SAFC Hitech™
Enabling Technology

technical bulletin

EpiPure™ TMA and EpiPure™ Solution TMI™ in the MOVPE of High Brightness LEDs

As MOVPE of high brightness LEDs and lasers goes into production, stricter and more stringent requirements have been placed on the purity of the metalorganic precursors. In particular, the oxygen content of the starting metals has been identified as critical to the performance of the final device. SAFC Hitech has developed the EpiPure™ grade of precursors to meet the demands of these rapidly growing markets and we present here typical data achieved in a production environment.

Significant effort was required to identify the exact nature of the oxygen contaminant species present and its precise concentration to establish the production processes for the EpiPure™ range of products. In this article, we focus on the indium and aluminum sources, due to their significant impact on layer quality and to illustrate the different methodologies required.

The main oxygen containing impurity present in the preferred In source, Trimethylindium (TMI), made by an ether containing route, has been identified as TMI.etherate, by Fourier transform nuclear magnetic resonance (NMR). This was confirmed by the novel gas chromatograph - atomic emission detector (GC-AED) technique, which was developed to provide state of the art analytical capabilities. In a detailed R&D project, the ether solvent was removed from the synthesis process to provide EpiPure™ grade material. Previously reported date showed the oxygen levels in MOVPE grown AlInAs, as measured by SIMS, were significantly reduced [1] when EpiPure™ TMI was used, either as a solid or as Solution TMI™. Improvements in NMR sensitivity to oxygen containing organic impurities (50 ppm reduced to 2-3ppm as the detection limit) have enabled the ether levels in older, now obsolete, batches of TMI to be measured. Qualitatively, these old batches gave worse growth and device results [2], and 77 K Hall measurements showed higher background carrier concentrations and lower mobilities, even in InP growth.

The main impurity in the conventional Al source Trimethylaluminum (TMA) has proved to be dimethylaluminum methoxide rather than a solvent adduct. Though this impurity can be removed to some extent, using careful fractional distillation to give “low oxygen grade” TMA, further improvements were necessary and a new chemical ‘getter’ purification route was developed to provide EpiPure™ grade material. Once again, state of the art analysis using NMR and GC-AED techniques were developed to monitor successful reduction in contaminant levels in EpiPure™ material when compared to older batches of “low oxygen grade” TMA. A quantitative study has previously correlated levels of dimethylaluminum methoxide with SIMS results on GaAs/AlAs quantum well [3].

Having shown significant improvement in the physical analysis results for the EpiPure™ grade products, a series of side-by-side growth tests were commissioned to demonstrate the benefits achievable using the new sources in a production environment. The same TMGa/AsH_3/PH_3 precursor batches and nominally identical deposition parameters were employed throughout, with combinations of the following sources: Adduct grade Solution TMI™, EpiPure™ Solution TMI™, “low oxygen grade” TMA and EpiPure™ TMA.

$Al_{0.85}Ga_{0.15}As$ structures were grown with EpiPure™ TMA and “low oxygen grade” TMA and the carbon and oxygen levels measured by SIMS. The carbon levels appeared to be independent of the aluminum precursor but the EpiPure™ TMA produced layers with about an order of magnitude lower oxygen levels (Figure 1). The same trend was seen in the PL of $Al_{0.3}Ga_{0.7}As$ - double hetero (DH) structures comparing the two sources with the EpiPure™ TMA providing a more intense PL (Figure 2).

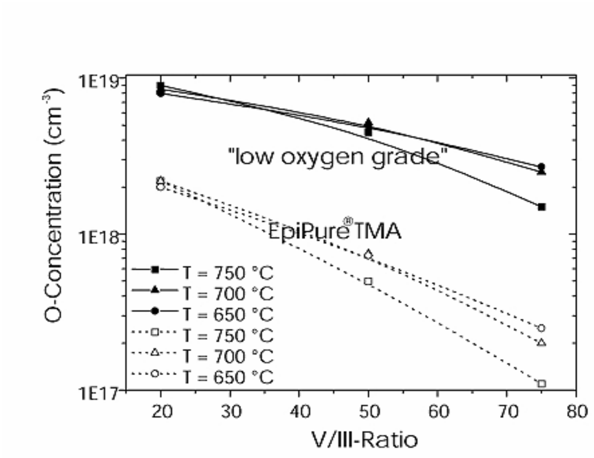

Figure 1: SIMS analysis of two $Al_{0.85}Ga_{0.15}As$ structures grown at various different growth conditions with “low oxygen grade” TMA and EpiPure™ TMA

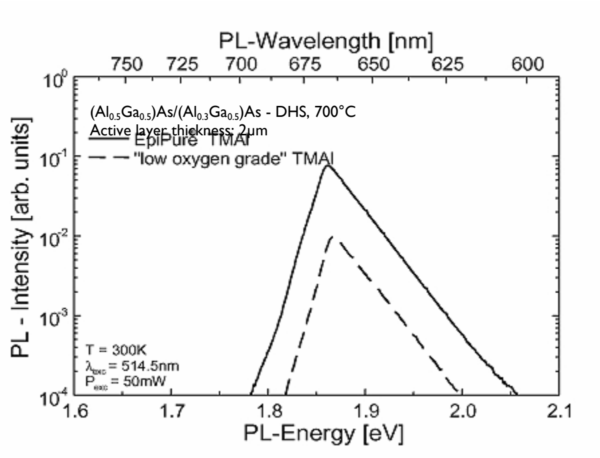

Figure 2: Room Temperature PL of two AlGaAs DH-structures, grown at 700°C with “low oxygen grade” TMA and EpiPure™ TMA

Two $(Al_{0.2}Ga_{0.8})_{0.51}In_{0.49}P$ double hetero structures with $(Al_{0.7}Ga_{0.3})_{0.51}In_{0.49}P$ barriers were grown with the following precursor combinations - “low oxygen grade” TMA, adduct grade Solution TMI™, EpiPure™ TMA and EpiPure™ Solution TMI™. The combination that gave the brightest PL, by a factor of two, was EpiPure™ TMA and EpiPure™ Solution TMI™ (Figure 3).

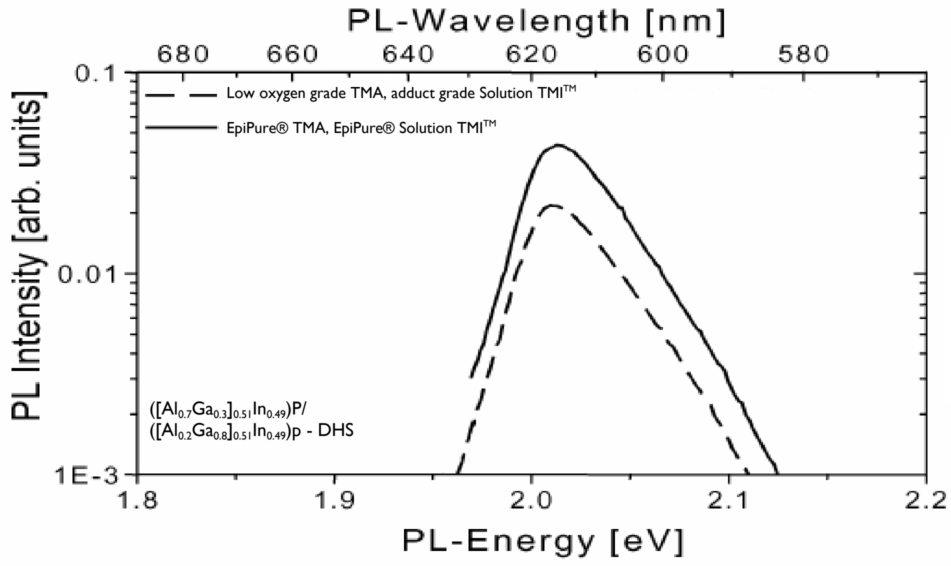

Figure 3: Room temperature PL of two AlGaInP DH-structures with 500 nm $(Al_{0.2}Ga_{0.8})_{0.51}In_{0.49}P$ active layer and $(Al_{0.7}Ga_{0.3})_{0.51}In_{0.49}P$ barriers, grown at 700°C with different precursor combinations as indicated.

These results confirmed the significant reduction in oxygen levels present in EpiPure™ grade TMA and EpiPure™ grade Solution TMI™ precursors and highlight their suitability for use in the production of the highest sensitivity systems where low contamination levels are critical.

References:

(1) Properties of Solution TMI™ as an OMPVE source, M.S. Ravetz et al, J. Electronic Materials, 29 (1) (2000) 157-161.

(2) The influence of trimethylindium impurities on the performance of InAlGaAs single quantum well lasers, J.S. Roberts et al, J. Crystal Growth, 195 (1998) 668-675.

(3) Oxygen incorporation in aluminum-based semiconductors grown by MOVPE, L.M. Smith et al, J. Crystal Growth, 134 (1993) 140-146.