technical bulletin

Technical Review on Solution TMI™

Introduction

Trimethylindium (TMIn) has been proven to be the precursor of choice in the fabrication of indium based alloys via metalorganic chemical vapor phase epitaxy (MOVPE or OMVPE or MOCVD) [1,2]. A bubbling process delivers TMIn to the deposition chamber via a high purity inert gas (such as hydrogen, helium). The carrier gas is saturated by the vapours of the TMIn as it passes through the bubbler. This bubbling technique is quite reliable for liquid metalorganics but has limitations with solid materials like TMIn. This material shows less than adequate reproducibility in the vapour pick-up rate, with adversely affects the composition control essential for ternary and quaternary layers.

Trimethylindium is a while crystalline solid (m.p. 88.4°C) which exists as a tetramer via methyl bridges. The inconsistent delivery of TMIn throughout the life of the bubbler is attributed to its physical state. It is conjectured that the crystal size reduces the surface area for evaporation. The vapour pick-up is further hampered by the formation of voids and channels as the carrier gas passes through the dip tube inside the bubbler. It has also been observed experimentally the TMIn tends to sublime elsewhere in the bubbler during extended usage causing inefficient saturation of the carrier gas.

Despite the vapour entrainment problems, the use of TMIn continued due to its favourable vapour pressure and the chemical reactivity. Several approaches were explored to address the delivery problem of TMIn, some of which were quite successful, particularly the dual bubbler configuration. These historical approaches range from bubbler improvements to alternate chemical compositions.

(1) The use of a diffuser in the bubbler allows for better distribution of carrier gas that increases the contact with TMIn [3].
(2) Packaging TMIn with Rasching rings, glass beads or SS tubing pieces in the bubbler. This has been known to increase the percent utilization of TMIn by reducing the channeling effect.
(3) The use of liquid TMIn at elevated temperatures—a solution that was proven to be inherently more difficult and risky. It required heating of the pipe, mass flow control.
(4) The use of a reverse flow configuration in which the carrier gas is passed through the outlet valve rather than the dip leg of the bubbler [4]. This warrants better diffusion of carrier gas through solid TMIn.
(5) Dual bubbler configuration to enhance the saturation of the carrier gas with TMIn [4,5]. This approach has been shown to be very effective with near 100% utilization of the bubbler at a steady rate.
(6) (The use of ethyldimethylindium as an alternative indium source [6] has limited applicability due to a narrow temperature range. At above 10°C this material begins to transport the individual constitutes, TMIn and TEIn. A liquid TMIn source was also proposed where TMIn was suspended in trialkylindium with bulky alkyl group [7]. The growth data on this system has not been forthcoming.
(7) The use of dimethylaminopropyl-dimethylindium (DADI) proved ineffective due to its poor volatility [8].
(8) It has also been proposed that the slurry of TMIn in hexadecane can deliver the vapors consistently due to the better bubbling of the carrier gas [9].

(9) The on-line use of ultrasonic monitor (EPISON) to continuously monitor the composition of TMIn has been widely accepted within the industry [10]. These monitors can be used with any of the approaches above with the advantage of having a feedback loop to adjust the carrier gas flow rate.

The precursor system offered by SAFC Hitech [11] is comprised of trimethylindium in an aliphatic amine of extremely low volatility labelled as 'Solution TMI^{TM}.'
This system is proven to be very effective in the epitaxial growth of ternary and quaternary layers with very tight compositional controls [12,13].

Results and Discussion
In this system (Figure 1), solid trimethylindium is suspended in a saturated solution of TMIn. dmda (dmda = N.N dimethyldodecylamine) This adduct is a liquid at ambient temperature with a density of 1.09 g/ml. The evaporated TMIn is continuously replenished by dissolution during usage. The feed rate variations are minimal as long as the rate of dissolution of TMIn is greater than the evaporation. Solution TMI^{TM} offers the following advantages:

- Constant output of TMIn vapours over nearly the entire life of the source
- Speedy response similar to other liquid metalorganics
- Lattice matching in the growth of ternary and quaternary materials
- Vapour pressure virtually the same as TMIn, $Log_{10}P$ (mmHg) = 10.52-3014/T(K)
- Maintains dynamic equilibrium between solid and liquid throughout

The chemistry of the amine adducts of group III alkyls have been studied in the detail [14,15]. The Solution TMI^{TM} system is a dynamic equilibrium where tow competing processes occur, i.e., adduct, formation and displacement reaction. The rate determining step is the dissociation of the adduct, when tertiary amine is the complexing agent. The rate law for this process is 1/ô AM=k_1 [A] with an activation energy of 19.7 kcal/mol. The exchange with the excess base is known to take place at as low as –60°C.

This precursor system has also been observed to reduce the trace level of oxygen containing impurities. This is due to somewhat weaker In-O bonds. It is well known in the literature that Me_3N can displace ether from $Me_3In.OEt_2$ to give $Me_3In.NMe_3$ indicating greater bond strength of In-N bond [16]. It appears that in-situ purification takes place when TMIn.dmda = TMIn dynamic equilibrium sets in. Some of the preliminary work on 808nm SQW laser structures using Solution TMI^{TM} has shown better PL intensities than the conventional TMIn source [17]. Many side-by-side evaluations are underway to substantiate these findings.

Solution TMI^{TM} behaves identically to the conventional TMIn source initially as measured by Epison. However, after 50% depletion, the output from the Solution TMI^{TM} was found to be more stable than the solid source. The delivery was stable even up to the last 5 grams of TMIn in the bubbler. The performance of the bubbler was measured by growing InP films and lattice matched InGaAs/InP. The In-P layers were grown in a low pressure (200 mbar) reactor at a substrate temperature of 650°C. The bubbler of Solution TMI^{TM} was kept at 40°C with the carrier gas flow rate of 200 sccm. The growth rate was about 3µm/hr. A V/III ratio of 260 was used for the In-P layers. The layers of InGaAs layers were grown in an atmospheric pressure reactor at 665°C while maintaining the bubbler at 30°C. The V/III ratio in this case was 5.5 with a growth rate of 3µm/hr.

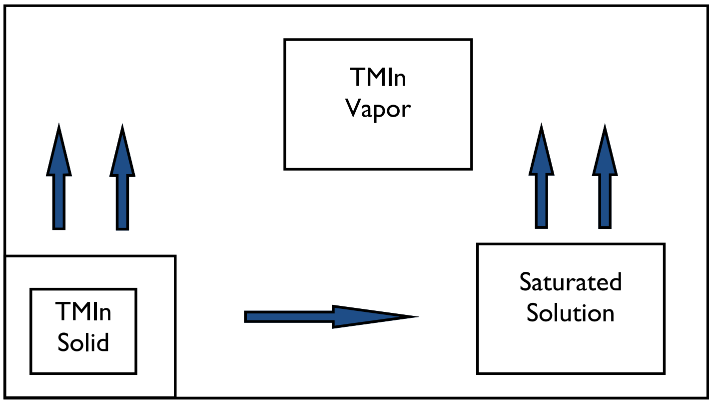

Figure 1.

The Hall characteristics for the films were as follows:
InP: n_{300} = -3.2 x 10^{14}cm^{-3}, μ77 = 181,000 cm^2/Vs

InGaAs/InP: n_{300} = -1.8 x 10^{14}cm^{-3}, μ77 = 44,000 cm^2/Vs

0 ppm mismatch, FWHM substrate/epilayer peak = 55 arcsec

A double crystal scan of a GaInAs2 layer on InP is shown in Figure 2. The FWHM for the epilayer is 35.5 arcsec, an excellent FWHM despite the lattice mismatch (substrate FWHM = 15.1 arcsec) Similarly, FWHM of the quaternary layer GaInAsP was 82.7 arcsec. The results indicate very good minority carrier diffusion lengths [12].

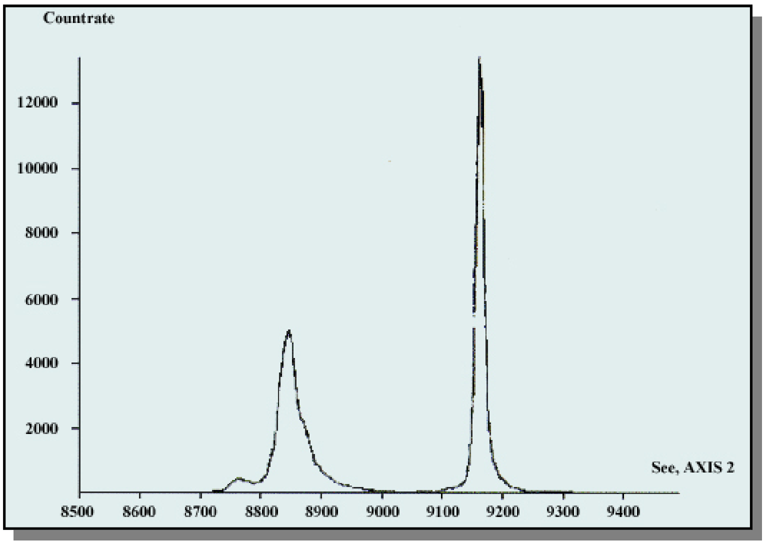

Figure 2: Double crystal scan of GaInAs$_2$ layer on InP

SAFC Hitech has initiated an internal research program to study the pick-up behavior of solid and Solution TMI™ as a function of temperature, time and carrier gas flow rate using an Epison monitor. The focus of this study is to optimise the parameters for larger bubblers to be used in production reactors. We encourage customers to come forward with particular issues they may have so that we can include them in our study.

References:

(1) G. Stringfellow, Organometallic Vapor Phase Epitaxy: Theory and Practice, Academic Press, Boston, MA 1989
(2) A.C. Jones, J. Cryst. Growth, 129 (1993) 728-773
(3) A. Micrea et al, J. Cryst. Growth, 77 (1986) 340
(4) N.D. Gerrard et al, J. Cryst. Growth, 121 (1992) 500-506 and the references therein.
(5) Patent on Dual Bubbler
(6) J. Knauf et al, J. Cryst. Growth, 93 (1988) 34
(7) R. Kanjolia, US Patent 5, 502, 227, 1996
(8) F. Scholz et al, J. Cryst. Growth, 107 (1991) 365-369
(9) L.W. Fannin et al, J. Electron. Mater. 23 (1994) 93-96
(10) Stagg et al, J. Cryst. Growth, 120 (1992) 98-102
(11) Frigo et al, WO 93.03196 International Patent Publication., US patent 5,232,869
(12) Frigo et al, Appli. Phys. Lett 61 (1992)531-533
(13) Frigo et al, J. Cryst. Growth, 124 (1992) 99-105
(14) K.L. Henold et al, Inorg. Chem. 7 (1968) 950-952
(15) D.C. Bradley et al, J. Cryst. Growth, 92 (1988) 37-45
(16) Souliere et al, J. Cryst. Growth, 124 (1992) 93-98
(17) J.S. Roberts, Private Communication, 1998