

# Real-time acoustic sensing and control of metalorganic chemical vapor deposition precursor concentrations delivered from solid phase sources

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We have investigated the performance and potential benefit of acoustic sensing for real-time monitoring and closed loop control of binary gas mixture compositions delivered from low vapor pressure metalorganic sources. Two solid phase sources were investigated in the presence of H<sub>2</sub> as a carrier gas: (1) trimethylindium (TMI) and (2) bis(cyclopentadienyl) magnesium (Cp<sub>2</sub>Mg), which have room temperature (25 °C) vapor pressures of 2.5 and 0.04 Torr, respectively. An acoustic sensor was implemented on the gas feed line to measure the concentration-dependent speed of sound in the gas mixture. This enabled sensitivity and control at precursor levels as low as 0.6 ppm in H<sub>2</sub>. Closed loop process control was implemented to maintain TMI and Cp<sub>2</sub>Mg concentration target in the presence of intentionally introduced long term temperature drifts. Despite induced variations of the precursor vapor pressure up to 50%, the delivered composition was controlled to within ±0.15% for TMI (at 0.5 mol% set point) and ±0.3% for Cp<sub>2</sub>Mg (at 0.01 mol% set point). Short term variability could also be substantially reduced by the control scheme. This work demonstrates the feasibility of sensor-driven control systems for stable delivery of low vapor pressure, normally problematic precursor materials. In turn, this opens the door to utilization of a broader range of species which can be synthesized as chemical precursors. © 2004 American Vacuum Society. [DOI: 10.1116/1.1776180]

## I. INTRODUCTION

Metalorganic (MO) precursors delivered from temperature- and pressure-controlled “bubbler” vessels have been used in an increasing variety of processes for the fabrication of high quality semiconductor materials and correspondingly high performance devices, including III–V and II–VI optoelectronic compound semiconductors deposited by metalorganic chemical vapor deposition (MOCVD), and high *K* dielectrics for gate and capacitor structures deposited by atomic layer deposition. The quality and reproducibility of devices grown by MOCVD (also referred to as metalorganic vapor phase epitaxy) depends markedly on control of precursor delivery: (1) to achieve the desired semiconductor composition and associated band gap; (2) to obtain multilayer heterostructures for band gap engineered devices; and (3) to produce desired dopant concentrations and vertical profiles in these semiconductor layer structures. Controlling delivery rates of MOCVD precursors is a significant challenge for several reasons, including their often low vapor pressures, the elevated source temperatures needed to increase vapor pressures, the changing surface area of the solid precursor material as it is consumed, and precursor condensation on colder internal surfaces of the downstream gas delivery system. This underscores the importance of equipment engineering upstream of the deposition reactor.

For common CVD precursors in Si technology (e.g., tetraethylorthosilicate) or compound semiconductor technology (e.g., trimethyl gallium, trimethyl aluminum), precursor concentrations and flow rates can be estimated from tabulated vapor pressure data as a function of temperature and measurements of carrier gas flow rates and operating pressure in the reactor.<sup>1</sup> While this procedure is generally adequate with liquid phase sources that have a sufficiently high and relatively stable vapor pressure, it becomes problematic for low vapor pressure sources and/or with sources whose effective volatilization rate changes as the source is consumed. For example, in solid phase sources (powders, small crystals), the change of partial pressure with time can be significant since the size and surface area of the source particles change as the source is consumed. As the available surface area of the source decreases, precursor concentration delivered downstream to the reaction region and wafer then decreases despite constant carrier gas flow.

One approach to maintaining constant precursor delivery rate for such sources is to use only a small fraction of the source, then replace it. However, this incurs drawbacks in terms of precursor cost and environmentally inefficient material utilization. On the other hand, calibration of delivered precursor mass flow as a function of time is tedious and subject to unpredictable short-term excursions associated with spatial redistribution of the solid source particles in the bubbler vessel.

Another approach to controlling the delivery of solid precursors is to suspend/dissolve precursor crystals in a solvent solution (e.g., trimethylindium (TMI) Epipure™).<sup>2–4</sup> While

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this has become a preferred option, it presents concerns about the influence of the solvent on the process, as well as the reproducibility of the solute/solvent mixture.

Clearly, the ability to exploit a variety of potential new synthetic precursors and to control delivery of these as well as conventional precursors would be substantially enhanced if suitable means were available for real-time measurements and control of precursor concentrations and flow rates. This would obviate the need for solvents, open the door to innovation in chemical precursor synthesis, and assure manufacturing and environmental benefits from advanced process control (APC) in the context of reliable, reproducible precursor delivery for chemical processes. Various sensor approaches capable of real-time/*in situ* application have been used to monitor and sometimes control the delivery of metalorganic (MO) precursors, such as spectroscopic ellipsometry measurements of the light polarization on the wafer,<sup>5,6</sup> infrared single wavelength,<sup>7</sup> Fourier transform infrared (FTIR),<sup>8-12</sup> and UV spectroscopy measurements<sup>13</sup> of the gas phase in the vicinity of the wafer.

Acoustic sensors, either based on time-of-flight or resonant frequency measurements, have also proven to be very well adapted to measure the composition of MOCVD binary gas mixtures due to their long-term reproducibility and high sensitivity, particularly that elicited by the high mass ratio between the heavy metalorganic precursor and the carrier gas (typically H<sub>2</sub>) as used in many MOCVD processes. It has been shown that acoustic sensing can be used to anticipate the behavior of a TMI (trimethylindium) solid source and to characterize its instability over time, i.e., predict the need to replace an exhausted source.<sup>1</sup> X-ray postgrowth measurements also showed significant improvements of the thickness and composition control in InGaAs films<sup>14</sup> and InP/GaInAs compound layers<sup>13,15</sup> with respectfully solid TMI and liquid trimethylgallium sources. Yamamoto *et al.* also reported successful utilization of acoustic sensing and feedback control in the synthesis of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> by MOCVD.<sup>16</sup>

The work reported here investigates the use of acoustic sensing to monitor and control solid sources with very low vapor pressure. Cp<sub>2</sub>Mg (bis(cyclopentadienyl)magnesium) was chosen as a case study as its vapor pressure is only 0.04 Torr at 25°C. Cp<sub>2</sub>Mg is used as a *p* dopant in many MOCVD applications with III-V alloys and is also used for the growth of complex quaternary II-VI alloys. It is also a well known source of problems due to its instability in delivery rate over time. The delivery of TMI reagent was also investigated. TMI is widely used in the fabrication of indium based alloys, especially for III-V GaInAs compound semiconductors. With a vapor pressure 15× higher than Cp<sub>2</sub>Mg at room temperature (2.5 Torr at 25°C), its utilization is not as challenging as Cp<sub>2</sub>Mg. However, TMI-based experiments permitted us to fine tune the system prior to using Cp<sub>2</sub>Mg while providing data that could be compared to previously published data obtained from acoustic sensing measurements.

This work demonstrates the efficacy of acoustic sensing and associated feedback control systems in delivering highly

controlled MOCVD precursor fluxes. This is shown in regard to both large, long-term drifts (50%) and smaller short-term fluctuations of source emission condition. Binary compositions were determined by gas speed of sound measurements, which provide higher precision and allow operation at lower pressures than with time-of-flight methods.<sup>17</sup>

## II. SENSOR OVERVIEW

The theory and sensor design for the Inficon Composer™ acoustic sensor used in this study have been previously described in detail.<sup>17,18</sup> Though primarily designed to monitor the arrival of precursor to a MOCVD reactor,<sup>19</sup> this sensor has also been used for in-line mass-flow controller calibration,<sup>20</sup> and for *in situ* chemical sensing downstream to a tungsten CVD reactor in order to provide real-time film thickness metrology as required for real-time advanced process control (APC).<sup>21-23</sup> The sensor measures the speed of sound by determining the fundamental resonant frequency for gas mixtures within a thermally controlled Helmholtz resonant cavity. The resonant frequency of the gas mixture is directly related to its average molecular weight, as shown in Eq. (1),

$$F = \frac{c}{2L} \quad \text{with} \quad c = \sqrt{\frac{\gamma_{\text{avg}}RT}{M_{\text{avg}}}}, \quad (1)$$

where  $F$ =gas resonant frequency;  $c$ =sound velocity;  $\gamma_{\text{avg}}$ =average specific heat ratio;  $T$ =gas temperature;  $M_{\text{avg}}$ =average molecular weight;  $R$ =gas constant;  $L$ =length of acoustic cell.

In order for the acoustic stimulation frequency to remain in resonance with the gas flowing through the cell, a signal processor is used to perform as a lock-in amplifier, the frequency range varying from 500 to 5000 Hz. Using these low frequencies minimizes acoustic damping, allowing a broad operational pressure range from 50 to 1000 Torr in H<sub>2</sub> carrier. Metallic diaphragms are used to protect the quartz crystal microphones from pressure bursts while providing a safely sealed environment. The acoustic cavity is maintained isothermal, heated by a microfilament coupled to a platinum resistance thermometer, at a user-defined temperature set point controlled to ±0.05°C.

Measurements are carried out at a 1 Hz rate, the composition being determined from the speed of sound measurements and values for gas properties provided by the user, i.e., gas molecular weights and specific heat ratios.

## III. EXPERIMENT

The precursor gas delivery system is depicted in Fig. 1, using 50 g Epicem V200FTPwell solid phase sources. The MO crystals were contained in a 300 cm<sup>3</sup> stainless steel vessel submerged in a 20 l bath whose temperature was controlled to ±0.1°C. The stainless steel gas lines upstream and downstream to the source were carefully thermally insulated and heated by ruban-type resistive tapes with a temperature accuracy of ±0.05°C. The acoustic cell temperature matched the temperature of the gas line, typically set 20°C above the

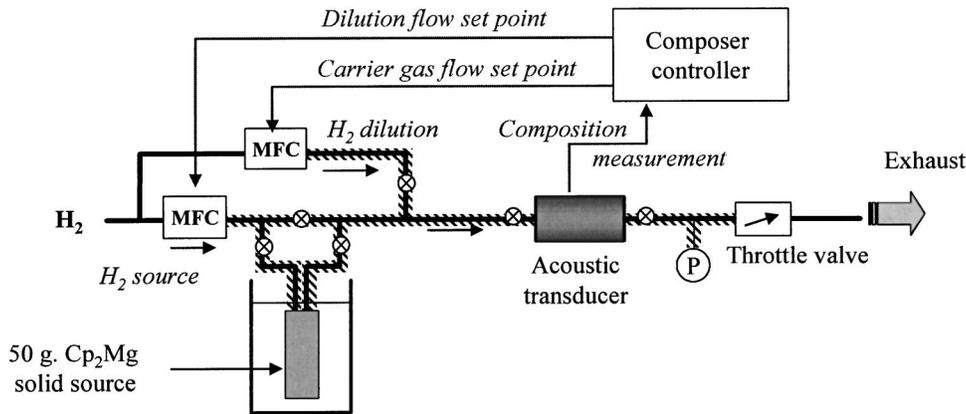


FIG. 1. Schematic of the metalorganic solid source delivery system. The binary gas composition is measured in the resonant cavity of the acoustic sensor. When closed loop control is exercised, the composition is regulated by actuating both the  $H_2$  source flow and the  $H_2$  dilution flow rates in tandem. The acoustic resonance chamber and heated feed lines (dashed sections) are maintained  $10\text{--}20^\circ\text{C}$  above the source bath temperature.

temperature of the source. Unless specified in the experimental part, the bath temperatures were  $24.5^\circ\text{C}$  for TMI and  $40^\circ\text{C}$  for  $\text{Cp}_2\text{Mg}$ , the estimated vapor pressures being, respectively, 2.44 and 0.159 Torr. The  $H_2$  carrier gas was preheated by passing through a gas line heated  $10\text{--}20^\circ\text{C}$  above the temperature of the source. It was then flowed through the source vessel to saturate the gas with MO vapor, the carrier flow rate for this  $H_2$  source being adjusted by a 100 sccm mass flow controller (MFC). A second MFC located downstream to the source allowed the dilution of the binary gas mixture with  $H_2$  dilution flow rates up to 200 sccm. The gas mixture was then fed into the  $18\text{ cm}^3$  resonant cavity of the acoustic sensor, the total pressure in the system (MOCVD source and sensor) being controlled by a throttle valve driven by a 1000 Torr heated capacitance pressure gauge. No attempt was made to deposit materials downstream for these experiments, and therefore the exiting gases were exhausted to a dry scrubber downstream to the throttle valve.

The Composer Monitor<sup>TM</sup> software application was used to monitor and save the data for postprocessing. Calibration of the composition was performed on a daily basis by flowing 150 sccm pure  $H_2$  through the cell and resetting the zero composition.

In closed loop control mode, source and dilution  $H_2$  flow rates were used as the primary control variables, with the relative flow amplitude in these two  $H_2$  streams being actuated by their respective MFCs to provide a constant MO molar flow rate. Flow set point voltages to the MFCs were determined by the sensor control unit based on predetermined control parameters, each MFC receiving a 0–5 V analog signal generated by the controller. A proportional integral derivative control algorithm was used to optimize these outputs so that the control system's response to an error between the measured and expected concentrations matched the time-dependent characteristics of the delivery system (i.e., flow rates, system volume, source vapor pressure). The control loop parameters, including controller gain, time constant and dead time, were determined by introducing a disturbance (i.e., variation of the flow rate through the source) and recording the system response in accordance with instructions provided with the sensor.<sup>24</sup> The controller gain was determined by the ratio of the change in concentration (in mol%) divided by the change in flow setting (in volts). Due to the signifi-

cantly different partial pressures of TMI and  $\text{Cp}_2\text{Mg}$ , the gain chosen was significantly different for the two sources, i.e., 0.42 and 0.0072 V/mol%, respectively. In both cases the system time constant  $t_c$ , corresponding to the time delay between a change in the carrier flow setting and a noticeable change in concentration, was estimated at 4 s. The dead time  $t_d$ , equal to  $(t_{0.63} - t_c)$  where  $t_{0.63}$  is the time between a change in the carrier flow setting and the time to achieve 63.2% of the new equilibrium concentration (i.e., point of maximum slope), was estimated at 3 s for a total flow rate ( $H_2$  source +  $H_2$  dilution) of 150 sccm.

## IV. CONCENTRATION PROCESS CONTROL

### A. Control strategies

In MOCVD gas delivery systems, the liquid is intended to reach equilibrium with the carrier gas, which is then saturated with the MO precursor in the gas phase. The presumption is then that the delivered gas is a mixture of the carrier gas at its partial pressure in the vessel together with the saturation vapor pressure of the MO source corresponding to the bath temperature of the source  $T_s$ . If  $p_s$  is the partial pressure of the MO source gas as delivered and  $p_{\text{svp}}$  is the vapor pressure of the MO source at the bath temperature  $T_s$ , then  $p_s(T_s) = p_{\text{svp}}(T_s)$ . With the carrier gas saturated at the vapor pressure of the MO source under any flow conditions used, the MO precursor concentration is fixed by the source temperature. Consequently, the delivery rate increases linearly with carrier gas flow, while concentration of the MO precursor in the carrier will be constant to the extent the temperature bath and subsidiary factors (e.g., condensation on delivery line walls) are maintained constant. This result also presumes that the saturation vapor pressure of the MO source is achieved under steady-state flow conditions, a requirement easily met with conventional liquid sources and bubbler delivery systems. Solid sources with sufficiently high vapor pressure could also meet these criteria. For such situations, MO source delivery is relatively stable, and if desired, control can be achieved using a composition sensor downstream to the source vessel and varying source temperature or carrier gas flow rate to maintain either constant MO concentration or constant MO delivery flux.

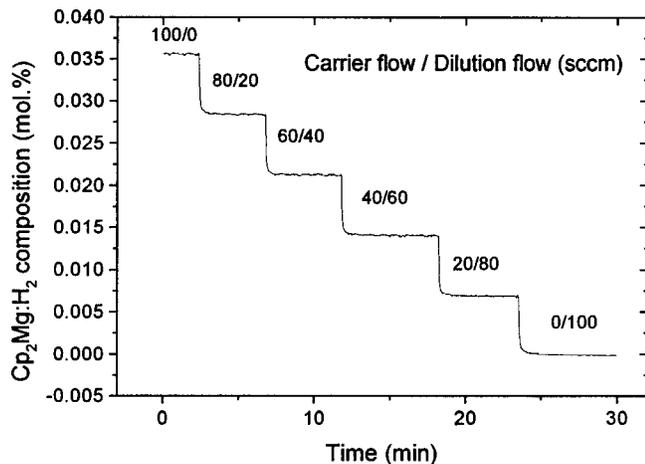


FIG. 2.  $Cp_2Mg:H_2$  gas composition as a function of  $H_2$  flow rates for the  $H_2$  source and dilution flows, each in sccm and indicated in the figure by source/dilution flow values for each condition. Total flow rate was maintained constant by adjusting the source to dilution flow ratio to achieve a constant 300 Torr pressure in the source. Source temperature of 40°C was used, corresponding to a partial pressure of 0.159 Torr.

The situation changes dramatically when low vapor pressure MO sources, particularly solid sources, are employed as MO precursors. If MO sources have vapor pressures too low, the source vessel will not achieve the saturation vapor pressure of the source material during the residence time characteristic of the source vessel. In contrast to the case for higher vapor pressure liquid sources, higher carrier gas flow rates will not increase precursor delivery and deposition rates since the volatilization of the source becomes rate limiting for low vapor pressure sources. In addition, MO concentrations in the delivered gas will drop with higher carrier gas flow rates, i.e.,  $p_s(T_s) < p_{svp}(T_s)$ . If MO precursor delivery is rate limited by source volatilization rates, stability of precursor delivery rates becomes more difficult. The problem is exacerbated in the case of solid sources, where the active area for volatilization decreases as the source is consumed, thus changing the precursor delivery rate as a function of time, and doing so at a rate which is unpredictable in its dependence on the specific morphology of MO powder/crystals present in the source vessel.

Significant drift of precursor flux is intrinsic to the use of low vapor pressure solid sources, and therefore a sensor-based control strategy is essential. Varying carrier gas flow through the source will not alter MO delivery rates when they are rate limited by MO evaporation from the source. To achieve MO concentration control in the presence of significant drift in MO fluxes, a second MFC-controlled carrier gas stream—termed the dilution flow—was added downstream to the MO source vessel as shown in Fig. 1.

However, given that the drifts are substantial, adjustment of the dilution flow rate alone will substantially vary the total pressure in the reactor, thereby modifying process performance. To maintain a constant total flow rate, the concentration was adjusted by varying the flow rate of  $H_2$  in the dilution line while maintaining a constant total carrier gas flow rate. Figure 2 depicts the  $Cp_2Mg:H_2$  gas composition as a

function of time as the  $H_2$  source and dilution flows were changed. The respective source and dilution flows are indicated as source/dilution flow values for each condition. Total flow rate was maintained constant by adjusting the source to dilution flow ratio to achieve a constant 300 Torr pressure in the source. Under these conditions and over a wide range of source/dilution ratios, the precursor concentration as delivered to the sensor was controlled easily, the influence of the dilution flow stream dominating over the weak influence of the source carrier flow.

## B. Precursor composition metrology

The sensitivity of the acoustic sensor was determined from the data in Fig. 2. The standard deviation (STD) of the composition over 100 data points and under fixed conditions of pressure and flows was estimated at  $3.0E-5$  mol%, meaning that concentration variations as low as 0.6 ppm (2X the STD) could be measured. It was also established from post-processing of these data that a variation of 0.1 sccm in the  $H_2$  dilution flow would result in a  $5.5E-5$  mol% change of the composition, a change that is within the range of the sensor sensitivity.

## C. Concentration process control under systematic temperature drift

The high sensitivity of the sensor and the potential to accurately control the composition of delivered gas by adjusting the ratio of carrier to dilution flow rates present a good prognosis for implementing real-time, in-line closed loop gas composition control. Therefore the real-time measurements of the gas composition were used as secondary control variables to dynamically adjust the mass flow set points to both the source and dilution MFCs as actuators to regulate the composition (i.e., the primary control variable).

To demonstrate the capability for composition closed loop control, a temperature drift was intentionally introduced in the system by turning off the heating element of the temperature controlled bath surrounding the bubbler vessel. The decrease of the bath temperature as a function of time is shown in Fig. 3(a). As the temperature dropped from 40 to 32°C over a 2 h period, the  $Cp_2Mg$  vapor pressure data suggest that the precursor partial pressure should decrease from 0.16 to 0.08 Torr, i.e., by 2X or 50%. As shown in Fig. 3(b), a 50% decrease of the  $Cp_2Mg:H_2$  composition was measured in an open loop configuration by the acoustic sensor, as expected, with  $H_2$  flows maintained constant at 100 and 50 sccm, respectively, for the dilution and source flow rates.

To evaluate the efficacy of a closed loop configuration, the same temperature drift was once again introduced, using the acoustic sensor as a real-time composition metrology and adjusting both dilution and source flow rates to maintain a constant precursor composition and total carrier flow rate. The data shown in Fig. 4(a) were obtained for  $Cp_2Mg$  with a composition set point of 0.01 mol% at 300 Torr and a total flow of 150 sccm. The 0.01 mol% set point corresponds to a standard concentration used in *p*-type doping applications ( $0.3 \mu\text{mol}/\text{min}$ ) in GaAs compound semiconductors. As the

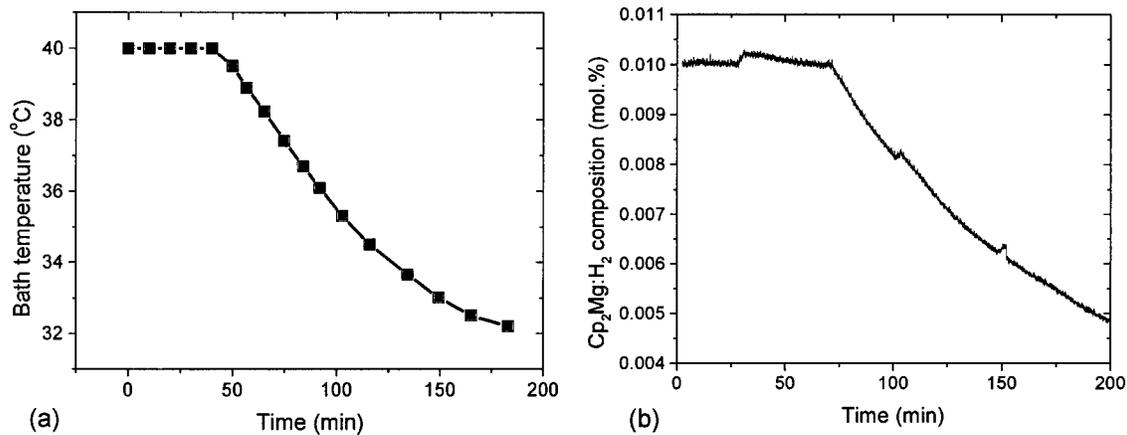


FIG. 3. Variations of  $\text{Cp}_2\text{Mg}:\text{H}_2$  composition in open loop configuration under conditions of long-term temperature drift. (a) Shows the temperature decrease experienced by the solid source over a 3 h period due to termination of power to the source heating bath (near 50 min.), with  $\text{H}_2$  flow rates and pressure kept constant. (b) Shows the resulting effect on the  $\text{Cp}_2\text{Mg}:\text{H}_2$  composition as measured by the acoustic sensor: the temperature drop resulted in a 50% decrease in precursor composition, consistent with the expected drop in vapor pressure.

temperature dropped from 40 to 32°C and the delivered precursor concentration decreased accordingly [as in Fig. 3(b)], the controller dynamically compensated these effects by decreasing the dilution flow rate while increasing correspondingly the source flow rate to maintain a constant gas throughout. Figure 4(a) shows the constancy of the  $\text{Cp}_2\text{Mg}$  precursor concentration as a function of time, along with the decrease in dilution flow rate and increase in source flow rate imposed by the control system as needed to achieve precursor concentration control. The acoustic sensor output of the  $\text{Cp}_2\text{Mg}:\text{H}_2$  composition is shown in more detail in Fig. 4(b). Despite the very large (estimated 50%) change in the  $\text{Cp}_2\text{Mg}$  vapor pressure, the data show that the standard deviation of the composition measurement over the 3 h period was  $3.0\text{E}-5$  mol% with an average value of 0.010 009 mol%. Thus the precursor concentration—even though only 0.01% of the total gas flow—is measured to a precision of 0.3%. The 50% change in precursor vapor pressure emulates a ma-

ajor modification of the solid source, as would be encountered in using such sources in manufacturing. In terms of stability of precursor delivery through the consumption cycle for the source, this represents the loss of half the material in the source. Thus the sensor and control system appears highly adequate in ensuring constant precursor delivery even in the presence of major decreases in the amount of source material remaining for use in the process.

An analogous control experiment was carried out with the TMI source, using a 0.5 mol% set point while the temperature decreased from 33 to 29°C. As shown on Fig. 5, the system response was very similar to that for  $\text{Cp}_2\text{Mg}$ , achieving an average value of 0.499 98 mol% and a standard deviation of 0.000721 mol% over a 3 h period. Thus the precursor concentration—even though only 0.5% of the total gas flow—is measured to a precision of 0.15%, roughly comparable to that for the  $\text{Cp}_2\text{Mg}$  case.

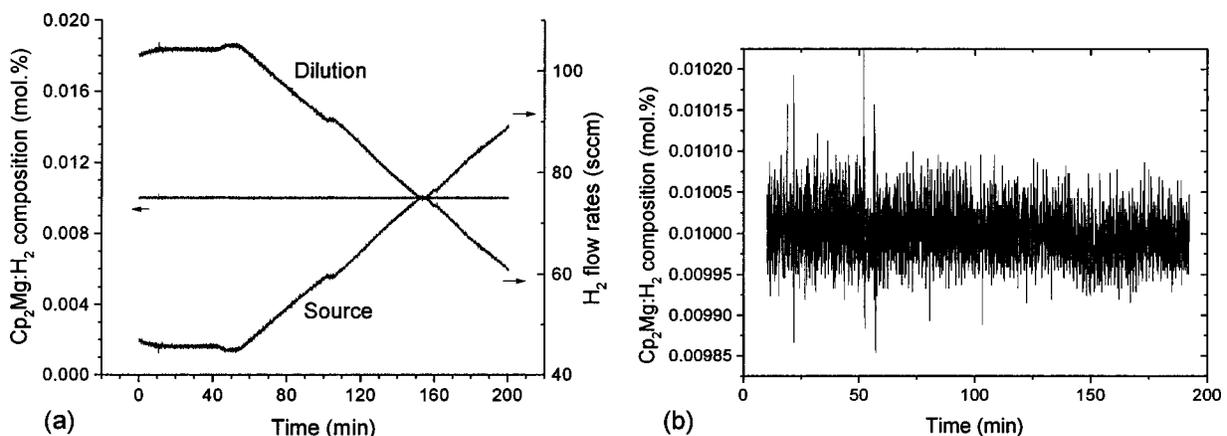


FIG. 4. Performance of the acoustic sensor and feedback control system under long-term temperature drift of the  $\text{Cp}_2\text{Mg}$  source. In (a), as temperature in the source drops, the system responds by regulating the  $\text{H}_2$  flow rates (right scale) in order to maintain the composition on target at 0.01 mol% (left scale). (b) Presents a close-up view of the composition. Standard deviation of the composition over the 3 h temperature drift was  $3.5\text{E}-5$  mol%, with an average value of 0.010 009, reflecting a precision in precursor composition stability of 0.3% of its value, despite the fact that the precursor constituted only 0.01% of the total gas.

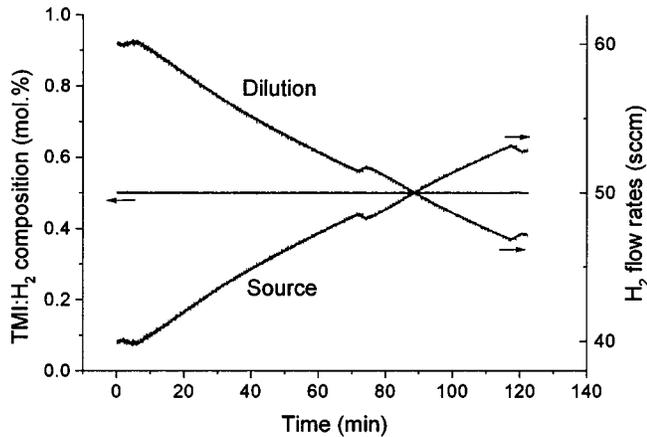


FIG. 5. Performance of the acoustic sensor and feedback control system under long-term temperature drift of the TMI source. Standard deviation of the composition over the 3 h temperature drift was 0.000 72 mol%, with an average value of 0.4999 mol%, reflecting a precision in precursor composition stability of 0.15% of its value.

#### D. Effects of short-term disturbances

To characterize the closed loop control performances under short-term disturbances, a section of the on/off heating tapes on the gas delivery line were programmed to generate temperature oscillations of  $\pm 1.5^\circ\text{C}$  over a 3 min period, the temperature raising sharply by  $3^\circ\text{C}$  over the first 30 s and then decreasing continuously by  $3^\circ\text{C}$  over the remaining 150 s. The section in question was located between the first half of the gas feed line from the source to the acoustic sensor (i.e., 20 in. long) while the other segments (line upstream to the source, dilution feed line, precursor vessel and acoustic cavity) were kept at a constant temperature.

Figure 6(a) shows the system's response in the case of  $\text{Cp}_2\text{Mg}$ , first under closed loop control over 30 min and then in open loop. In this case, the bath temperature was established at  $40^\circ\text{C}$  while the gas feed lines and acoustic cell temperature were set at  $50^\circ\text{C}$ . In closed loop mode, the control system minimized the effect of the temperature oscillations by adjusting the  $\text{H}_2$  flow rates (right Y scale) in order to

maintain the  $\text{Cp}_2\text{Mg}$  concentration on target at 0.01 mol% (left Y scale). In the absence of control (open loop), the  $\text{H}_2$  flow rates remained constant and the amplitude of the concentration oscillations resulting from the temperature perturbations increased by a factor of  $\times 2.6$ . The composition standard deviation under closed loop control was 4.6 and  $12.1\text{E-}5$  mol% without control.

Figure 6(b) shows a set of data acquired during a similar experiment but with the temperature of the gas feed lines and acoustic sensor raised from  $50$  to  $60^\circ\text{C}$ , the bath temperature remaining the same at  $40^\circ\text{C}$ . As there is no significant change in closed loop mode compared to the data in Fig. 6(a), it clearly appears that in the absence of control, the amplitude of the concentration oscillations was significantly reduced ( $\sim 25\%$ ) when operating at  $60$  vs  $50^\circ\text{C}$ . In addition, to maintain the same composition at 0.01 mol%, the dilution flow rate was increased from 101 to 114 sccm, i.e., a 13% increase. This suggests that in this transient regime, a larger amount of  $\text{Cp}_2\text{Mg}$  reached the sensor when the temperature of the line was increased from 10 to  $20^\circ\text{C}$  above the temperature of the source. Additional experiments showed that no noticeable oscillations were detected when flowing pure  $\text{H}_2$  (with no MO precursor) in the presence of the temperature perturbations, as it might have been assumed that the oscillations monitored by the acoustic sensor were the result of the change of the gas temperature. Considering the origin of the perturbation, it must be assumed that a non-negligible amount of  $\text{Cp}_2\text{Mg}$  condensates on the walls of the stainless steel feed line, this condensation effect on concentration being minimized at higher temperature. Further experiments at higher temperature could not be carried out, our acoustic sensor version being limited to a  $65^\circ\text{C}$  maximum temperature.

#### V. DISCUSSION

By correcting for changes occurring in the MO delivery system, either as a result of time dependent thermodynamic alteration of the source or perturbations induced by the equipment state, *in situ* monitoring by acoustic sensing and

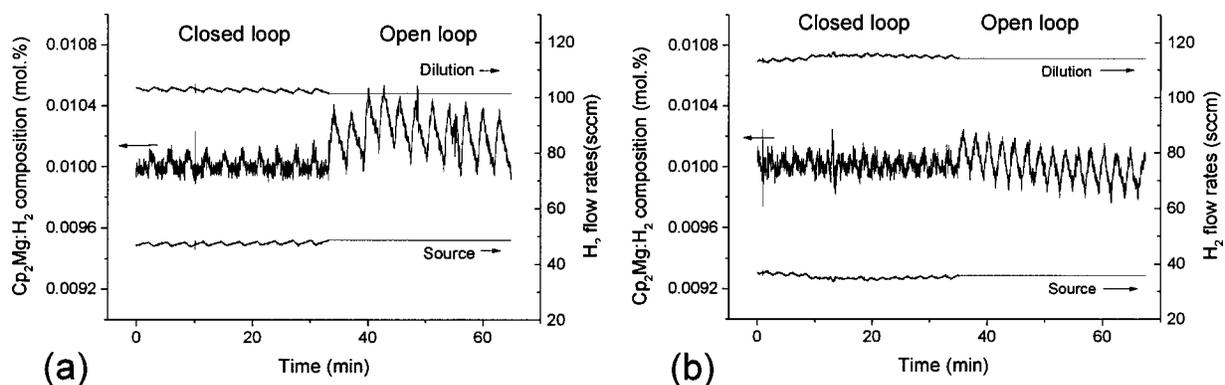


FIG. 6. Effects of short-term disturbances under open and closed loop control. Disturbances were introduced with  $\pm 1.5^\circ\text{C}$  temperature oscillations over a section of the gas feed line. The sensor and feed line temperatures were set at  $10^\circ\text{C}$  (a) and  $20^\circ\text{C}$  (b) above the  $\text{Cp}_2\text{Mg}$  source temperature (at  $40^\circ\text{C}$ ). In closed loop mode, the composition (left scales) is regulated by adjusting the  $\text{H}_2$  flow rates (right scales). In open loop mode, the disturbances are significantly lowered with higher feed line temperatures.

real-time feedback control of the MO reagent concentration can offer significant benefits, including improved process reproducibility, minimized equipment downtimes to calibrate or replace the source, or reduced costs by increasing the source usable lifetime. It can also offer greater flexibility in process design which can exploit new MO sources that might not have been usable without the sensing, metrology and control capabilities demonstrated here.

The notion of coupling MO concentration measurement by acoustic sensing with feedback control via the actuation of two sets of mass flow controllers (source and dilution) was investigated by Yamamoto *et al.*<sup>16</sup> in the case of  $\text{YBa}_2\text{Cu}_3\text{O}_x$  MOCVD. They showed that concentration oscillation due to temperature variation in the  $\text{Cu}(\text{DPM})_2$  source, with a concentration set point around 0.02 mol%, could be minimized with feedback operation. However, these authors did not report the quantitative precision and controllability of their method, e.g., the standard deviation or precision of their measurement, either in open or closed loop. Comparing our estimates of the data they displayed graphically to the quantitative results presented above for our  $\text{Cp}_2\text{Mg}$  concentration measurements at 0.01 mol%, we infer that we have improved precision and controllability by an order of magnitude compared to Yamamoto's work. Explaining this difference in detail is beyond the scope of this work, but at least two possibilities can be noted. First, two different acoustic sensor approaches were used: our work employed sensing based on low resonant frequencies (400–4000 Hz) in an acoustic cavity, while Yamamoto's data are based on time-of-flight measurements obtained at relatively high frequency (15 kHz). Second, the detailed actuator and control system performances may be different.

Our results show that in the case of a  $\text{Cp}_2\text{Mg}:\text{H}_2$  gas mixture the standard deviation of the composition measurements was the same, i.e.,  $3.0\text{E-}5$  mol%, either under fixed process conditions of flow, pressure and temperature, or when introducing a strong temperature drift over a 3 h period resulting in a  $50\times$  drop of the metalorganic precursor vapor pressure. This demonstrates that the control system was able to compensate very accurately for the drift in the source as the composition was maintained on target at 0.01 mol%  $\pm 0.3\%$  for  $\text{Cp}_2\text{Mg}$  and 0.5 mol%  $\pm 0.15\%$  for TMI.

Furthermore, these results show that the limiting factor for the control performance of this system did not reside in the sensitivity of the sensor but in the reproducibility of the actuators. Indeed, general purpose MFCs such as the MKS 1179 used for this experiment are specified to have a repeatability of  $\pm 0.2\%$  of full scale, i.e.,  $\pm 0.4$  sccm in the case of the 200 sccm dilution MFC. Based on the  $0.0072$  mol% / V value of the process gain determined in the case of  $\text{Cp}_2\text{Mg}:\text{H}_2$ , a  $\pm 0.4$  sccm variation of the  $\text{H}_2$  dilution flow would result in a change of the composition by  $\pm 7.2\text{E-}5$  mol%, which is twice the value determined for the standard deviations of our measurements. We therefore conclude that the accuracy of the mass flow control is a critical factor in the overall accuracy of our control system. This is consistent

with the fact that system performance was only slightly improved when using the higher vapor pressure source (TMI), where the composition was controlled at  $0.5$  mol%  $\pm 0.15\%$  in comparison to  $0.01$  mol%  $\pm 0.3\%$  for  $\text{Cp}_2\text{Mg}$ . Once again, the reproducibility of the actuators is critical: even though the concentration was  $50\times$  higher for TMI than for  $\text{Cp}_2\text{Mg}$ , comparable composition control toward the respective targets is achieved in the two cases.

From process development and manufacturability perspectives, close attention is generally given to the control of the source temperature, since the thermal stability of MO precursors is normally critical in achieving stable delivery rates. For example, in the case of  $\text{Cp}_2\text{Mg}$  at  $40^\circ\text{C}$ , a  $0.1^\circ\text{C}$  variation will result in a 0.8% variation of the vapor pressure and therefore of the flux to the wafer (assuming constant flow rates and pressure). We showed that such temperature induced variations could be corrected by implementing real-time feedback control of the concentration, easing the requirements on the stability of heating elements normally needed to achieve reproducible process conditions.

In contrast, much less attention is normally devoted to optimizing the temperature of delivery lines downstream to the MO source in order to control adsorption, desorption, and condensation phenomena which occur on internal surfaces of the delivery lines for reactive MO precursors. By accurately monitoring the gas composition while intentionally modulating the temperature of the gas feed lines and keeping the rest of the process metrics constant, we were able to partially quantify the effect of the average temperature on these surface reactions. By increasing the gas line temperature from  $10$  to  $20^\circ\text{C}$  above the temperature of the source, the effect of the induced temperature perturbation was reduced in open loop mode by 25%, and simultaneously more  $\text{Cp}_2\text{Mg}$  was actually being delivered to the acoustic cell (as revealed by the increase of the  $\text{H}_2$  dilution flow rate). We believe that this approach could be employed to optimize the thermal profile of MO gas delivery systems with respect to the intrinsic adsorption/desorption/reaction properties of the MO precursors.

## VI. CONCLUSION

Sensor-based process control using feedback control driven by a resonant-frequency acoustic sensor can insure stable gas feed rates when using metalorganic solid phase sources such as TMI or  $\text{Cp}_2\text{Mg}$ . With a  $\text{Cp}_2\text{Mg}$  vapor pressure of 0.159 Torr at  $40^\circ\text{C}$ , the binary gas mixture  $\text{Cp}_2\text{Mg}:\text{H}_2$  was used as a particularly challenging and technologically relevant test bed to demonstrate the performance of the sensor-based metrology. Sensitivity levels of 0.6 ppm were achieved, corresponding to  $\pm 3\text{E-}5\%$   $\text{Cp}_2\text{Mg}$  in  $\text{H}_2$ . Long-term temperature drifts were used to simulate MO source aging effects. Despite 50% change of the vapor pressure over a 3 h period, the  $\text{Cp}_2\text{Mg}:\text{H}_2$  composition remained constant at the target 0.01 mol% with variation of only  $\pm 0.3\%$  of this value. Controllability was limited by the reproducibility of the  $\text{H}_2$  mass flow controllers used as actuators. Acoustic measurements were also used while applying

short-term disturbances and the control scheme reduced the resulting composition oscillations by  $>2\times$ ; these investigations showed that gas feed lines and sensor should be maintained at temperatures at least  $20^\circ\text{C}$  above the temperature of the source in order to minimize condensation of the metalorganic compound and to limit the effect of short-term disturbances due to potential temperature oscillations.

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