

Ultrasensitive Absorption Spectroscopy  
by Intracavity Laser Techniques

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INTRODUCTION

Diagnostic techniques which can be used to monitor spectroscopically the gas phase during the chemical vapor deposition (CVD) of material on a substrate are of significant value both in the analysis of reaction mechanisms and in the real time control of deposition conditions. The *in situ* detection of gas phase intermediates during CVD is of special importance in obtaining a realistic understanding of the mechanism(s) underlying the preparation of a specific deposited material. These *in situ* diagnostic measurements also can be utilized to optimized processing conditions.

Laser induced fluorescence (LIF) has often been used to monitor reaction intermediates because of its high sensitivity for detecting gas phase molecules. Many chemical conditions which facilitate CVD, however, are not well suited for LIF spectroscopy due to highly reactive environments and pressure conditions which quench emission yields or because of the large amounts of background emission created by the dissociative processes, e.g., during plasma discharge. By contrast, absorption spectroscopy has long been recognized as a widely applicable technique which can be readily utilized in chemical, pressure, and radiation conditions not conducive to LIF detection. The major limitation is sensitivity which in conventional absorption spectroscopy has prevented its application to monitoring low concentrations of molecules and radical concentrations.

Recently, the limited detection sensitivity of absorption spectroscopy has been addressed through the development of intracavity laser spectroscopy (ILS) [1,2]. ILS techniques have been used in a variety of instrumental configurations to demonstrate enhanced detection sensitivities for absorption measurements of many orders of magnitude relative to conventional absorption spectroscopy [1,2]. The enhanced sensitivity derives from the competition between the gain in the laser medium and the wavelength-dependent losses within the laser resonator. By placing the species of interest inside the optical resonator cavity of a longitudinally multimode laser, the absorption spectrum of the intracavity atomic or molecular species is superimposed on the wavelength-dispersed spectrum of the laser output.

EXPERIMENTAL

The ILS laser system is shown schematically in Figure 1. A modified dye laser (Coherent 590) is pumped by an argon ion laser (Coherent I-53-8 or Coherent I-53-18). The pumping radiation is attenuated as a function of time (33 Hz) by passing it through an acousto-optic modulator (AOM1). AOM1 diverts enough pump power to prevent the dye laser from reaching threshold conditions. When AOM1 is switched off, the pump laser brings the dye laser rapidly above threshold ( $\sim 0.15 \mu\text{s}$ ). The dye laser output passes through a second acousto-

optic modulator (AOM2) which deflects part of the dye laser output to the spectrometer. The wavelength-dispersed radiation exiting the spectrometer is focused onto the face of an intensified vidicon camera. Such multichannel detection makes it feasible to monitor substantial portions of the rovibronic absorption spectrum of the intracavity species in real time.

The period of time during which the dye laser operates above threshold and AOM2 remains open determines the generation time,  $t_g$ , of the ILS laser system [3]. It has been shown that the intracavity absorption obeys a Beer-Lambert relationship with the equivalent pathlength of absorption,  $L_{eq}$ , given by  $L_{eq} = R \cdot t_g \cdot c$  where  $R$  is the ratio of the pathlength of the laser through the intracavity absorber to the length of the laser resonator cavity and  $c$  is the velocity of light. For the results presented here,  $L_{eq}$  was in the range of 3 - 50 km.

The wavelength of the ILS dye laser is controlled by angle tuning an intracavity pellicle. The spectral bandwidth of the dye laser is 0.8 nm ( $22 \text{ cm}^{-1}$ ) and the overall spectral resolution of the detection system is about 95000 ( $0.18 \text{ cm}^{-1}$ ). The spectra presented here are a composite of a number of individual spectra obtained from overlapping wavelength regions.

Contained within the 1 m long cavity of the dye laser is the sample cell. It is equipped with 0.5 inch thick, fused-silica windows positioned at Brewster's angle. During the CVD process, these windows are continuously flushed with hydrogen or argon to prevent contamination by any particulate products of the decomposition which would render the cell windows opaque to the transmission of the laser radiation. The sample cell is modular in design consisting of sections of quartz tubing joined together using stainless steel fittings (Cajon Ultra-Torr). Decomposition of the source material in the intracavity cell is accomplished by (1) a microwave discharge in an Everson-Broida cavity operated at ~100 W and in a geometry concentric with the laser axis or (2) pyrolysis in an 1500 W tube furnace surrounding the central 6" section of the cell. The various gases used are introduced into the cell by stainless steel handling systems which include flowmeters and mass flow controllers.

In order to examine resulting deposited films, 1/4" x 1/2" sections of oxidized (~1  $\mu\text{m}$  thick) silicon wafer are placed inside the decomposition zone of the intracavity CVD cell. The surface composition of the films prepared by the CVD processes are examined by XPS analysis.

## RESULTS AND DISCUSSION

We have previously reported the ILS detection of silylene ( $\text{SiH}_2$ ) in the microwave discharge decomposition of silane in argon [4,5]. Electronically excited argon and  $\text{H}_2$  species are observed also under some of these conditions. Different concentrations of  $\text{SiH}_2$  are observed by ILS in the microwave discharge decomposition of phenylsilane, ethylsilane and ethyltrichlorosilane under similar experimental conditions. Since several studies [6] have indicated that  $\text{SiH}_2$  is a dominant precursor to Si and  $\alpha\text{-Si-H}$  deposition, its detection is of special importance in examining source materials for the preparation of silicon.

Figure 2 shows a section of the ILS spectrum observed during the pyrolysis of silane at 750 °C and with a total pressure of 6.2 Torr in a 1:1 mix with H<sub>2</sub>. The wavelength region is within the (0,3,0)-(0,0,0) vibronic band in the A-X transition of SiH<sub>2</sub>. Almost all the absorption features in this spectrum are due to known transitions of SiH<sub>2</sub>. Spectra in this wavelength region also have been obtained during the pyrolysis of a number of organosilanes. Different relative intensities of SiH<sub>2</sub> absorption transitions are observed under similar pyrolysis conditions. For example, more intense SiH<sub>2</sub> absorptions can be observed in the pyrolysis of ethylsilane than in the pyrolysis of silane.

A primary obstacle to the use of organosilanes for the CVD of silicon is the seemingly inevitable incorporation of carbon in the resulting silicon films. It is thought that carbon deposition under these conditions occurs via a polymeric process [7]. As a consequence, the radical C<sub>2</sub> is a possible gas phase precursor to carbon incorporation in the films. Figure 3 shows a section of the ILS spectrum obtained of the microwave discharge decomposition of 0.1 Torr of acetylene in 0.8 Torr of argon in the region of the 0-1 band head of the C<sub>2</sub> Swan system [8].

Both the SiH<sub>2</sub> and C<sub>2</sub> ILS absorption spectra are recorded under real time, *in situ* CVD conditions which produce deposited films. In the case of pyrolysis of silane (Figure 2), XPS analysis of the deposited material show that it is essentially pure crystalline silicon. The XPS analysis of the films produced during the plasma discharge of acetylene demonstrate a pure carbon composition. The short (1-5 sec) accumulation times for these ILS data facilitate the control and optimization of CVD conditions through diagnostic measurements of gas phase species.

Stable molecules also can be monitored directly by ILS through either allowed (e.g., visible electronic transitions of NO<sub>2</sub> [9,10]) or forbidden absorptions (e.g., vibrational overtone transitions in the ground electronic state of CH<sub>4</sub> [11,12]). Although the latter overtone transitions are of particular interest in astronomical spectroscopy [13], they also may be used in absorption diagnostics via ILS. Figure 4 presents the overtone absorption spectrum of CH<sub>4</sub> recorded by ILS near 682 nm for a room temperature sample (610 Torr). The absorption strength of this line has been measured by ILS [11,12] as have collisional broadening parameters [12].

The diagnostic capabilities of ILS in CVD have one additional experimental characteristic which can be of significant practical advantage. Since the spectral information is contained on the laser beam which exits the dye laser cavity, the ILS data can be transmitted over optical fibers. It has recently been demonstrated that absorption data recorded by ILS can transverse an optical fiber without significant distortion [14].

#### REFERENCES

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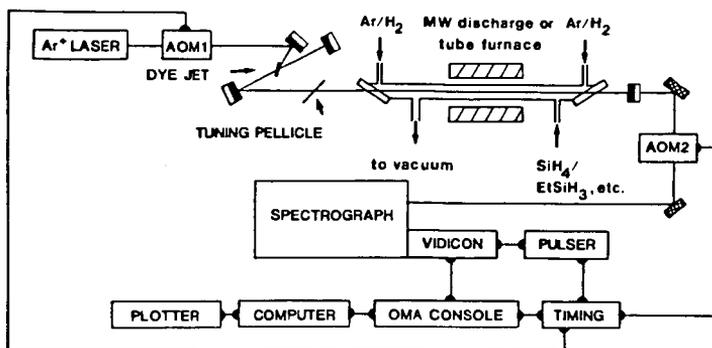


Figure 1. Instrumentation used for intracavity laser spectroscopy of gaseous species produced in the pyrolytic and/or microwave discharge decomposition of source compounds for  $\text{SiH}_2$ .

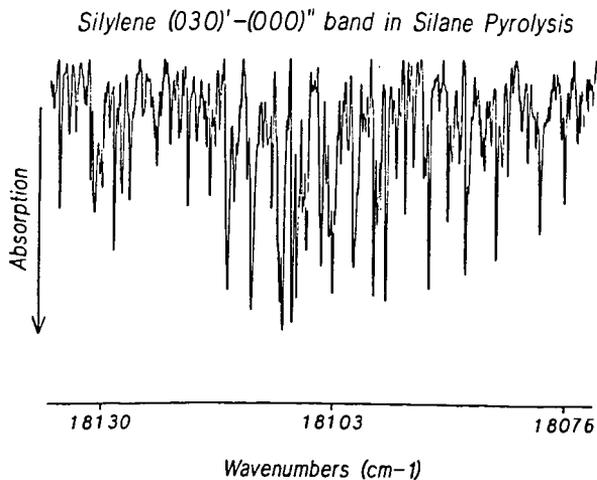


Figure 2. ILS spectrum for the pyrolysis of 52% silane in  $\text{H}_2$  at 8.5 Torr of total pressure and with  $T_0 = 800^\circ\text{C}$  ( $t_0 = 125 \mu\text{s}$ ). This spectrum is in the region of the strongest transitions of the  $(030)^+ - (000)^+$  band of  $\text{SiH}_2$ . The base line corresponds to zero laser intensity, i.e., 100% absorption.

*(0-1) band head of C-C Swan system*

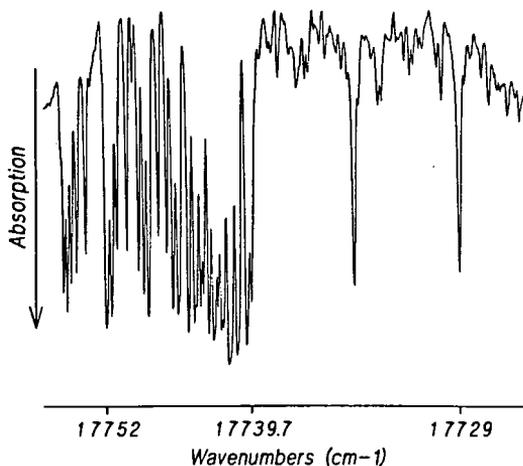


Figure 3. ILS spectrum of a microwave discharge of  $\text{C}_2\text{H}_2$  acetylene in argon at 0.7 Torr total pressure. The spectrum is centered at the (0-1) bandhead of the C, Swan system.

*ILS spectrum of Methane at 610 torr & 295 K*

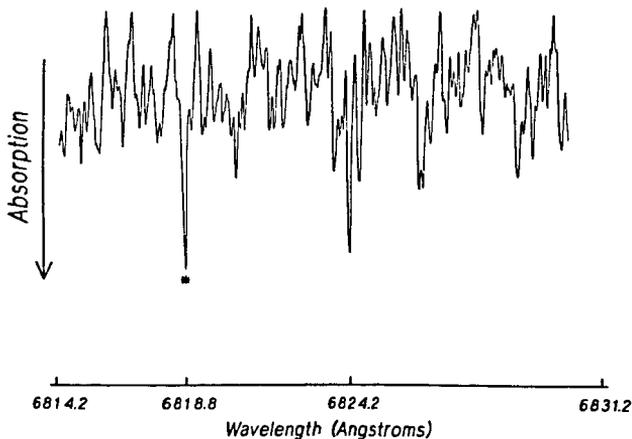


Figure 4. The ILS spectrum of a part of the 682 nm band of methane (assigned as  $2\nu_2 + 3\nu_3$ ). This spectrum is a composite of individual spectral profiles and is obtained by joining together spectral profiles recorded for overlapping spectral regions. The most prominent feature is labeled by an asterisk (\*).