Advances in nitride precursors pave way to HB-LED mass production

SAFC Hitech discusses the demands on nitride MOCVD precursor manufacturing from the rapid development in application areas such as solid-state lighting, including the delivery of triethylindium for high-quality indium nitride growth.

One of the fastest-growing sectors in the III-V materials market is currently nitride-based high-brightness LEDs (HB-LEDs). With significant growth in demand for HB-LEDs for use in applications such as LED televisions, automotive and architectural lighting, market forecasts for this area predict steady growth over the coming years to about $12bn in 2012, as illustrated in Figure 1. In particular, instrumental in this rise has been the research into nitride-based devices that has expanded potential solutions to enable access to the whole visible spectrum (i.e. to the output wavelength of devices spanning the visible range of the electromagnetic spectrum using a single material system). Exciting new applications in solid-state lighting are moving towards commercialization, adding further to the demand for increasing numbers of products across more application areas, as highlighted in Figure 2.

To keep pace with the growth of this industry, the precursors employed to deposit the thin films required must be made available in significantly larger volumes to meet demand. Such increases in material quantity must be achieved without compromising product quality, and technical excellence must be maintained to ensure that performance meets exceptionally high standards. For example, proprietary equipment and handling protocols must be developed, installed and commissioned to ensure that parts per million (ppm) levels of contamination are not introduced to 100kg lots. In particular, oxygen and silicon impurities at these levels have an extremely detrimental effect. Significant effort over many years has seen contamination levels in group III organometallic compounds decrease from 0.5ppm to 5ppb (parts per billion). These advances are what have made possible the ultra-high-brightness devices that are driving the LED market forward.

The importance of delivery systems

Achieving the best quality compound semiconductor layers and structures for device fabrication requires the correct combination of ultra-high-purity chemicals. However, in order to achieve the most cost-effective process, the most reliable delivery systems are needed. The introduction of chemicals to the deposition system must be performed in a fully controlled manner with no contamination in order for users to develop the most efficient methods to manufacture competitive products. SAFC Hitech has undertaken extensive research into all

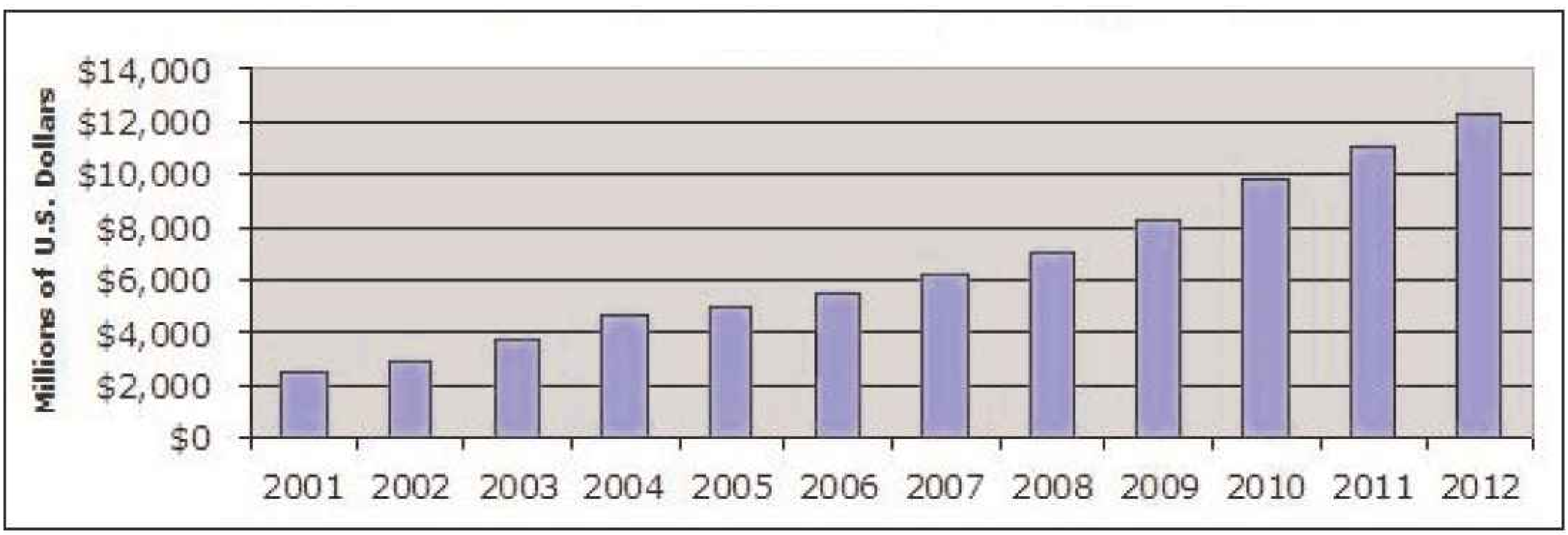

Figure 1. Total LED market 2001–2012 (millions of dollars). Source: iSuppli Corp (November 2007).

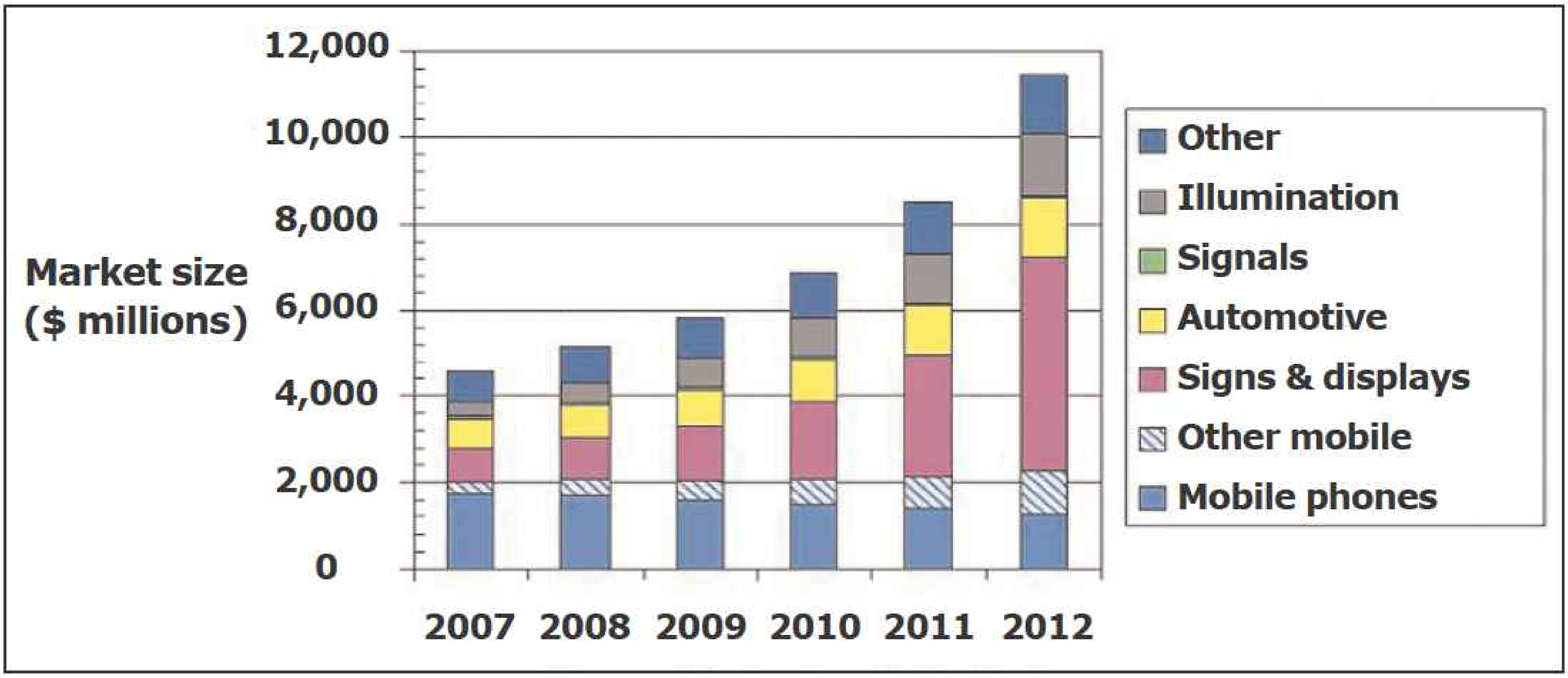

Figure 2. Predicted LED applications 2007–2012. Source: Strategies Unlimited.

aspects of the precursor delivery technology needed to offer complete solutions for customer applications.

The deposition of gallium nitride (GaN) and aluminum nitride (AlN) by MOCVD has been well established using the conventional liquid precursors trimethylgallium (TMG or Me_3Ga) and trimethylaluminum (TMA or Me_3Al) in combination with ammonia (NH_3) and the production of these group III molecules in high volume. Their delivery in bulk has been addressed using a variety of proprietary techniques. Production and subsequent treatments, including SAFC Hitech's unique adduct purification, has ensured that high-purity routes are available that can be scaled effectively to increase capacities. Robust chemistry has been combined with in-house plant engineering, resulting in plant capacities in the tonnes per year range. SAFC Hitech's EpiFill delivery tool allows users to handle large volumes of chemical in a safe, controlled fashion. In the EpiFill system, liquid precursor is pumped from a bulk reservoir to a tool unit on demand to minimise the kit modifications required to upgrade the precursor delivery system and to take advantage of reduced bubbler change-out time and qualification run requirements, resulting in reduced system downtime. The savings from such a system can make the difference between profit and loss in this highly competitive market, where strong price pressure is evident.

In the case of gallium and aluminum, the starting compounds, along with the target nitride layers, are reasonably well matched, easing the choice of deposition parameter that will ensure a compatible process that affords a wide range of mixed metal alloy compositions. The situation is not the same with regards to indium, due to the solid nature of the preferred precursor, trimethylindium (TMI or Me_3In), and the instability of the target indium nitride (InN) layers with respect to GaN and AlN. In particular, the

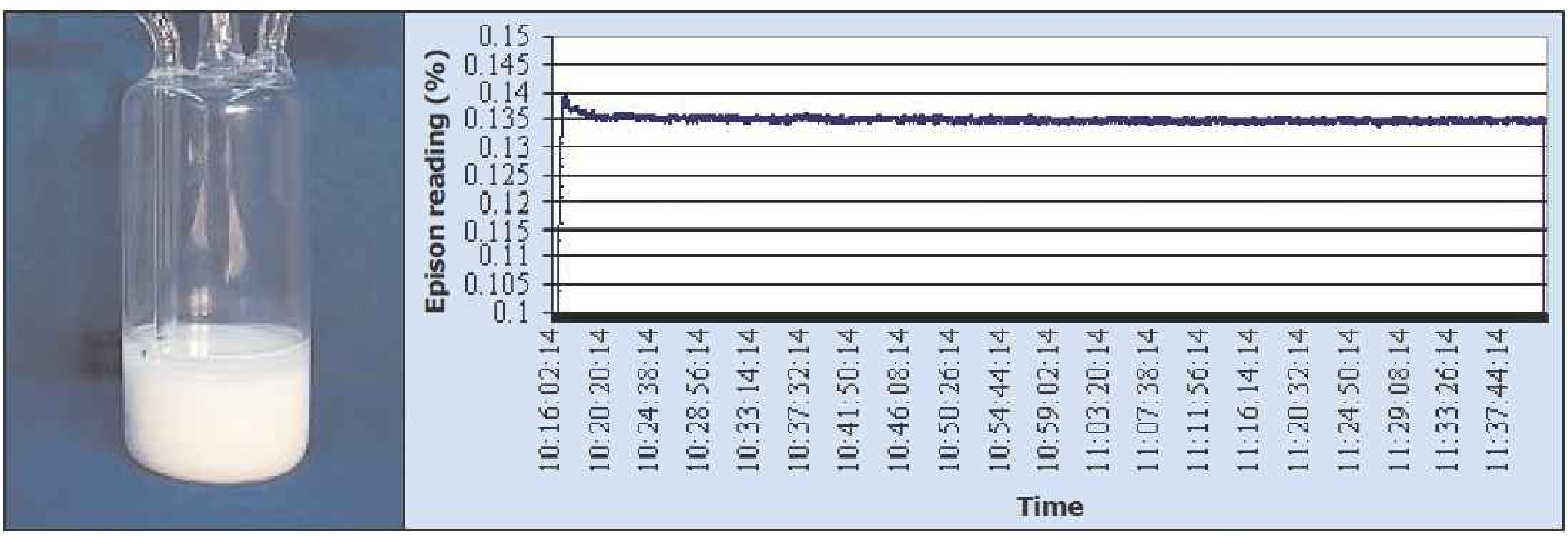

Figure 3. Solution TMI (left) physical appearance and (right) performance (standard, 10°C, 300sccm, 500mbar in crossed dip leg bubbler).

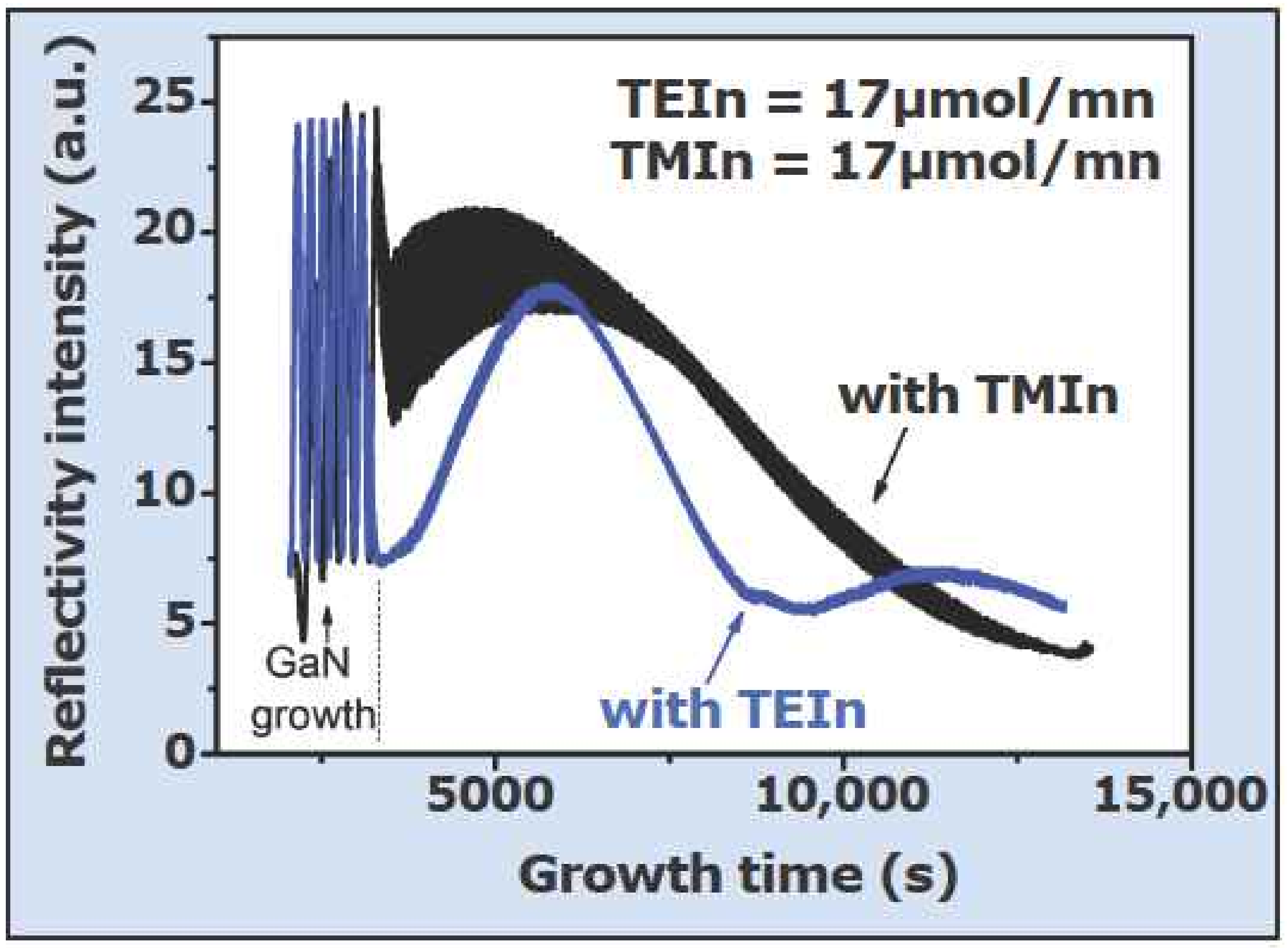

Figure 4. In-situ reflectivity measurement during MOCVD growth of the InN layers grown with TEIn and TMIn, with ammonia as the nitrogen precursor.

requirement to reduce deposition temperatures from 1050ºC to 600ºC or below (in order to avoid layer decomposition) leads to problems in finding conditions where mixed In/Ga/Al nitrides can be formed controllably. It is well known that the very interesting inclusion of InN into devices — in order to allow the full spectrum of visible LED output wavelengths to be accessed using a single material family (nitrides) — has been hampered by the above issues, and this is an area where SAFC Hitech has focused significant effort in working to develop new technologies.

Bubbler design

When we look at precursor handling and delivery, the solid nature of TMI makes it impossible to simply pump liquid samples from one place to another, as we can for TMG or TMA. Transport, therefore, must be targeted in the form of vapor. In small volumes, vapor pick-up from the ampoule can be achieved with excellent consistency and supply results from all of the bubbler options available are comparatively similar. However, for bulk delivery, numerous obstacles must be overcome to provide stable, reliable output fluxes. To address this issue, bubbler design has received significant attention in recent years, with a number of innovative approaches being studied. Currently though, for high volumes no single bubbler method can meet customer demands. However, SAFC is developing an innovative, scaleable approach to this issue and will launch new products in 2010.

Historically, to obtain reproducible 'bubbling' transport of TMI, the formation of a TMI solution has been highly successful. The patented Solution TMI product provides liquid-like saturation efficiencies for the solid precursor and slurry transfer of larger batches offers the potential to increase lot size accordingly. Excellent growth results are routinely achieved with this approach, although for a very high-volume delivery system a true liquid is more desirable to be fully compatible with the existing TMG/TMA bulk delivery technologies mentioned previously.

In order to further develop this methodology SAFC Hitech recently returned to TEI (Et_3In) studies that were halted a number of years ago due to the relatively low thermal stability of the source. In the previous studies, the adduct purification approaches that were investigated required such excessive temperatures to isolate the final product that partial decomposition was observed during collection, causing safety concerns in the laboratory-scale experiments and hence limiting production scale up potential. Since returning to the study of TEI to access the technologically important InN films, fabrication at SAFC Hitech has employed alternative methodologies and, in studies conducted recently, high-purity product has been isolated successfully using low-temperature protocols that are much better suited to this compound, thus solving a number of safety, delivery and quality issues in a major step forward.

The TEI produced at laboratory-scale using these new methodologies was also studied as part of the recently completed European project INDOT. This three-year project was a collaboration between SAFC Hitech, Aixtron, France's Montpellier University and SAES Getters which focussed on InN and InGaN film deposition and their quality improvements. The TEI that was isolated was found to significantly aid the ability of a team at Montpellier University to grow advanced InN films. High-quality, homogeneous layers were deposited reproducibly to high standards of precision, making the fabrication of full operational devices integrating this material a possibility for the first time. In detail, highly crystalline films with a full width at half maximum (FWHM) of 600 arc sec in the (0002) x-ray diffraction (XRD) peak rocking curve and 1600 arc sec in the (1000) peak rocking curve were achieved at more than double the growth rates possible with TMI. This is shown in Figure 4, where the in-situ reflectance oscillations correlate to the film thickness. Coupled with the breakthrough use of bromotrichloromethane ($CBrCl_3$) as a co-reagent to smooth the deposited layers, ultra-high-quality InN is now a reality.

A different solution to precursor vapor delivery is to provide a saturated gas reservoir for supply to a number of kits. Provision of a constant composition requires excellent vaporization control and a feedback system to ensure any fluctuations due to the solid nature of the TMI are compensated for. Of course, this delivery technology can also be applied to liquid sources so that, rather than pumping liquids to the tool and then using bubbling to vaporize the group III sources (as in the EpiFill system), controlledconcentration gases can be generated and transported. To achieve this goal, the TMG and TMA is fed to liquid vaporizers in the bulk delivery system itself and then to a manifold for direct dispensation to one or more kits. The controlled introduction of the liquid to the vaporizer via a feedback loop and demand control system is such that a highly uniform output of vapors is produced for feeding directly into a number of deposition kit manifolds simultaneously, as demonstrated by the EpiVapor system schematic in Figure 5.

This approach eliminates the requirements for kit bubblers and the requisite heating/cooling baths and gas handling systems, and offers the potential for several much simpler solely vapor-fed tools to be linked to a single remote precursor supply point in the same way that process gases are currently connected. Safety is a large and very important factor when developing production lines, and the ability to contain the bulk hazardous chemicals in remote bunkers is attractive, provided that no loss of process control is introduced. Indeed, the flexibility of precursor supply in the vapor phase to several kits enhances usage monitoring and streamlines all supply mechanisms.

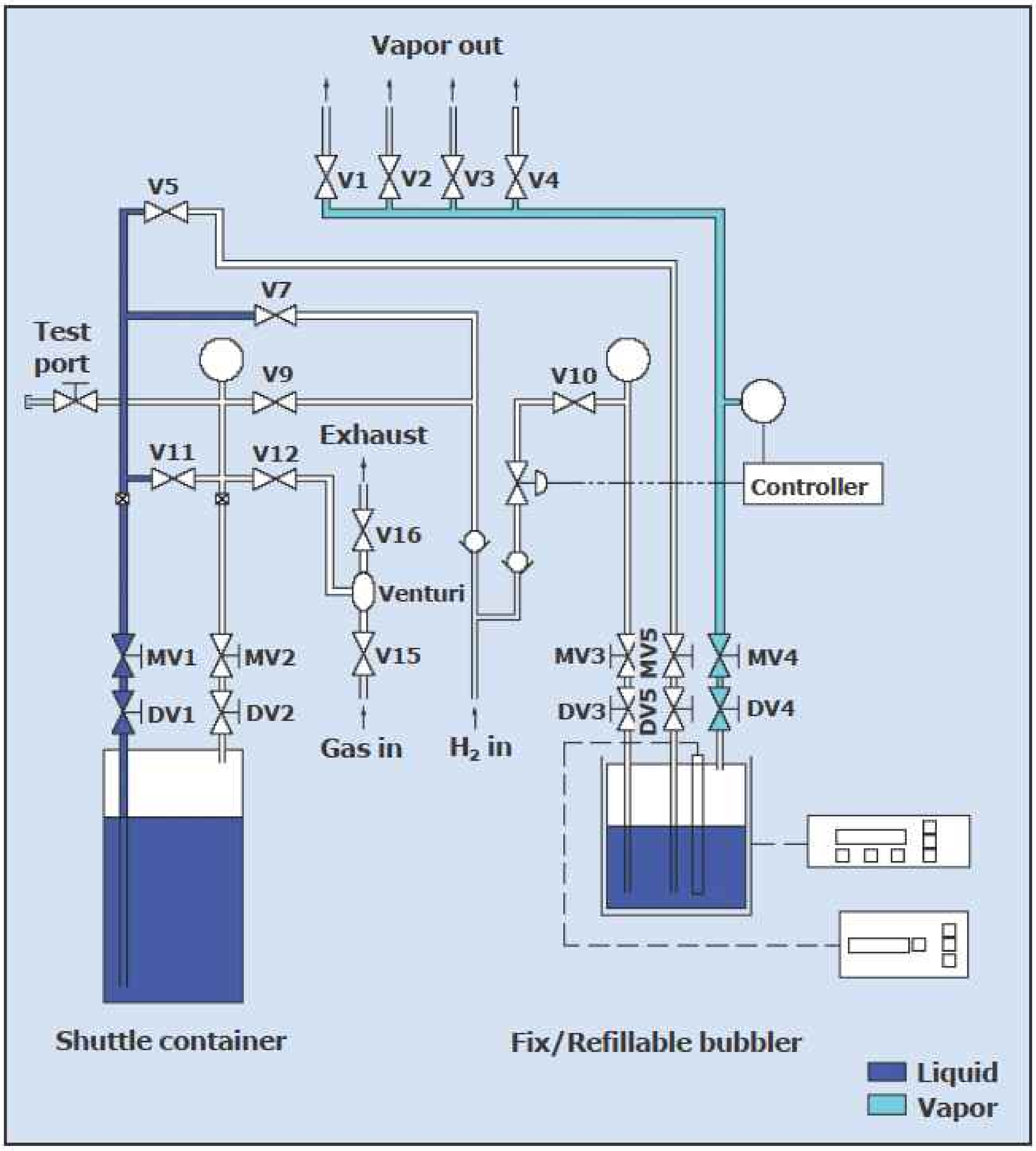

Figure 5. Schematic of EpiVapor system.

The choice of delivery system largely depends on the existing customer equipment and the relative costs to install upgrades. The EpiFill system is easy to retrofit to existing equipment and does not affect current process parameters, as the bubbling of carrier gas through the tool bubbler is still the control source for the precursor transport rate, while the EpiVapor system is more suited to new facilities where substantial simplification of tool precursor introduction systems can be made (saving capital investment). A simple gas manifold on each local deposition system can be employed to meter all chemicals controllably from an all-vapor bulk supply.

Finally, from SAFC Hitech's perspective as a precursor supplier, significant investment in new laboratory and plant capacity around the globe enables the manufacture of high-purity chemicals in localized facilities, ensuring the highest levels of service for customers in each market. This local manufacturing is required due to the pyrophoric nature of the chemicals and the resulting transportation limitations that prohibit air freight and cause unacceptable time delays when shipping products over long distance. In particular, production in Taiwan has been expanded in recent years to meet the growing customer requirements in the Far East as high-efficiency LED manufacturing increases year on year. This policy is also being pursued in other countries to complement the existing sites and to maintain unparalleled access to high-purity precursors worldwide. ■

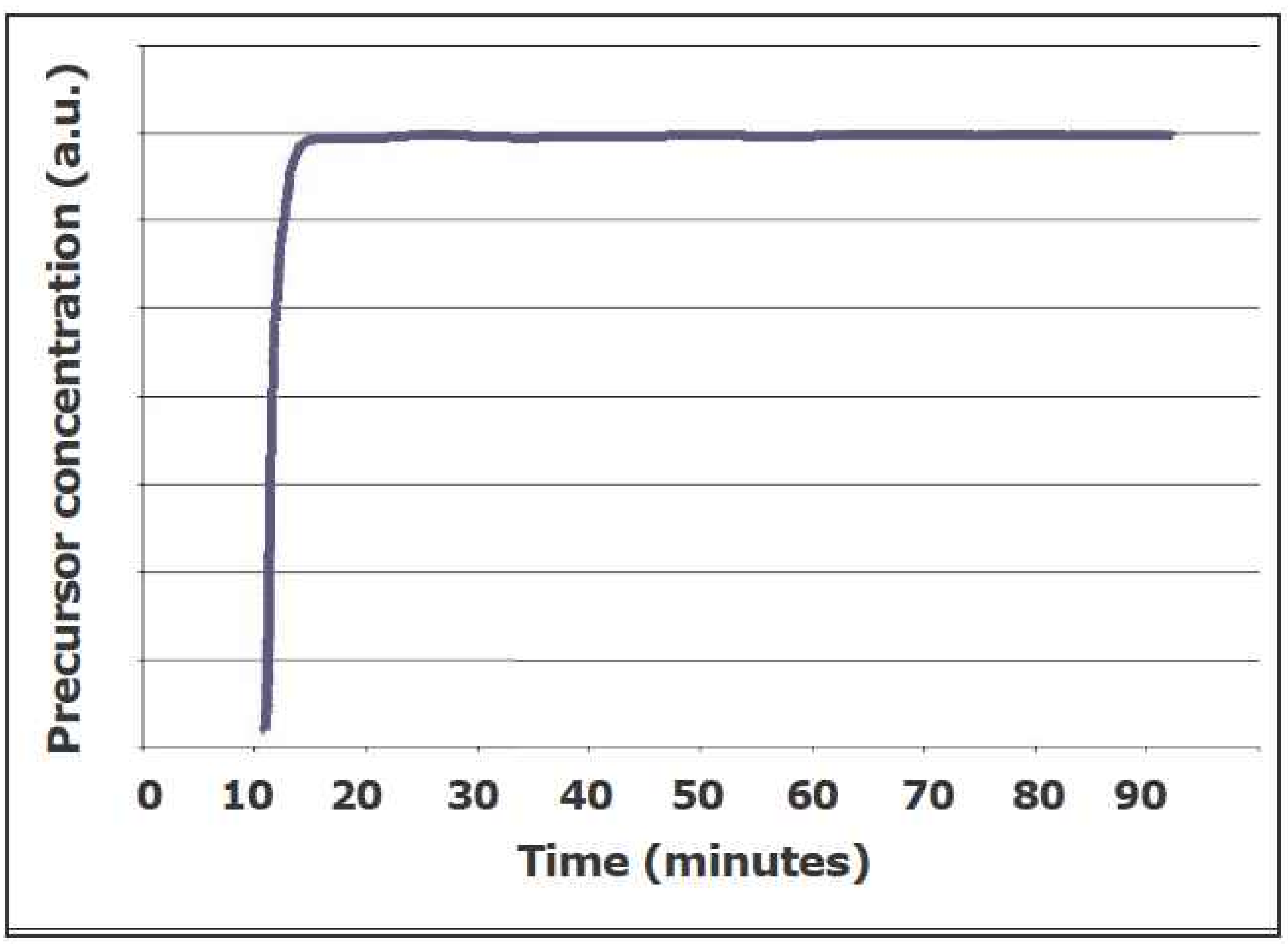

Figure 6. EpiVapor system output performance.