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Infrared single wavelength gas composition monitoring for metalorganic vapour-phase epitaxy

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Abstract

We discuss the use of fixed wavelength infrared absorption measurements as a means for observing compositional changes in MOVPE process gas mixtures using relatively simple instrumentation consisting of an incandescent lamp, a narrow bandpass filter matched to the CH stretch modes of the alkyl precursors, and an infrared detector. An advantage of this setup is that the low energy of the infrared radiation does not induce photolysis reactions on the analyser cell windows in contrast to ultraviolet-based techniques. We present preliminary data on gas composition measurements obtained in the alkyl lines of an MOVPE reactor and show that useful information can readily be obtained on absolute gas concentrations, gas switching transients, and reactor line memory effects. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The measurement and control of alkyl concentrations in a metalorganic vapour-phase epitaxy (MOVPE) reactor is an area of growing importance. The first report using an optical-based technique actually in the growth chamber involved an infrared (IR) diode laser in the 7–20 μm region [1,2]. The technique was sufficiently sensitive to monitor brief instabilities in the switching of an

unbalanced vent-run system, but not sensitive enough to monitor individual alkyl concentrations at a level that would allow feedback control. Following on from the original work at Sandia National Labs [3], we have previously described the use of 190 nm ultraviolet (UV) absorption across the front of the liner as a technique for quantifying the stability of the reactor and manifold [4]. Others have described similar work and have used the output signal in feedback mode to control the line concentration of trimethylindium [TMIn] [5] (a particularly awkward alkyl to stabilise). Whilst having the advantage of a very rapid response it is a difficult technology to implement in an alkyl line as there is always the need for

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a purge flow to keep the windows clean of photolysis products, especially for TMI_n. Others have approached the problem using ultrasonic sound waves, with two commercial systems now available [6,7]. The drawback with these is the large volume that has to be sampled in the line and the speed of response, which might not be able to pick up short-lived transients (of order 1 s or less) that can be very important during switching at interfaces. Fourier transform infrared (FTIR) absorption has been studied [8] and has the advantage that the photon energies are not sufficient to cause photolysis even of TMI_n. Despite the variety of approaches to the measurement of alkyl concentrations there is still a need for a cheap, easy to install monitoring technique that would be adaptable to a variety of alkyls and suitable for the more concentrated environment of the alkyl line. To date no one has reported the use of a specific IR wavelength in this context. Unlike ultrasonic speed-of-sound analysers commonly used in the MOVPE environment, the alkyl concentration can be measured independently of the carrier gas species. In this study we report for the first time a low-cost single-channel IR monitoring system that gives very useful information regarding gas composition changes in MOVPE alkyl lines. We have chosen tertiarybutylphosphine (TBP) and trimethylgallium (TMGa) as exemplars for all group V and group III alkyls. In the first example, we show a calibration of TBP pressure against IR transmission, and also show that the technique can detect concentration transients due to line memory effects. In the second example we present the observation of composition transients in a TMGa bubbler due to downstream gas switching and correlate them with UV absorption transients obtained using a previously described system [4].

2. Experimental procedure

The apparatus is extremely simple to set up. The IR source is an incandescent light source either with a quartz envelope (a commercial projection lamp) or CaF₂ window (Cal Sensors). Care was taken not to perturb the air flowing around the lamp otherwise changes in heat output could be

observed. The light is incident upon a stainless-steel optical cell equipped with sapphire windows. The optical path lengths for the cells were 12 and 200 mm for the TBP and TMGa channels, respectively. IR radiation was detected using a liquid nitrogen-cooled InAs detector equipped with a 3.38 μm narrow bandpass filter. The CH₃ groups on all common alkyls absorb from the C–H vibrations in this region. Fig. 1 shows a schematic of the setup. The signal-to-noise ratio is enhanced by the use of a lock-in amplifier and chopper. To monitor the stability of alkyls in the growth liner a beam of 190 nm light passes through the front of the cell through purged windows [4].

3. Results and discussion

Fig. 2 shows a plot of transmission coefficient versus TBP partial pressure as calculated from the vapour pressure curves provided by Epichem Ltd. These data were obtained by varying the TBP bubbler temperature over the range 4.5–10°C. The transmission was fitted to Beer's law:

$$I = I_0 + (1 - I_0)e^{-aLC}.$$

This form constrains the fit to 100% transmission at zero TBP flow. L is the cell path length (12 mm), C is the TBP concentration in atoms/cm³. The fit has two adjustable parameters, the absorptivity a and a background constant I_0 , which reflects the fact that the transmission can never reach zero even at the high concentration limit because the bandwidth of the filter (160 cm⁻¹) is greater than that of

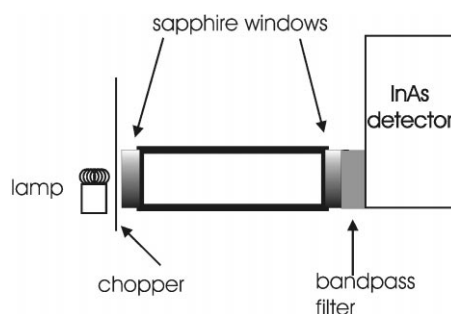


Fig. 1. Schematic of IR alkyl analyser cell and optical components.

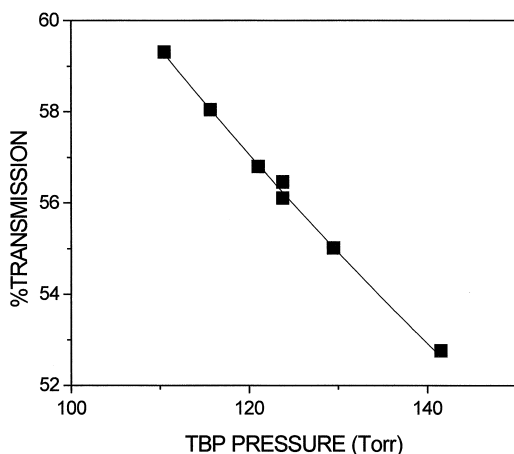


Fig. 2. Plot of 3.38 μm IR transmission versus TBP concentration obtained by varying the TBP bath temperature between 4.5°C and 10°C. Solid line represents a fit to the equation in the text.

the absorption line profile (estimated to be around 100 cm^{-1} and likely offset from the filter centre frequency by a small amount). The fit in Fig. 2 yielded a value of $I_0 = 28\%$ and $a = 2.1 \times 10^{-19} \pm 4\% \text{ cm}^2/\text{atom}$, which is about 25% lower than the result reported by Salim et al. using FTIR [8]. The relatively small discrepancy may be due to inadequate alkyl bath equilibration times between measurements. The transmission levels shown in Fig. 2 correspond to very high levels of absolute absorption. Most other alkyls will have substantially lower signals than this. For example the signal in a TMIIn bubbler at 18°C will be approximately 1% of this level. Nevertheless, with appropriate reference beam normalisation techniques this should not present a problem.

The use of in situ monitoring on individual channels permits observation of the time to equilibrate various alkyls in the delivery lines, all of which have different interaction response times with the stainless-steel tubing. Fig. 3 shows an IR transient obtained in a cell located on a TBP bubbler channel. The IR cell was located 300 mm downstream from a TBP bubbler via 6 mm diameter stainless-steel tubing. At $t = 0$ a H_2 flow of 20 sccm was diverted into the bubbler and results in the large drop in transmission indicated. At $t \sim 32$ min the H_2 flow was diverted out of the TBP bubbler and just into

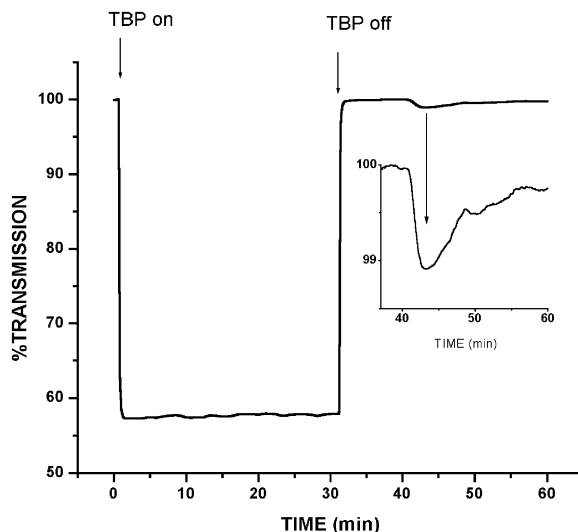


Fig. 3. IR transient obtained by switching 20 sccm of hydrogen into the TBP bubbler ($t \sim 0$), and into the bubbler bypass line ($t \sim 32$ min). At $t \sim 36$ min the nominally pure H_2 flow is reduced to 4 sccm. The inset shows the resulting transient due to memory effects in the line.

the stainless-steel line. Initially the H_2 flow was maintained at 20 sccm resulting in a return to the previous 100% transmission level. At 35 min, the H_2 flow is reduced to 4 sccm. After a brief delay of approximately 2 min, a clear absorption transient (see inset) is observed due to the presence of residual TBP in the lines. The observed transmission drop corresponds to an effective partial pressure of about 1.6 Torr of TBP and is attributed to desorption of TBP from the tubing walls. The effect becomes much more pronounced at low flows as the TBP desorption rate remains constant while the H_2 flow is reduced. This rather surprising result indicates that the equilibrium in an alkyl line is not a simple one and any attempt at changing the flow to change the bubbler output may not have the desired effect immediately. Further work is in progress to study this phenomenon.

In our previous report on the use of UV in the growth liner, we reported instabilities [4] of alkyl concentration in the liner just before the susceptor. These instabilities were observed when the reactor was modified to accommodate pusher flows to reduce the time taken to equilibrate the bubbler and

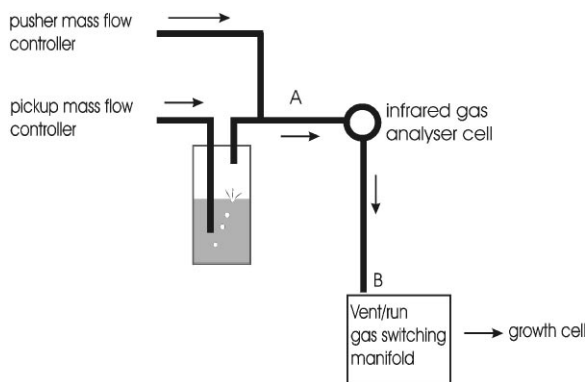


Fig. 4. Schematic of pusher and pickup MFCs and the position of the analyser cell and orifice positions.

lines [9]. The arrangement of the mass flow controllers (MFCs) and the position of the IR gas analyser cell are shown in Fig. 4 schematically. The length of the TMGa gas analyser cell was 200 mm. We could detect any instability in the growth liner by monitoring the UV absorption as before, and in the TMGa line using this new IR setup. It is important to note that the reactor is equipped with a vent–run pressure balance configuration [10] and at no time was the pressure difference between the reactor and vent line observed to exceed 0.1 Torr. The run pressure is 760 Torr.

The analyser was mounted just downstream from where the pusher (dilution) and pickup (through the bubbler) flows joined together. The TMGa bubbler bath temperature of 15°C corresponds to a TMGa partial pressure of 145 Torr. A switching sequence of 60 s to run, and 10 s to vent was established for the TMGa line. Initially we used 10 sccm in both the pickup and the pusher lines. These conditions had previously been shown to give stable flows and interface switching [4].

In Fig. 5 the IR absorption trace exhibits a stable concentration of alkyl in the TMGa line manifold and an approximate square wave in the absorption of the UV light in the growth cell. There is also the expected slow turn on (arrow in Fig. 5) due to the small flow in relation to the dead space (approximately 1 cm³) in the switching manifold [9].

When the pusher flow is increased to 100 sccm (a more reasonable flow for a dilution line, which also speeds up the equilibration in the alkyl line) an

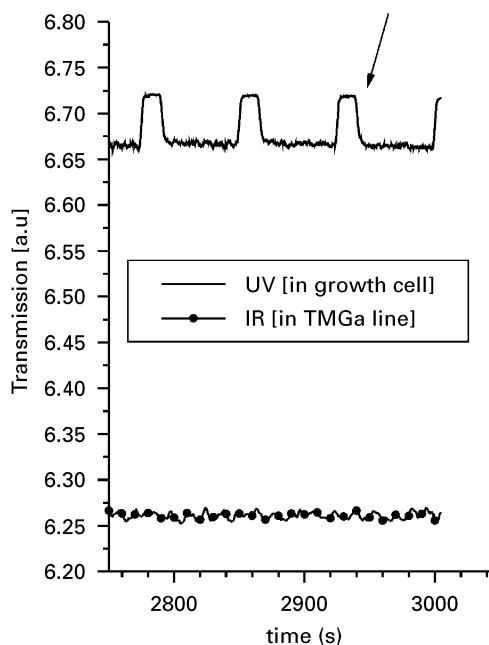


Fig. 5. Transmission of UV and IR light in the growth liner and TMGa line, respectively. Switching 60 s TMGa on, 10 s off. Flow of 10 sccm in both the pusher and pickup MFCs.

anomaly on the otherwise perfect square wave of alkyl concentration appears some 15 s after switching (arrow in Fig. 6). It is obvious from the IR signal that this anomaly can be traced back to an instability in the TMGa line some 15 s earlier during the switching of the gallium in and out of the manifold, despite the fact that the vent–run pressure imbalance was less than 0.1 Torr during the switching. Thus, any improvement gained in the turn-on and turn-off of the alkyl in the cell, due to the increased pusher flow, has been gained at the expense of the overall stability of the alkyl in both the line and the cell. Any attempt to alter the balance between the vent and the run pressures either introduced spikes (excess vent pressure) or a sluggish turn-on (excess run pressure). The anomaly seen in Fig. 6 is of considerable amplitude, about 30% of the TMGa concentration in the liner, and nearer 50% in the TMGa line (after which it is smeared out somewhat on the way to the liner).

Two possible explanations for this phenomenon are postulated. Either the pickup alkyl vapour flow and the pure hydrogen pusher flow is insufficiently

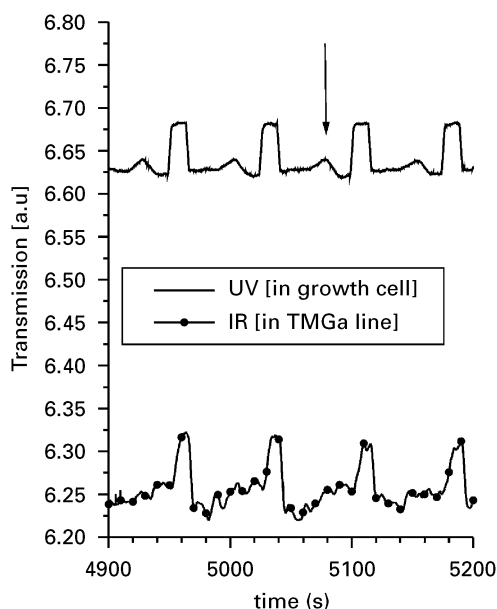


Fig. 6. Transmission of UV and IR light in the growth liner and TMGa line, respectively. Switching 60 s gallium on 10 s off. Flow of 100 sccm in the pusher and 10 sccm in the pickup MFCs and a frit at A in Fig. 4.

mixed or the line is allowing pressure transients in the hydrogen to propagate back from the perturbation in the valve manifold. To distinguish between these hypotheses we placed a stainless-steel frit with $2\mu\text{m}$ pore size in two positions in the TMGa line. Initially, it was placed upstream of the analyser cell (A in Fig. 4) in an attempt to turbulently mix the pusher and pickup flows. We have previously shown this to be a very effective method of mixing alkyl vapour and hydrogen in the manifold [11]; only a small pressure drop of 20 Torr is needed. In this position the frit had no effect on the instability in the TMGa line so it was moved downstream of the analyser cell (just upstream of the manifold, some 2 m of 6 mm pipework away, position B in Fig. 4). The results are shown in Fig. 7.

Under these conditions, when the measurements were repeated the IR signal is flat even during switching events in the manifold, indicating that the TMGa is being smoothly transferred to the growth cell. This is reflected in the very high quality of the square wave monitored by the UV absorption showing much-improved sharpness of turn-on and

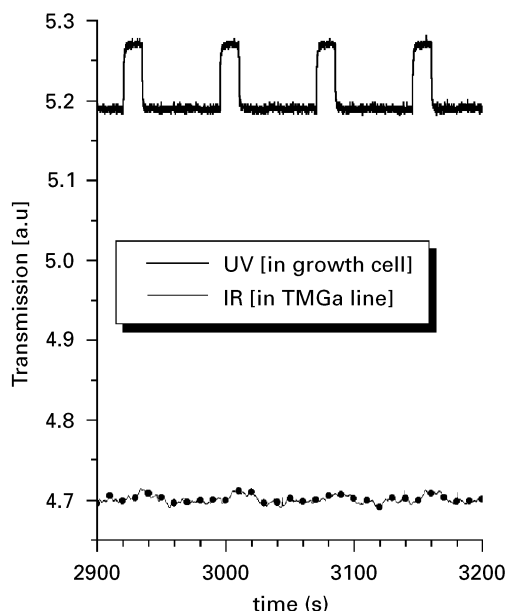


Fig. 7. Transmission of UV and IR light in the growth liner and TMGa line, respectively. Switching 60 s gallium on 10 s off. Flow of 100 sccm in the pusher and 10 sccm in the pickup MFCs and a frit at B in Fig. 4.

turn-off of the TMGa signal in the growth cell, compared to Figs. 5 and 6. It seems that placing the frit near the manifold has created a sufficient pressure drop (about 15 Torr) to prevent the pressure pulse back from the manifold into the TMGa line. The postulate of a pressure pulse is a likely explanation, although the manometer on the TMGa line shows no fluctuation during the gas switching.

4. Conclusions

This paper illustrates for the first time the use of single-channel in situ organometallic gas concentration monitoring in the alkyl lines of an MOVPE reactor. This technique offers a low-cost alternative to ultrasonic monitoring with some specific advantages over that technique. In addition, the rather primitive implementation used in this study could be greatly improved at modest cost by implementing more sophisticated measurement techniques. In the present implementation, the detected signal was affected slightly by room temperature

fluctuations, which couple directly to the lamp output. While this does not present a problem at the relatively high gas concentrations used in this study, a more sophisticated set-up would employ a reference beam at a nearby wavelength in order to normalise the output signal.

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