# A Method to Extract Physical Properties from Raman Scattering Data in a CVD Reactor

Jang Hwang, Chinho Park*, Min Huang, and Tim Anderson
University of Florida, Department of Chemical Engineering, Gainesville, FL 32611, U.S.A.
*Yeungnam University, School of Chemical Eng. & Tech., Gyongsan 712-749, KOREA

The design and operation of metalorganic chemical vapor deposition (MOCVD) reactors strongly influence film properties. To develop a realistic reactor model, accurate kinetic information for chemical reactions in the reactor is required. In this study, a method to extract physical parameters, including homogeneous rate constants, from *in situ* Raman scattering measurements was established.

For the experimental results reported here, precursors and carrier flows were introduced to an upflow cold-wall CVD reactor through either the center tube of a two-concentric inlet geometry or through the annulus of the middle inlet in a three-concentric tube inlet design. The entering gases impinged on a resistively heated susceptor, which faced the inlets at an adjustable distance. A Ramanor U-1000 Raman spectrometer was used to collect the $90^o$ scattered light. A 2D, axisymmetric reactor model was combined with both genetic and Simplex algorithms to estimate physical parameters from experimental data, i.e. Raman intensities as a function of position. Control parameters for the genetic algorithm were determined by solving several test problems.

The parameter estimation procedure was validated by comparing estimated values of the gas diffusivity and relative Raman cross-section from data for methane in $N_2$. Experiments were conducted in the three-inlet geometry at 23 $^o$C for several gas velocities; 2.5, 3.5, and 4.5 cm/s. For all three velocities, the estimated values of the relative Raman cross-section and diffusivity were in reasonable agreement with those predicted by semi-empirical models or measurements and reproduced experimental concentration profiles well. It is noted that the estimation procedure was able to simultaneously extract Raman cross-section and other properties. In particular, the cross-section is important for quantitative analysis of Raman scattering data.

Data on the pyrolysis of trimethylindium (TMIn) using the 2-inlet design were analyzed to estimate the relative Raman cross-section and first order reaction rate constant for the homogenous decomposition of TMIn. The rate equation was reparameterized to reduce the correlation between frequency factor and activation energy (1). The estimation procedure provided a good fit to the TMIn concentration profile (Fig. 1). The frequency factor and activation energy were found to be $10^{11.8}$ $s^{-1}$ and 34.0 kcal/mol, respectively. The relative Raman cross-section was also estimated as 23.3. Confidence intervals for the best estimates were numerically evaluated as $7.5\times10^{10}$ $s^{-1}$ and 1.2 kcal/mol with 95% confidence. The estimated rate constant parameters are compared to the previously reported values in Table 1. As shown in this table, the pre-exponential factor and activation energy estimated from measurements reported in the two studies using hydrogen as the carrier gas were quite different. Although inert, reducing, or a free radical scavenger were used as a carrier gas in previous studies, no chemical influence of the carrier gas is evident. Apparently the method of estimating the parameters resulted in a high degree of correlation between these two parameters. It was also noted that with the conditions used in this study, TMIn decomposition occurred only in the gas phase as evidenced by no observable TMIn just below the susceptor, supporting the assumption of purely homogeneous reaction. Furthermore, the concentration and temperature profiles were measured without the influence of an external probe.

The authors would like to thank Jim Hinnant and Dennis Vince for their kind support.

## REFERENCES

1. R. Mezaki and J.R. Kittrell, Ind. Eng. Chem., **59**, 63 (1967).
2. M.G. Jacko and S.J.W. Price, J. Cryst. Growth, **42**, 1198 (1964).
3. C.A. Larsen and G.B. Stringfellow, J. Cryst. Growth, **75**, 247 (1986).
4. N.I. Buchan, C.A. Larsen and G.B. Stringfellow, J. Cryst. Growth, **92**, 591 (1988).

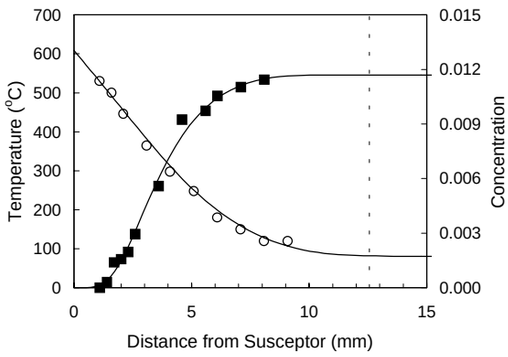


Fig. 1. TMIn decomposition in the cold-wall CVD reactor: TMIn (■) and temperature (○). The dashed line indicates the position of the gas inlet.

Table 1. Rate parameters for the 1st order decomposition of TMIn.

| | Frequency factor ($s^{-1}$) | Activation energy (kcal/mol) | Carrier |
|---|---|---|---|
| Present work | $10^{11.8}$ | 34.0 | $N_2$ |
| Jacko & Price (2) | $10^{15.7}$ | 47.2 | Toluene |
| Larsen & Stringfellow (3) | $10^{12.6}$ | 40.5 | $N_2$ |
| | $10^{12.0}$ | 35.9 | $H_2$ |
| Buchan *et al.* (4) | $10^{17.9}$ | 54.0 | He |
| | $10^{13.4}$ | 39.8 | Deuterium |
| | $10^{15.0}$ | 42.6 | $H_2$ |