.

## SUMMARY

In summary, it was shown that the epitaxial growth method (MBE vs. MOCVD) did not affect the wet-thermal oxidation rate of  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  for  $x = 0.90$  to  $0.98$ . It was also found that the V/III ratio, for relatively clean systems, and impurity levels below 10 ppm did not affect the oxidation rate. Apparent differences between samples were found to result from compositional non-uniformities in the AlGaAs layers. These results emphasize the importance of having precise control of the Al concentration in  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  layers so that reproducible oxidation rates can be achieved.

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