Identification and Quantification of Impurities Critical to the Performance of Nitride Semiconductor Devices

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Abstract

AlGaN/GaN HEMT devices were grown under specific experimental conditions designed to elucidate the effects of purification of the ammonia gas. Two different, commercially available, purifiers were tested under identical growth conditions along with three different grades of ammonia. After growth of the AlGaN/GaN layers, the wafers were subjected to Hall measurements where the sheet concentration, and mobility, were determined. The results clearly showed significantly enhanced performance for the inorganic based purifier compared to the resin based organometallic purifier for all experimental parameters tested. Additionally, the nitride devices were subjected to SIMS analysis with depth profiling in an attempt to identify the elemental nature of the impurities that caused the discrepancy in performance results between the various samples. Results from the Hall measurements and the SIMS analysis are presented and correlated to the conditions controlled during the growth of the nitride devices.

Keywords: A1. Characterization; A1. Impurities; A1. Purification; A3. Metalorganic chemical vapor deposition; B1. Nitrides.

1. Introduction

Performance of Gallium Nitride based semiconductor devices can be adversely affected by the presence of entrained impurities. Oxygenated impurities have been investigated and found to be a significant concern to wafer fabrication [1, 2,]. In addition to oxygenated containing impurities, it is expected that electron donating or electron accepting impurities such as silicon, germanium, tin, antimony, sulfur and carbon, can have a negative effect on device performance. The source of the impurities incorporated into the semiconductor layers are thought to originate inherently from the raw materials such as organometallics, ammonia, and hydrogen. Although these source materials are carefully analyzed and fully characterized with the best possible analytical techniques, the levels of impurities determined are typically below detection limit. In cases where the impurity concentration is observable above detection limit, the typical concentration range is ppb to ppt levels. These levels are not typically considered detrimental to device performance. In addition to analyzing and controlling the impurities within the raw source materials, point of use (POU) has also been implemented to minimize impurities incorporated into the semiconductor devices. POU purification has traditionally been used to reduce oxygenated impurities in ammonia, hydrogen, and purge gases such as nitrogen. Furthermore, POU purification has been previously reported to be effective in reduction of oxygenated impurities as observed analytically and with actual device performance results [3]. As reported earlier, the reduction of oxygenated impurities had a direct impact on the forward voltage and light output of LED devices. In addition to oxygenated species removed, the purifier used in this study had the capability to remove dopant impurities. However, the dopant impurities were not studied or characterized during this investigation.

In the current study, oxygenated and dopant impurities have been investigated to determine which impurities are present in the GaN layer, which impurities have a direct impact on performance and what is the critical level of impurities identified within the device. After growth of the AlGaN/GaN layers, the wafers were subjected to Hall measurements where the sheet concentration, mobility, and sheet resistance were determined. Although Hall measurements can be a good indicator of device quality under controlled growth parameters, Hall measurements cannot determine the responsible elemental impurities that cause the performance degradation. As a result, the nitride devices were subjected to SIMS analysis with depth profiling in an attempt to identify the elemental nature of the impurities that caused the discrepancy in performance results between the various samples.

2. Experimental Information

The investigation focused on several different parameters to elucidate the factors that had the greatest impact on device performance. The variables considered within the scope of the investigation included two different purifiers that operate on different principles of operation, three different grades of ammonia gas, and the cylinder level (full or near empty). The purifiers investigated were commercially available models that operate on two different mechanisms for impurity removal. The first purifier was an organometallic resin based purifier (Nanochem® OMA) that operates on the principle of chemisorption. In this type of purifier, the oxygenated species are removed via an irreversible chemical reaction to produce a solid phase product that is not volatile and is not removed from the purifier housing. The second type of purifier used during this study was an inorganic based purifier (Nanochem® NHX-Plus™) that operates on the principle of physisorption. In this type of purifier, the oxygenated species are removed via a reversible adsorption or chemical reaction that captures the desired impurities and the impurities are not released from the purifier housing. The impurities can be released from the purifier if the purifier medium undergoes a regeneration step specifically designed to release the impurities and re-new the purifier for further use.

The ammonia gas used for this study consisted of three different grades. The high grade ammonia used was Matheson Tri-Gas Ultima™ ammonia with a total purity level of 99.99994%. The mid-grade ammonia used was Matheson Tri-Gas ULSI™ ammonia with a total purity level of 99.9995%. The low grade gas was of unknown purity level provided by a local Taiwanese manufacturer and expected to have lower purity level than the high or mid-grade ammonia used for the investigation.

A recent study has demonstrated that gas phase delivery of ammonia can be problematic due to increasing levels of moisture observed as the container is consumed [4]. This effect of increasing impurities is believed to be due to a concentration of moisture in the condensed or liquefied phase of the ammonia as the ammonia is being withdrawn from the gas phase. Towards the end of the cylinder usage, the dissolved moisture is released from the cylinder as the amount of liquefied ammonia diminishes and approaches the point wherein no liquid remains within the cylinder. This commonly observed effect can be detrimental to the device manufacturing and can ultimately cause performance degradation. Therefore, the amount of ammonia remaining in the cylinders during the course of this investigation was carefully monitored and the design of experiments contained herein have attempted to capture this variable in the results obtained. As defined herein, the beginning of the cylinder refers to cylinders that have less than 15% of the gas consumed compared to a full container. The end of the cylinder refers to cylinders that have less than 15% remaining compared to a full container.

All devices were fabricated using an Aixtron

AIX 200 RF MOVPE tool. Wafer diameters were 2 inches and the tool was commercially specialized with a high temperature reactor (1,200℃) for nitride applications. The device structure can be observed in Fig. 1.

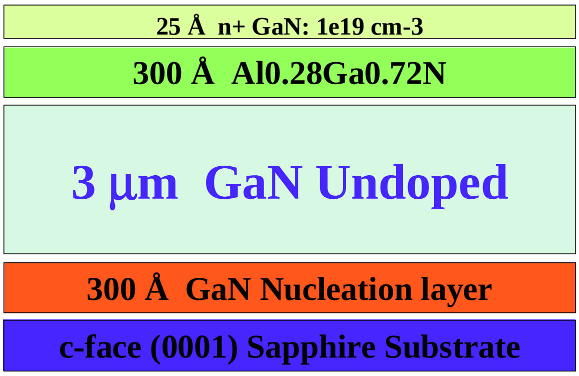

Fig. 1. Structure of devices used for all samples involved with current investigation. Schematic not drawn to scale.

3. Comparison of device performance

The device performance was determined by conducting Hall measurements and comparing the mobility, and sheet concentration of the free charge carriers within the semiconducting device. Furthermore, since the mobility is influenced by the sheet concentration and the vice versa, the product of the mobility and sheet concentration was established as a "Performance Factor." The Performance Factor was then used to compare one sample to another to determine overall device performance. Fig. 2 shows the measured carrier mobility for all the samples included in the investigation. Fig. 3 displays the measured sheet concentration of carriers measured for all the samples included in the investigation. Fig. 4 compares the performance factor for all samples involved with the current investigation.

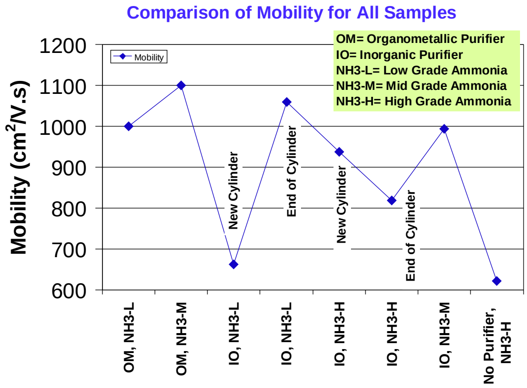

Fig. 2. Carrier mobility results for all samples included within the current investigation.

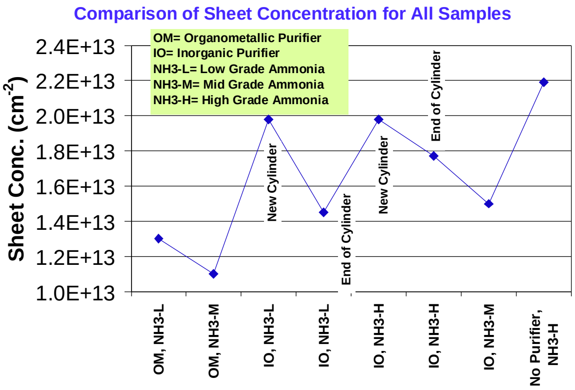

Fig. 3. Sheet carrier concentration for all samples included within the current investigation.

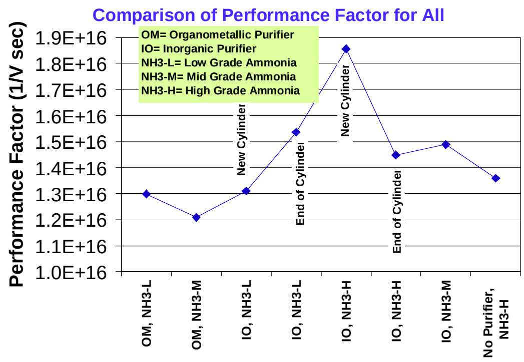

Fig. 4. Comparison of performance factor for all samples included within the current investigation. The performance factor consists of the product of mobility and sheet concentration.

The results from Fig. 4 revealed that the sample with the best overall performance was the device manufactured at the beginning of a high grade ammonia cylinder while the inorganic purifier was used to purify the ammonia gas at the point of use in the gas distribution system. When experimental variables were isolated and samples were compared directly to each other, the following results were obtained. For the first comparison, results obtained from use of the organometallic purifier was compared to results obtained with the inorganic purifier used for low grade ammonia at the end of the cylinder. The results are shown in Fig. 5 and show that the performance factor is larger for the device manufactured with the inorganic purifier with all other variables held constant.

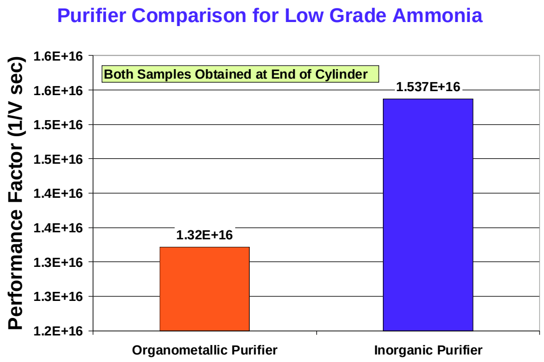

Fig. 5. Performance factor comparison of two different ammonia purifiers using low grade ammonia at the end of the cylinder.

Similar results were obtained with mid-grade ammonia since the performance factor was determined to be 1.21E16 $V^{-1}sec^{-1}$ for devices fabricated with the organometallic purifier compared to 1.49E16 $V^{-1}sec^{-1}$ for devices grown with the inorganic ammonia purifier. Fig. 6 shows results from the performance factor under conditions where the three different grades of gas were used from new cylinders with only the inorganic ammonia purifier. Results indicate that the device performance is improved with improving quality of ammonia gas.

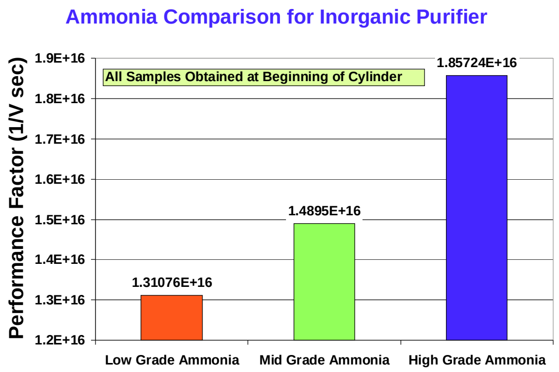

Fig. 6. Performance factor comparison of three different ammonia sources at the beginning of the cylinder while purifying with the inorganic purifier medium.

For the final purifier comparison, devices were fabricated under conditions using high grade ammonia at the end of the cylinder while using an inorganic purifier and comparing these results to the performance factor for devices grown under the same experimental circumstances, however no purifier of any kind was used. The performance factor data for this comparison is shown in Fig. 7.

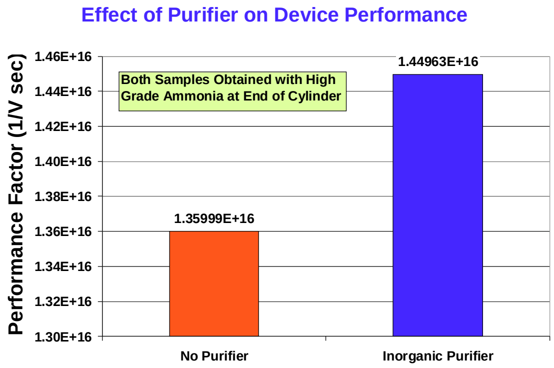

Fig. 7. Performance factor comparison for GaN device grown with an inorganic purifier compared to a device grown without ammonia purification of any kind. The devices were fabricated using high grade ammonia at the end of the cylinder.

The results indicate that use of the inorganic purifier can enhance the device performance even for high purity ammonia. Overall, the inorganic purifier out-performed the organometallic purifier in all situations under all circumstances.

4. Secondary ion mass spectrometry results

SIMS results were obtained on all samples that were measured for performance factor. The SIMS analysis was conducted for C, O, Si, S, Ge, Sn, and Sb. Relative concentration differences were observed for C, O, and Si, however no difference was observed for S, Ge, Sn, and Sb and results for these elements are not reported. The results obtained for carbon were obtained from samples fabricated with low grade ammonia at the beginning of the cylinder. One sample was grown using the organometallic purifier resulting in a carbon level of 1.8 E16 atoms/cc, while the other sample was grown with the inorganic purifier resulting in a carbon level of 3.0 E16 atoms/cc. The results showed a minor difference in the carbon levels between the purifiers, however it is clear that the organometallic purifier did not contribute excess carbon levels to the GaN device. The results obtained for Si and O from samples grown with inorganic purification compared to samples grown without ammonia purification showed significant differences. The results in Fig. 8 showed elevated levels of silicon and oxygen for the unpurified ammonia sample.

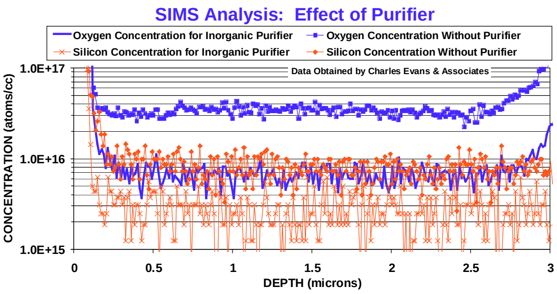

Fig. 8. SIMS results for samples fabricated with and without purification of ammonia.

Similar results were observed for silicon when samples were compared for high grade versus low grade ammonia when both samples were grown with the inorganic purifier. The silicon level for the sample grown with the high grade ammonia was determined to be 2.8E16 atoms/cc and 0.45E16 atoms/cc for the sample grown with the low grade ammonia. Interestingly, the oxygen levels were the same for these two samples, indicating that the purifier removed the oxygenated species to the same level but not the Si levels. In order to ensure the Si concentration fluctuations were not an artifact of the analysis, a single sample was analyzed twice for a measure of repeatability. The results showed that the Si levels were nearly identical with one sample characterized to have a Si level of 0.5 E16 atoms/cc while the Si level from the second sample was determined to be 0.48E16 atoms/cc. The silicon concentration was then measured for four different samples and four different results where selected wherein the Si concentration varied the greatest between the samples. Then the Si concentration was then compared to the performance factor for that sample and the results displayed in Fig. 9.

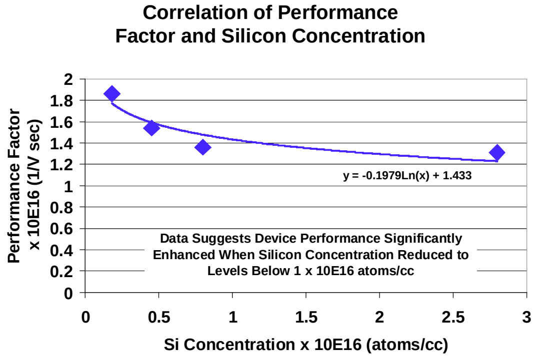

Fig. 9. Correlation of Si concentration to Performance factor for samples tested.

It roughly appears that a logarithmic correlation exists between Si levels and performance factor for the samples tested. Although there appears to a slight correlation between Si concentration and performance factor, there are many other variables that could affect device performance. Therefore the reader is cautioned from drawing strong conclusions from this correlation and the phenomenon requires additional detailed study.

4. Summary

AlGaN/GaN HEMT devices were grown under variable experimental conditions such as ammonia quality, usage level of the cylinder and type of purifier. The two different, commercially available, purifiers were tested under identical growth conditions and results showed that the highest performance factor was achieved with high grade ammonia and the inorganic purifier. When the inorganic purifier was compared directly to the organometallic purifier, the results showed superior performance from the inorganic purifier when tested with low grade and mid grade ammonia while all other variables were held constant. When comparing different ammonia gas grades with the inorganic purifier, the results showed that the performance factor improved as a function of ammonia gas quality. SIMS results of the devices showed a significant difference in Si and O for devices fabricated with and without purification of the ammonia. Similar results were observed for silicon when samples were compared for high grade versus low grade ammonia when both samples were grown with the inorganic purifier. The Si levels of four different samples were then plotted against performance factor and the results showed a possible logarithmic correlation wherein the performance factor appears to increase rapidly if the Si level is below 1 E16 atoms/cc. Additional studies are required since the performance factor can be influenced by many factors involved in the wafer manufacturing process.

References

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