

Spatially resolved measurements of absolute CH₃ concentration in a hot-filament reactor

E.H. Wahl^{a,*}, T.G. Owano^a, C.H. Kruger^a, Y. Ma^b, P. Zalicki^b, R.N. Zare^b

^a Department of Mechanical Engineering, Stanford University, Stanford, CA 94305, USA

^b Department of Chemistry, Stanford University, Stanford, CA 94305, USA

Abstract

Methyl radicals are generated in a hot-filament diamond synthesis reactor using a resistively heated tungsten filament (20 mm long) in a slowly flowing mixture of 0.5% CH₄ in H₂. The UV absorbance of CH₃ is measured during deposition using a line-of-sight optical technique called cavity ring-down spectroscopy (CRDS). Measurements are carried out at 213.9 nm, a wavelength at which the CH₃ absorption cross section has been shown, by others, to be independent of temperature over a large range. We observe a strong sensitivity of the methyl radical concentration throughout the reactor to the substrate temperature. At some operating conditions, we also observe the methyl radical concentration to peak at a location several millimeters from the filament surface. This behavior of CH₃ with distance from filament is in qualitative agreement with two-dimensional models of the deposition environment, and is attributed to the effect of Soret diffusion on the balance of the primary methyl production/destruction reaction. © 1997 Elsevier Science S.A.

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1. Introduction

The methyl radical has fundamental importance for studies of diamond film growth by chemical vapor deposition (CVD) because it is regarded as a gas-phase precursor of the diamond film [1–3]. Therefore, starting with the first report in 1988 on infrared detection of CH₃ during filament-assisted growth of diamond [4], several techniques have been applied to monitor methyl radicals in a CVD reactor, including REMPI spectroscopy [4–8], UV absorption spectroscopy [9,10], and mass spectrometry [11]. These techniques, however, can be intrusive (as in the case of REMPI) and of limited spatial resolution (mass spectroscopy) and sensitivity (absorption). The CH₃ mole fraction in a CVD reactor has been modeled [12], and the relation between the model predictions and growth rate and film quality has been studied [13,14].

We have developed diagnostics for the methyl radical based on the cavity ring-down spectroscopy technique (CRDS) [15–20]. CRDS is a highly sensitive absorption

spectroscopy that determines the absolute absorbance of a laser pulse passing through a sample. In a manner similar to single-pass laser absorption spectroscopy, this measurement is performed with two-dimensional spatial resolution; however, unlike the case of single-pass absorption spectroscopy, CRDS measures absorbance as low as 10⁻⁵–10⁻⁷ and is insensitive to shot-to-shot power fluctuations in the laser pulses. These features make CRDS suitable for high sensitivity measurements in the near UV spectral region where pulsed lasers are commonly used.

In this report we present measurements of the methyl radical which provide absolute CH₃ concentration profiles in a hot-filament reactor. Our technique takes advantage of the high sensitivity measurement of methyl radical absorbance at 213.9 nm made possible by cavity ring-down spectroscopy. The CH₃ absorption cross-section (σ) at 213.9 nm has been measured by Hwang and coworkers [21,22], who found σ to be insensitive to gas temperature within the range of 1250 to 2000 K ($\sigma = 1.04 \pm 0.13 \times 10^6$ cm²/mol).

* Corresponding author. Fax: +1 415 723 1748.
e-mail: ewahl@saha.stanford.edu.

2. Experimental setup

The experimental setup for cavity ring-down spectroscopy of methyl radicals in a hot-filament reactor has been described in detail elsewhere [23]. In the present study, the ring-down cavity is 62 cm long with mirrors mounted in 1.5 inch thick aluminum blocks separated with four stainless steel rods 0.75 inch in diameter for cavity stability. The reactor is placed inside this cavity frame and connected to the mirror mounts by means of flexible bellows. A laser pulse injected into the cavity circulates back and forth along the same path between the cavity mirrors, crossing the reactor parallel to the filament and substrate. The distance between the filament and the pulse path is controlled with a micrometer that moves the reactor on a translation stage.

The schematic of our CRDS setup is shown in Fig. 1. An excimer-laser-pumped dye laser (Lambda-Physik) working with coumarin 440 was used as the pulse source. The pulses were 15 ns long with 0.18 cm^{-1} linewidth. After frequency doubling in a BBO crystal with an Inrad Autotracker, the 214 nm pulse was shaped with the system of pinholes and lenses to match approximately the TEM_{00} transverse mode of the optical cavity. The quasi-hemispherical optical cavity was 62 cm long with a flat entrance mirror and a 2 m curvature concave back mirror. The mirrors were coated by Lightning Optical

Corp. and achieved 98.9% reflectivity at 213.9 nm, as determined directly by the ring-down time τ_0 of the empty cavity. The TEM_{00} cavity mode has approximately a cylindrical form with a waist of 0.5 mm in diameter.

The light transmitted through the back mirror of the cavity was collected by a photomultiplier (PMT) and the PMT signal as a function of time was recorded on an HP 54510A digitizing oscilloscope with 2 ns temporal resolution. The ring-down waveforms digitized on the oscilloscope were transferred to a PC, averaged, and the ring-down time τ was obtained from a real-time computer fit. The CH_3 absorbance is then obtained from Eq. (1)

$$\alpha L_s = \frac{t_r}{2} \left(\frac{1}{\tau} - \frac{1}{\tau_0} \right), \quad (1)$$

where τ_0 is the empty cavity ring-down time, α is the sample absorption coefficient, and L_s is the sample length. In our experiment L_s is assumed to be equal to the filament length. With α thus determined, the absolute number density of the absorber, n , may be ascertained via knowledge of the cross-section σ and the relation $\alpha = \sigma n$.

The hot-filament reactor consists of a five-way stainless steel cross 4 inches in diameter. A two-stage

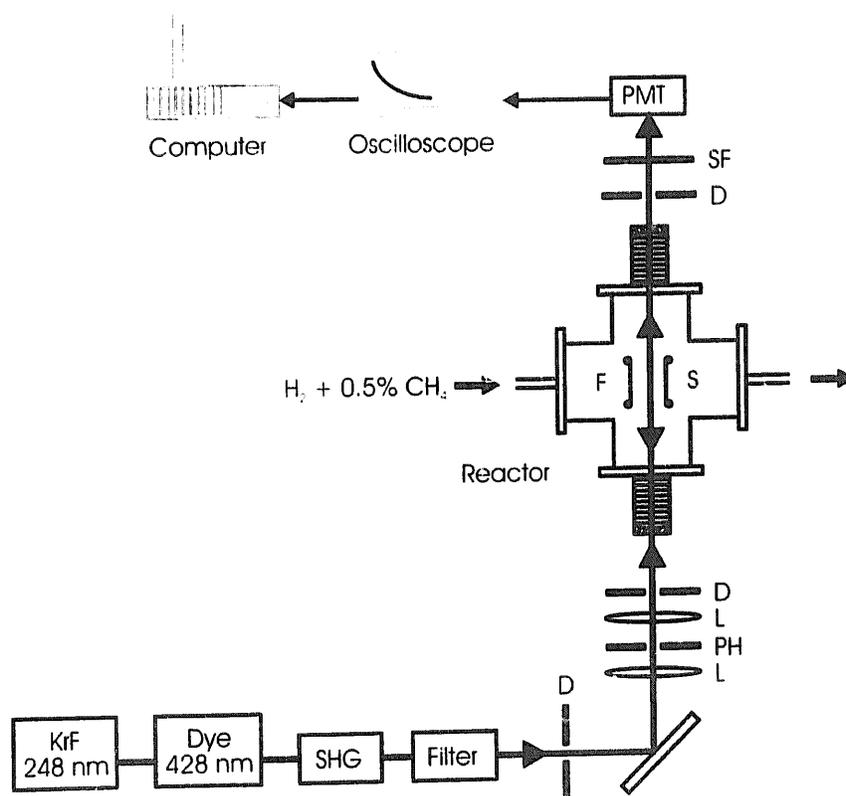


Fig. 1. Schematic of the CRDS system and the hot-filament reactor. PMT, photomultiplier tube; D, iris diaphragm; L, lens; PH, 50 μm pinhole; SF, spectral filter; F, filament; S, substrate.

mechanical pump (E2M40, Edwards) is used to evacuate the chamber to the minimum pressure of 4×10^{-3} Torr. The chamber is filled with 20 Torr mixture of H_2 with 0.5% of CH_4 flowing at a rate of 100 sccm. The tungsten filament is 20 mm long and 200 μm in diameter. It is positioned horizontally inside the chamber using two tungsten posts, 4 cm long and 1.5 mm in diameter, mounted on water-cooled copper electrodes. The filament is resistively heated with dc current to a brightness temperature of 2300 K, which is monitored with a disappearance pyrometer (Pyro Micro-Optical Pyrometer). The substrate is made of a molybdenum strip (4 mm \times 20 mm \times 250 μm) and is resistively heated. The substrate temperature is monitored with a K Type thermocouple which is welded to the rear surface. The front surface is scratched with 10 μm diamond paste. The reactor condition is stabilized for at least 12 h before CRDS measurements are performed.

3. Results

We have applied CRDS to measure methyl radical concentration in two different reactor geometries. In the first geometry, the axis of the circulating CRDS beam is aligned parallel to the filament, and is translated in the plane defined by the filament and the substrate's long axis. In this manner, absorbance as a function of lateral position is mapped out, and converted to absolute number density as described above. Fig. 2 shows the spatial profiles of the CH_3 number density (absorbance)

measured in this manner within the hot-filament reactor at two different substrate temperatures. In this study, the filament temperature is held constant at 2300 K, the total pressure is 20 Torr, and the gas mixture is 0.5% CH_4 in H_2 flowing from left to right at a flowrate of 100 sccm. One can observe that the concentration of methyl radicals falls rapidly with increasing distance from the filament, and that the methyl radical concentration increases significantly at the higher substrate temperature. It is interesting to note that the methyl concentration well upstream of the filament is strongly influenced by the substrate temperature, possibly due to an overall increase in the reactor temperature field and hence methyl radical production. One can also observe that for the 900°C substrate condition the peak methyl concentration occurs at a distance away from the filament (approx. 2 mm). This peaked result agrees qualitatively with the behavior of the CH_3 REMPI signal as a function of distance from the filament reported by Ota and Fujimori [6], but the peak CH_3 concentration we find is two orders of magnitude higher than their estimate. Goodwin et al. [8] also measured spatial profiles of the CH_3 REMPI signal in the hot-filament reactor; however, their data do not extend to positions close to the filament and cannot be directly compared with our observations.

Fig. 2 also shows the methyl radical concentration profile predicted by the two-dimensional model of Mankelevich et al. [24,25] for the same reactor conditions probed experimentally. In this two-dimensional model conservation equations for species, mass, momen-

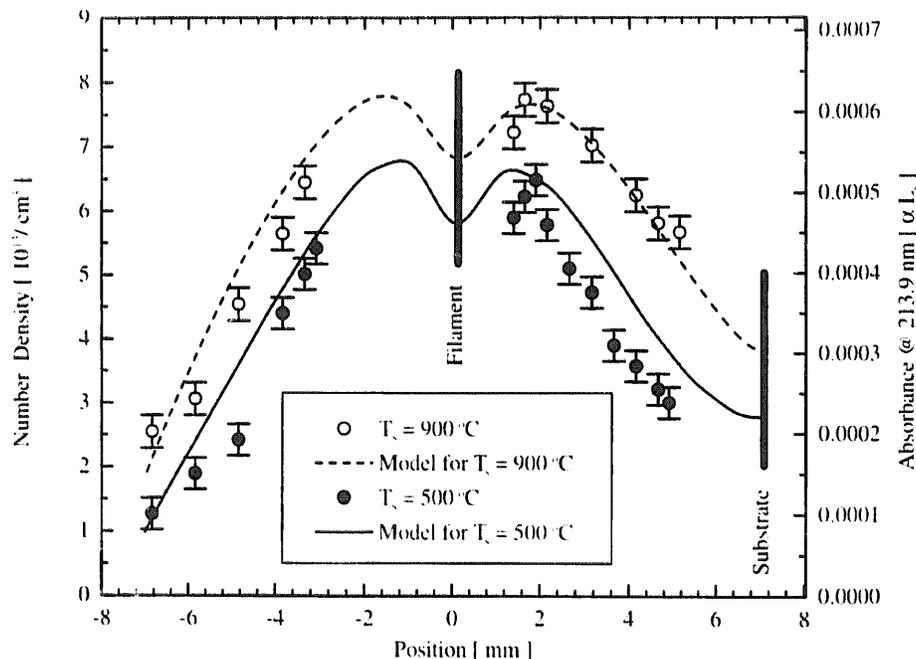


Fig. 2. Spatial profiles of the measured CH_3 number density (absorbance) within the hot-filament reactor at two different substrate temperatures along with the model predictions of Mankelevich. The filament temperature is 2300 K, the total pressure is 20 Torr, and the gas mixture is 0.5% CH_4 in H_2 flowing from left to right at a flowrate of 100 sccm.

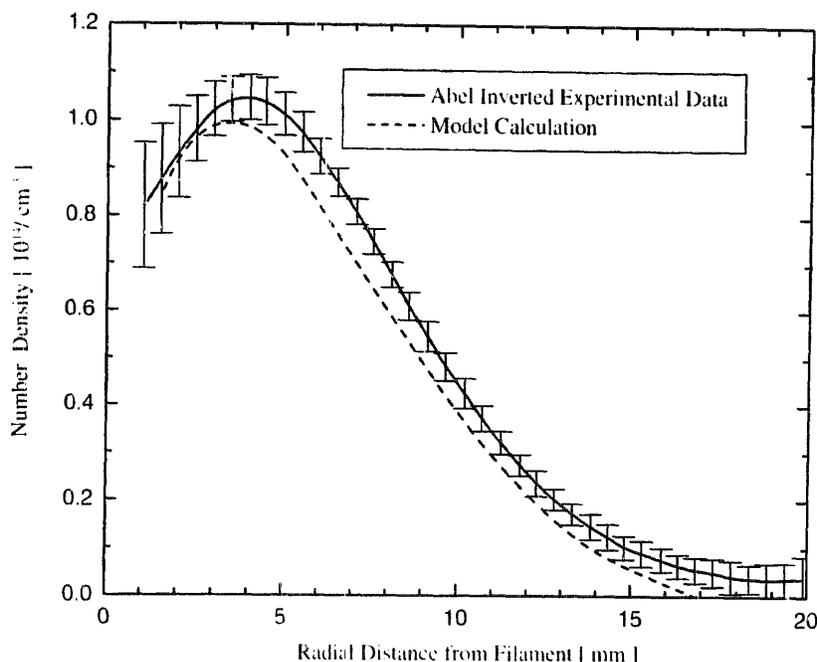


Fig. 3. Radial distribution of the CH_3 concentration near the hot filament obtained by the Abel inversion of the absorbance profile (error bars indicate the effect of experimental uncertainties on the inversion). The filament temperature is 2400 K, the reactor pressure is 20 Torr, and the gas mixture is 0.5% CH_4 in H_2 with a flowrate of 100 sccm.

tum, and energy are solved including molecular and thermal diffusion, along with chemistry for 15 species via 38 reversible reactions. Temperature “slips” at the filament and substrate surface are prescribed from a separate Monte Carlo simulation. The largest uncertainty in this model is the production rate of atomic hydrogen at the filament surface. The results of the model prediction are in good agreement with the experimental measurements both in shape and relative magnitude for the two cases presented. Deviation of the model and experimental data near the substrate in the case of $T_{\text{sub}}=500^\circ\text{C}$ is most likely due to the sensitivity of methyl radical production to the local gas temperature.

McMaster and coworkers [26] discuss the limitations of many of the HFCVD diamond reactor models. One-dimensional models are limited in their ability to account for the true geometry of reactors, often neglecting reactor walls or other surfaces that affect the gas-phase composition and leaving out the three-dimensional character of diffusion. Proper modeling of the hot-filament environment requires sufficient knowledge of the interaction of the hot-filament surface with the gas phase. Despite the fact that much of the gas-phase species are dominated by the effects of the hot filament, little work has been done to assess this interaction.

The second reactor geometry investigated was aimed at understanding the production mechanism of the methyl radical near the filament surface. In this geometry the substrate was removed to provide an axisymmetric temperature and concentration field about the axis of the filament. (The slight asymmetry introduced by the

slow motion of gas through the reactor has been demonstrated in our reactor to be negligible in an experiment where the flow direction was reversed.) The axis of the CRDS circulating beam was then aligned perpendicular to the axis of the filament at its approximate midpoint. In this configuration the CRDS beam was translated away from the filament, effectively probing various chords of the axisymmetric methyl radical field. With the aid of an Abel transform [27] these lateral data can be converted into a profile of the absolute methyl radical concentration as a function of radial distance from the filament. Results of this study are shown in Fig. 3 for a 200 μm diameter filament at a temperature of 2400 K, a reactor pressure of 20 Torr, and a mixture of 0.5% CH_4 in H_2 .

In Fig. 3 we can see the methyl radical concentration peak at approximately 10^{14} molecules/ cm^3 some 4 mm radially away from the filament surface. Also shown in Fig. 3 is a simplified model calculation for this geometry and operating parameters performed by Roozbehani [28], who solved the one-dimensional radial species conservation equation including molecular and thermal diffusion (assuming that the production of methyl is spatially constant). The results of this model are in good agreement with the experimental data (although Roozbehani suggests that the *absolute* agreement is probably fortuitous) and the calculation yields a similar decay and location of the maximum in the methyl radical concentration.

To understand this off-filament peak of the methyl radical concentration we must consider several

mechanisms. First, atomic hydrogen is produced at the filament surface, while CH_4 (and CH_3) are converted to C_2H_y species at the filament surface [29,30] – hence the filament is an effective sink for these hydrocarbons. Secondly, thermal (or Soret) diffusion of species within the reactor causes the lighter components such as atomic hydrogen to diffuse toward hotter regions of the reactor, while heavier species such as methane diffuse toward the cooler regions [28,31]. This creates a tendency toward thermal segregation of the mixture components, with atomic hydrogen remaining near the filament, and methane moving away from the filament. Finally, the production of methyl radical is dominated by the fast reaction: $\text{H} + \text{CH}_4 \leftrightarrow \text{H}_2 + \text{CH}_3$, which is in partial equilibrium throughout most of the reactor and strongly links the methyl radical concentration field to that of atomic hydrogen and methane. The net effect of these various mechanisms is to create a rising concentration of atomic hydrogen as one approaches the filament, a declining concentration of methane towards the filament, and a production mechanism for methyl that swings from production to destruction depending upon whether hydrogen rises faster than methane declines. Roozbehani [28] has shown in his 2D simulation of his HFCVD reactor [28] that without the effect of Soret diffusion the balance shifts towards a monotonic rise in production as one approaches the filament (hence no peak in methyl concentration), and that by including the effects of Soret diffusion the experimentally measured peak in methyl concentration is accurately predicted.

4. Conclusion

On the basis of our observations we conclude that the CRDS technique can be used for quantitative diagnostic of methyl radicals with high sensitivity. We have applied CRDS to the measurement of methyl radicals generated in a hot-filament reactor. We have observed a strong sensitivity of the methyl radical concentration throughout the reactor to the substrate temperature. The methyl radical concentration field is found to be in good agreement with recent two-dimensional models of the hot-filament environment. At some operating conditions, we also observe the methyl radical concentration to peak at the location several millimeters radially away from the filament surface. This peak in methyl radical concentration is successfully reproduced by a model of the filament environment, and is attributed to the effect of thermal (Soret) diffusion on the balance of the primary methyl production/destruction reaction.

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