Advances in ammonia purification

SAES Pure Gas outlines the role of improved ammonia gas purification systems in eliminating impurities and variability from nitride LED manufacturing, hence improving LED characteristics.

Light-emitting diodes (LEDs) have begun to gradually replace conventional lighting due to their improvement in light efficiency, superior lifetime, color quality, and the absence of mercury.

The epitaxial growth of gallium nitride (GaN) layers is one of the most challenging steps in the LED manufacturing process. Process gases of a defined quality and reliability are essential in order to continue improving the LED's characteristics. Gas purification is hence commonly used to eliminate variations generated by the gas source and the gas distribution system.

Improved ammonia (NH_3) purification systems have been developed to expand the range of impurities that can be eliminated. This article presents the results obtained with these new NH_3 purification systems using the most advanced analytical techniques.

Introduction

Worldwide energy consumption continues to increase due to the development of emerging economies. Despite the push in many countries for the adoption of renewable energy sources, fossil fuels are by far the primary sources for energy production. In addition to greater adoption of renewable energy sources, a way of decreasing the usage of fossil fuels is to reduce overall energy consumption. It is estimated that lighting consumes approximately 19% of the energy produced worldwide. Significant improvements in the conversion efficiency of electric energy into light will result in an overall reduction in energy usage and thus fossil fuel consumption. Newly developed LED light sources are a great advancement in this direction: the efficiency of LEDs continues to increase and they now exhibit energy consumption that is more than five times lower than the most common tungsten bulbs. The efficiency of LED lighting is also exceeding the efficiency of fluorescent tubes, with the additional advantage of not containing toxic components (such as mercury) that are dangerous for the environment.

For the reasons stated above, the process of replacing conventional light sources with LEDs has started and will almost certainly proceed at a much faster rate in the next 2 or 3 years. In certain applications, such as the backlighting of displays, LEDs have already replaced virtually all traditional lighting.

The lifetime of LED light sources is predicted to be in the range 30,000–50,000 hours. In order to achieve this, the light source must be designed with the following characteristics: an efficient semiconductor material to convert electric energy into light, good thermal management to dissipate the heat and prevent dangerously high operating temperatures, and reliable electronics capable of lasting through countless on/off cycles. Any one of the above parameters can cause premature lamp failure if not properly addressed.

The growth of the epitaxial layers is the most critical step in the preparation of the semiconductor device. The presence of impurities during the deposition steps can alter the quality of the device by increasing the unwanted resistance effect, decreasing the conversion of the input energy into light, and reducing the expected lifetime. Utilizing the correct deposition conditions such as flow rate distribution, temperature, uniformity on the wafer and between wafers ensures good quality epitaxial layer growth. However, gas purity is still essential to minimize defects. In consideration of the above, gas purifiers for N_2, H_2 and NH_3 are normally used in the metal-organic chemical vapor deposition (MOCVD) process not only to minimize the impurity content but also to eliminate the variability between batches of gases, thereby improving the reliability of the final product.

Ammonia purification

NH_3 is the precursor used for the deposition of the GaN layers by MOCVD. Typical specifications for NH_3 purifiers require the removal of oxygen-containing impurities such as oxygen and moisture. Other impurities such as hydrocarbons and metal contaminants can also be present in NH_3, with detrimental effects on the final product.

Since NH_3 is not an inert gas and interacts with the purifier media, the characterization of the purification media must be performed in NH_3 and not in inert gases to avoid incorrectly estimating the capacity of the purifier to remove impurities. However, to avoid high NH_3 consumption and safety-related problems, the correct purifier functionality can be carried out in N_2 instead of

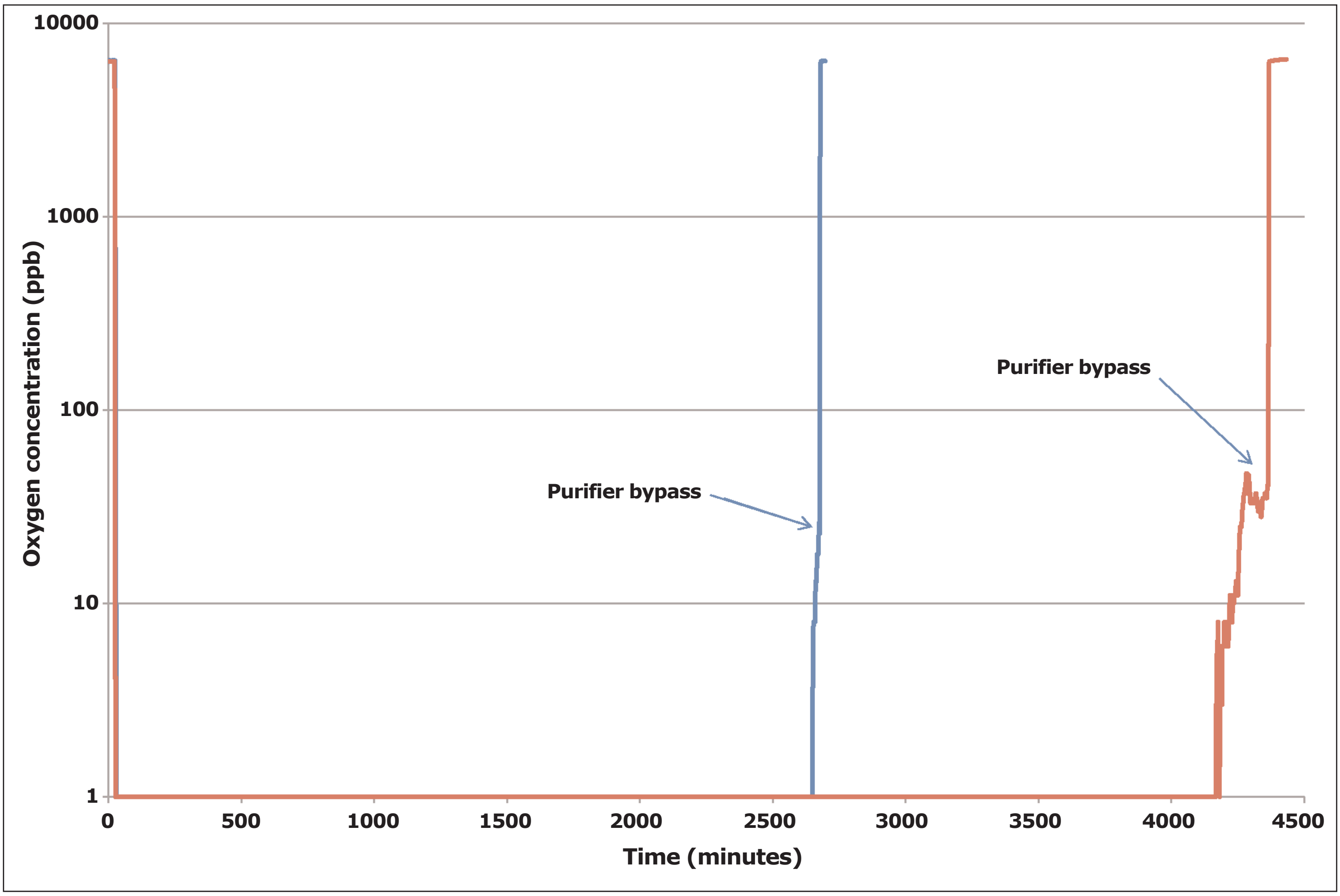

Figure 1, O_2 breakthrough curves in NH_3 for two different NH_3 flow rates and 6ppmV inlet O_2.

NH_3 while still resulting in the same kind of reliability. Testing of the gas line integrity, valve and heater operation, and system dry-down have the same value if carried out in N_2 rather than in NH_3.

This work describes the study of an NH_3 purifier focusing not only on its oxygen and moisture capacity but also on other contaminants that could potentially be present in NH_3. For oxygen and moisture analysis in NH_3, state-of-the-art analyzers like the Delta F DF-740 with a 10ppbV detection limit for water vapor in NH_3 and a Teledyne Ultra Trace 3000 Micro Fuel Cell analyzer — also with 10 part-per-billion (ppbV) detection limit for oxygen in NH_3 — allows real-time measurements of these impurities. In order to measure organic and metal contaminants it is necessary to use a sampling technique to collect and concentrate the impurities to be able to quantify them at a low concentration. Metallic impurities are detected by collecting the metallic compounds with deionized water impingers then analyzing the resulting solution by using inductively coupled plasma mass spectrometry (ICP-MS). Organic contaminants were analyzed by means of a CollectTorr sampling system, which concentrates the organic impurities onto a high surface media, which is then analyzed by thermal desorption gas chromatography mass spectrometry (TD-GC-MS).

The CollectTorr sampling system, which is based on solid sorption material, is also suitable to analyze NH_3 organic contamination in the field. The procedure for sample collection is very straightforward and does not require personnel from the analysis laboratory to be present for sample collection. Once the sample is collected it will then be analyzed in a controlled laboratory environment. The CollectTorr is a suitable and simple way to verify organic contamination in NH_3 used for LED manufacturing.

Results

To limit the amount of NH_3 required for the purifier evaluation, a scaled-down version of an actual purifier was used. The sample of the purification media was tested by flowing purified NH_3 through the unit with the addition of 6 part-per-million (ppmV) of oxygen and 2.5ppmV of moisture. The levels of the impurities used during this testing are higher than those seen in typical NH_3 to avoid carrying out excessively long tests. Figures 1 and 2 show breakthrough curves for oxygen and water vapor, respectively, at two different flow rates. As soon as the purifier is on line, the impurity levels drop down to the detection limit of the analyzers. Once the impurities progressively fill up the capacity of the purification media they start appearing at the purifier outlet. In this way it is possible to know, with a good

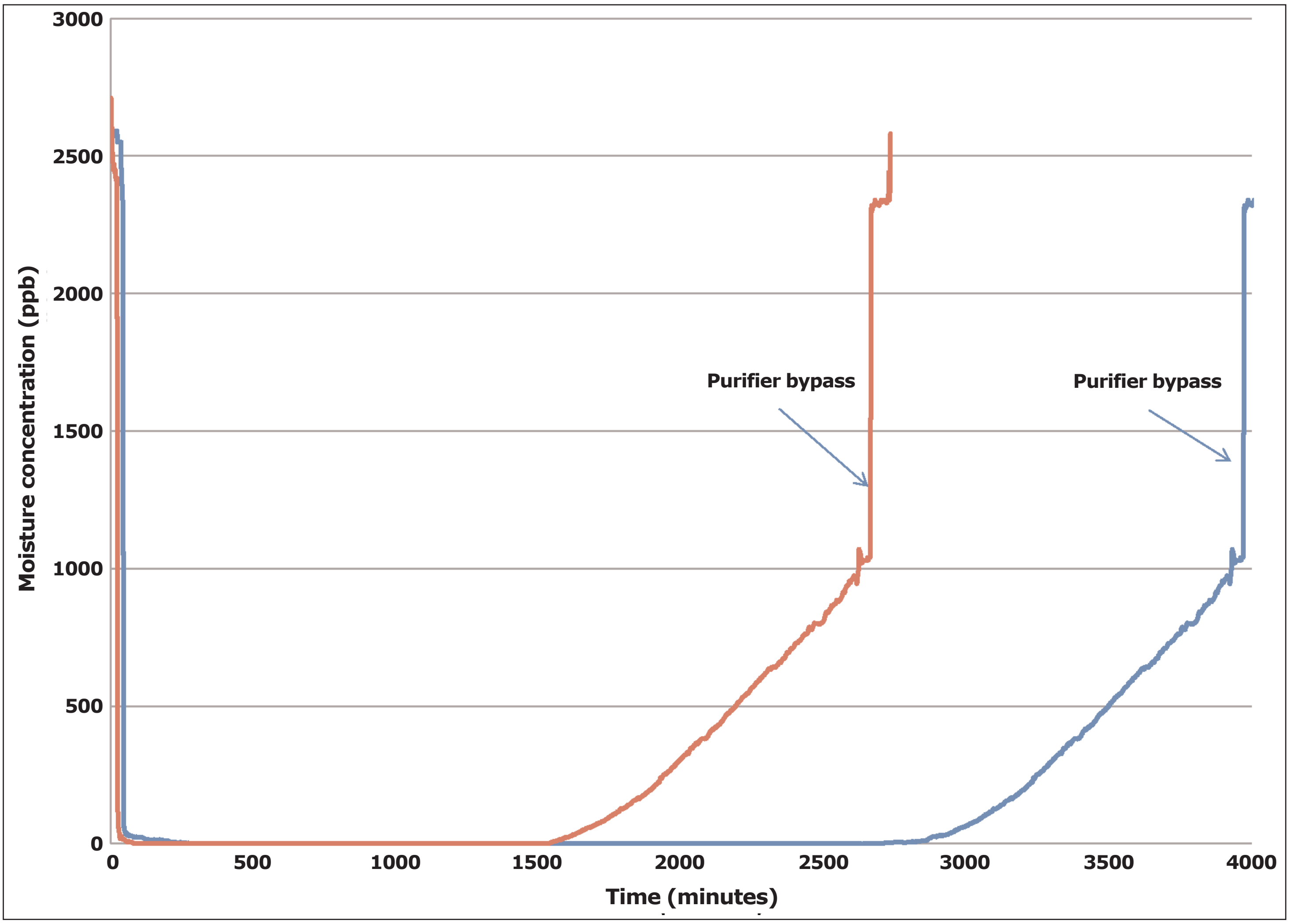

Figure 2. H_2O breakthrough curves in NH_3 for two different NH_3 flow rates and 2.5ppmV inlet H_2O.

degree of accuracy, the quantity of NH_3 that can be purified before regenerating the purification media.

Since the generation of organic compounds is not as easy as the introduction of oxygen and moisture, a sample of low-quality NH_3 was used for evaluating the removal of organic contamination. In this test the purifier was challenged with the 'dirty' NH_3 and the level of contamination of the organic compounds was monitored by means of the CollectTorr sampling system and subsequent TD-GC-MS analysis. Simultaneously, a second CollectTorr sampler was used to collect the organic contamination seen in the unpurified NH_3 gas. Figure 3 shows a direct comparison of the results and how efficiently the purifier can eliminate the organic contamination.

A similar test was carried out to monitor metals removal. The CollectTorr sampling system was replaced by liquid impingers containing deionized water. Table 1 compares the metal contents at the inlet and outlet of the purifier. Although the inlet concentration of the metal contaminants was already quite low, the purifier was able to fully eliminate the measured metals. In addition, the test clearly proved that the reaction between NH_3 and the purification media does not generate any additional metallic contamination.

While it is extremely difficult to correlate the impact of the concentration of an impurity with the quality of the LED epitaxial layers due to the multiple parameters that can affect the epilayers, it is certainly true that the use of a reliable and clean gas can eliminate one of the many variables that could deplete epitaxial layer quality. The

Table 1. Metallic impurities measured in both unpurified and purified NH_3. The following metals were not detected in either sample: Sb, As, Ba, Be, B, Cd, Cr, Co, Cu, Ga, Ge, Au, Fe, Pb, Li, Mg, Mn, Mo, Ni, K, Ag, Sr, Ti, V, and Zr.

Parameter	RL	Units	Purified NH_3 gas	Unpurified NH_3 gas
Aluminum (Al)	0.05	ppb	*	0.42
Calcium (Ca)	0.1	ppb	*	0.3
Sodium (Na)	0.05	ppb	*	0.18
Tin (Sn)	0.01	ppb	*	0.05
Zinc (Zn)	0.05	ppb	*	0.14

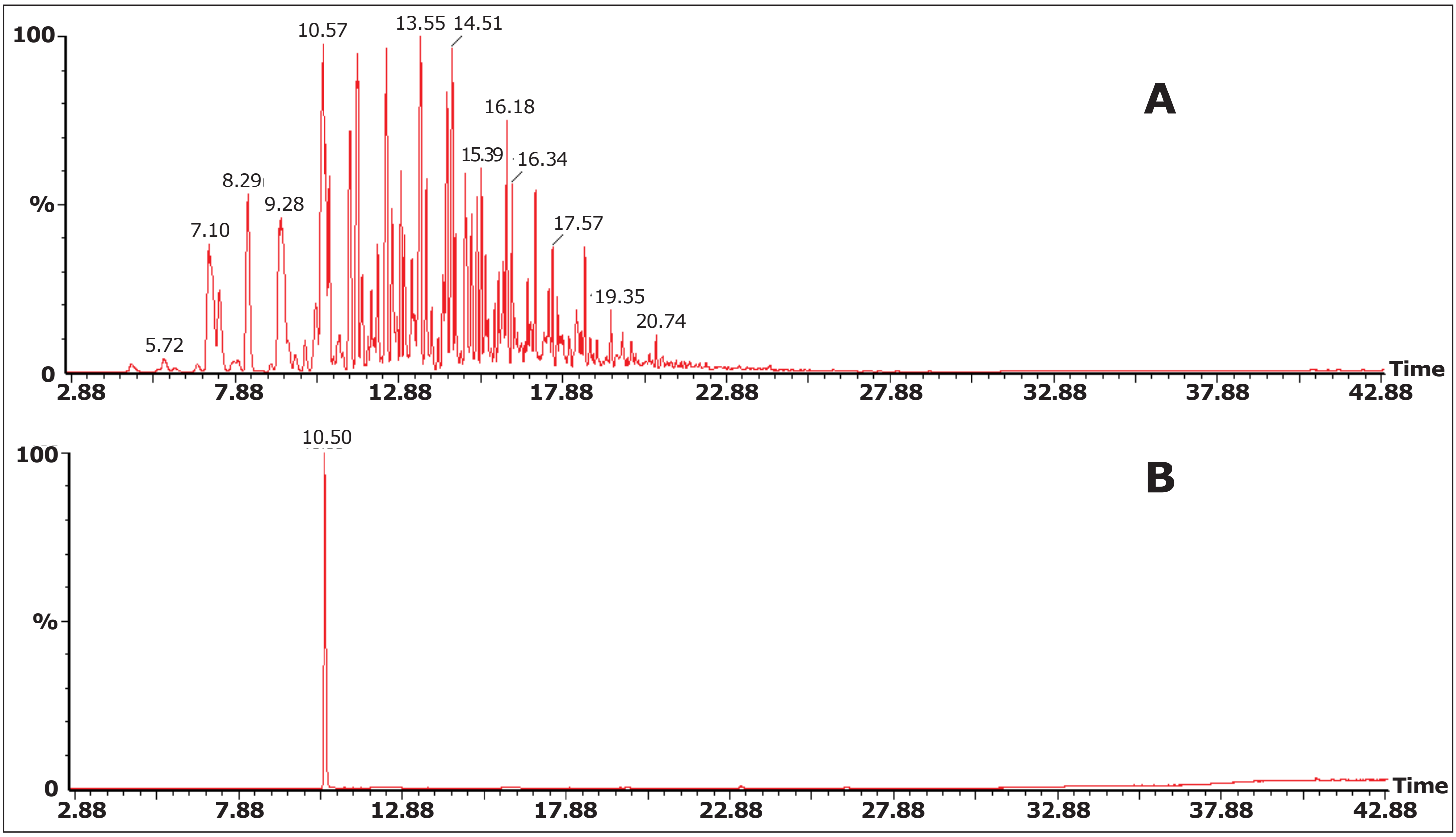

Figure 3. Hydrocarbon levels before (A) and after (B) the purifier. A total of 45ppbV hydrocarbon contamination was observed in the unpurified NH_3. The large peak present in the chromatogram of the purified NH_3 is due to the internal standard toluene-d8.

wider the range of impurities that are removed and controlled by the purifier, the lower the risk is for introducing uncontrolled contamination into the LED process chamber.

Purifier considerations

The purification media can be packaged into point-of-use purifiers, normally used on board or at the proximity of the MOCVD tools, or into regenerable purifiers that can supply the NH_3 required for many tools. An example of a regenerable purifier is shown in Figure 4.

While the lifetime of the point-of-use purifiers depends on the impurity loading and the actual flow rate passing through the purifier, the regenerable purifier has a theoretical indefinite lifetime because the purification medium is periodically regenerated. The use of regenerable purifiers leaves open the possibility for the user to use a lower grade of NH_3 without compromising the NH_3 purity at the point of use, thus reducing the cost of ownership.

Conclusions

The introduction of LEDs is expected to dramatically change the type of light sources over the next few years, with a resulting decrease in the worldwide energy consumption used for lighting. The ramp up of LED manufacturing must also be coupled with a reduction in production cost in order to be price competitive with the present light sources. It is expected that LED manufacturing will follow a path similar to the one seen by the more mature silicon industry, where the adoption of large-scale gas purifiers has enhanced the reproducibility and reliability of production as well as reduced the cost. The expected growth in LED markets will further increase the need for NH_3 of high purity. Thus it is critical to provide the market with purifiers capable of removing the widest range of impurities. ■

Figure 4. Regenerable NH_3 purifier.

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