Pulsed UV laser Raman spectroscopy of silane in a linear-flow chemical vapor deposition reactor

W. G. Breiland and M. J. Kushner[a)]
Sandia National Laboratories, Albuquerque, New Mexico 87185

(Received 11 October 1982; accepted for publication 9 December 1982)

For the first time, spatially resolved relative concentrations of silane inside a chemical vapor deposition reactor have been measured with spontaneous Raman spectroscopy using the third harmonic of a Q-switched neodymium:yttrium aluminum garnet laser. Concentration profiles were obtained under both atmospheric and low total pressure conditions. Considerable depletion of silane in the gas phase was observed.

PACS numbers: 81.15.Gh, 82.80.Di, 68.55. + b, 33.20.Fb

Chemical vapor deposition (CVD) is used widely for producing coatings and has many applications in microelectronics, electrooptics, superconductors, and wear/corrosion-resistant films.[1] Despite the development of CVD as a sophisticated technological art, very little is known about the fundamental physical and chemical processes that lead to deposition. This lack of detailed information is understandable because the CVD environment is quite difficult to study analytically. Over the years a number of *in situ* analytical techniques have been applied to the CVD problem. Mass spectrometry[2] and vapor chromatography[3] both require physical probes and/or remote sensing apparatus and therefore may not record the true distribution of chemical species inside the reactor. Infrared absorption and emission spectroscopy[4] do not have high spatial resolution.

Ideally, one requires a nonperturbing pinpoint probe that can accurately measure sub-Torr concentrations of highly reactive chemical species in the presence of rapidly changing chemical and temperature fields. cw Raman spectroscopy meets most of these requirements and was first proposed as a CVD diagnostic tool by Sedgwick *et al.*[5] They used this technique successfully to measure WF_6 and NH_3 profiles.[6,7] However, attempts to measure silane and chlorosilane densities were thwarted by strong fluorescence from an intermediate species, assumed to be $SiCl_2$, which overwhelmed the Raman signal.[5]

In this letter we report the first nonperturbing, spatially resolved measurements of relative silane concentration profiles inside a CVD cell during atmospheric-pressure and low-pressure deposition of silicon, $SiH_4(g) \rightarrow Si(s) + 2H_2(g)$. The measurements were made using pulsed UV laser Raman spectroscopy. This technique has two advantages over cw Raman methods that typically employ argon-ion lasers. First, one can use gated detection with apertures as short as 15 ns. Continuous sources of photomultiplier current such as susceptor blackbody radiation and dark current are thus effectively suppressed by six orders of magnitude for 10-Hz repetition rates. Second, in the absence of resonant effects, the Raman signal detected by a photomultiplier tube is proportional to the third power of the laser frequency. Thus, for equal average powers, 355-nm radiation will produce a Raman signal that is 2.6 times larger than the signal from 488-nm radiation.

The experimental arrangement is an adaptation of the one used by Hargis[8] to measure trace amounts of nitrogen. A horizontal CVD research cell was constructed by centering a 10-cm-long SiC-coated graphite susceptor inside a 1-m pipe made from standard 10-cm-diam stainless-steel vacuum fittings. One end of the pipe was equipped with a window for the laser and an injection port for the reactant gases. Gas flow inside the cell was restricted to a semicircular cross section by 45-cm-long ceramic plugs placed at the front and back edges of the susceptor and flush with its surface. The susceptor was heated resistively and its surface temperature was monitored with an optical pyrometer through a window on top of the cell. The entire cell was placed on a precision X-Y-Z mount that could be reproducibly positioned to ± 0.001 in.

A frequency-tripled (355 nm), Q-switched neodymium :yttrium aluminum garnet (Nd:YAG) laser delivering 4-ns-long, 40-mJ pulses at 10 Hz was used for the light source. In order to prevent laser burns on the input window, the light was first beam expanded to 50 mm in diameter and then focused to a line above the susceptor with a 1-m focal length lens. The beam entered the cell near the gas inlet and traveled in the same direction as the gas flow. Scattered light was collected at 90° through a 10-cm-diam quartz window located 20 cm from the center of the susceptor using two 50-mm-diam lenses in an infinite-conjugate configuration and focused on 200-μm slits of a 0.75-m monochromator. The probed volume was $0.2 \times 0.2 \times 10$ mm. The monochromator was equipped with a 1200-g/mm grating blazed at 300 nm and an uncooled RCA 31000M photomultiplier tube. A low-fluorescence Schott KV-370 filter was used to suppress scattered light at the laser wavelength. The PMT output was fed directly into a boxcar integrator with a 15-ns gate and a 3-s time constant. Profiles were obtained by translating the cell vertically. No interfering fluorescence was observed. The detection limit for this system was ≈ 10 mTorr of room-temperature silane, with a signal-to-noise ratio of 2/1.

Figure 1(a) displays a series of vibrational Raman spectra of silane (2187 cm^{-1}) and nitrogen (2331 cm^{-1}), taken under atmospheric pressure conditions, as a function of height above the susceptor. The Raman signal is directly proportional to gas density. Temperature gradients within

[a)] Present address: Lawrence Livermore National Laboratories, Livermore, California.

 © 1983 American Institute of Physics

Downloaded 27 Mar 2003 to 128.174.115.149. Redistribution subject to AIP license or copyright, see http://ojps.aip.org/aplo/aplcr.jsp

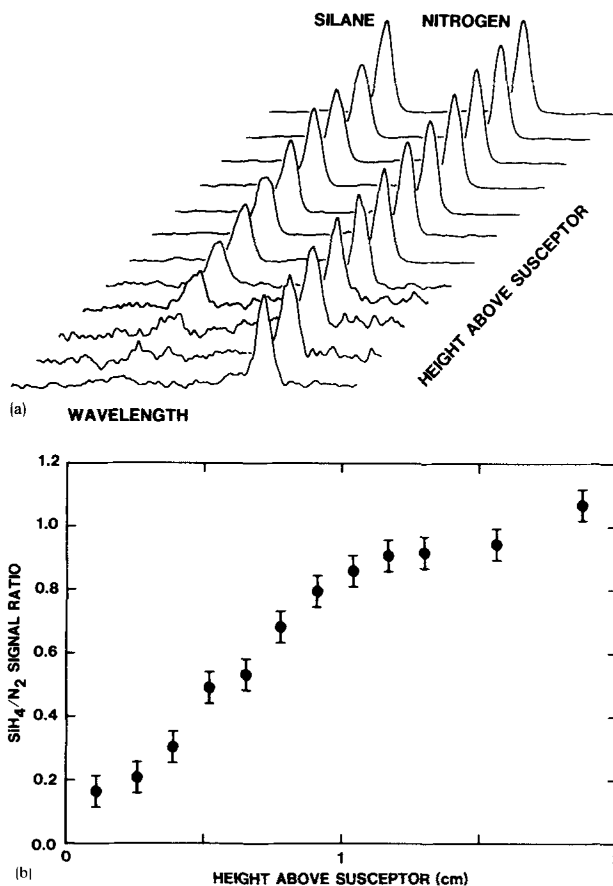

FIG. 1. (a) A series of pulsed UV laser Raman spectra of the vibrational Q branches of silane and nitrogen taken at 0.05-in. intervals starting at 0.05 in. from the susceptor surface. Background signal far from the resonance peaks is zero except for some points near the surface, as discussed in the text. 0.6 Torr silane, 13 Torr nitrogen, 627 Torr helium, 745 °C, 15 cm/s flow velocity. The nitrogen signals have been scaled to the same height to eliminate ideal-gas density effects due to temperature gradients. (b) Ratio (silane/nitrogen) of integrated Q branch Raman signals, taken from the atmospheric pressure data of (a), as a function of height above the susceptor. This ratio is proportional to the partial pressure of silane.

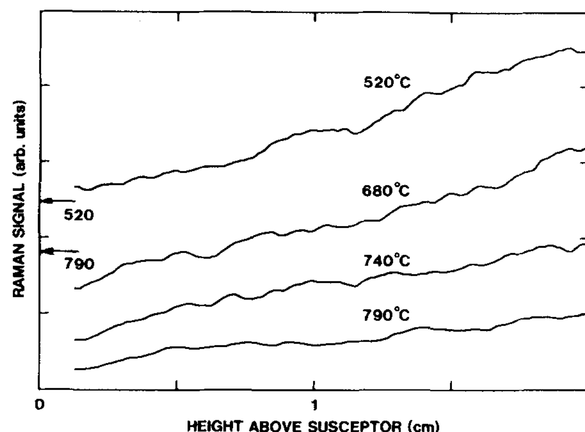

FIG. 2. Silane profiles for low-pressure conditions at various temperatures, obtained by continuously monitoring the 2187 cm^{-1} silane Raman signal as the cell was moved vertically. 0.6 Torr silane, 6 Torr helium, 13 cm/s flow velocity. Arrows indicate zero-height Raman signals expected if the decrease in silane density resulted from ideal-gas thermal expansion only.

the cell cause variations in the Raman signal that are due simply to gas expansion. This uninteresting effect has been cancelled by scaling the spectra such that the nonreactive nitrogen peak heights are equal. Figure 1(b) displays the data of Fig. 1(a) in a quantitative plot normalized to be proportional to the partial pressure of silane. Figure 2 is a series of profiles of silane taken under low-pressure conditions. In this case no normalizing technique could be used, so the profiles contain contributions from both density and silane depletion effects. A number of interesting effects can be seen from this preliminary data.

First, Fig. 1(b) clearly shows that the silane partial pressure near the surface falls to about 20% of its bulk-gas value, demonstrating that silane is substantially depleted in the gas phase. This depletion extends to 1 cm above the susceptor. Depletion could be caused by a diffusion-controlled concentration gradient as silane reacts on the surface, and/or by gas-phase chemical reactions. By changing flow, temperature, and pressure conditions, it may be possible to unravel these two contributions to the deposition mechanism using pulsed-laser Raman profiles.

Second, the silane profiles are dramatically different for atmospheric-pressure and low-pressure conditions. Since the gas-phase temperature profile has not been measured in the low-pressure experiment, no quantitative normalizing scheme is possible, but it can be deduced qualitatively that considerable depletion occurs throughout the gas phase at high temperatures. This is seen by referring to the arrows in Fig. 2 in which the substrate surface temperature T_s was used to calculate an expected zero-height "ideal-gas" Raman signal, given by $(294/T_s)$ times the room-temperature Raman signal. At 520 °C little depletion occurs, but at 790 °C the entire profile is below the expected zero-height ideal-gas signal.

Finally, it can be seen in Fig. 1 that the background noise increases as one nears the susceptor. This is due to stray light at the laser wavelength caused by strong Tyndall scattering from particulates that are formed in the gas phase. These particulates are readily observed when visible 532-nm frequency-doubled Nd:YAG radiation is used. The background decreases as one approaches very close to the susceptor. Visually, this appears as a "dark layer" in the scattered light, about 1 mm thick, above the susceptor. Similar dark layers have been observed in laser Doppler velocimetry, and are attributed to thermophoretic forces that push the particulates away from the heated surface.[9] No particulate scattering was observed at low pressures.

In conclusion, pulsed UV laser Raman spectroscopy has been used to profile a reactive gas species, silane, during chemical vapor deposition. Considerable gas-phase depletion of silane is observed under both atmospheric and low-pressure conditions. The technique used in this study combines the selective, nonintrusive, quantitative, and spatially resolved features of Raman spectroscopy with the added benefits obtained from a high-power pulsed UV laser, providing sensitivity, speed in data acquisition, and elimination of continuous background signals.

The authors would like to acknowledge Philip Hargis, Jr. for considerable help in adapting the pulsed UV laser technique to a working CVD reactor, and James Dishman

Downloaded 27 Mar 2003 to 128.174.115.149. Redistribution subject to AIP license or copyright, see http://ojps.aip.org/aplo/aplcr.jsp

for his expert technical assistance in construction of the apparatus and data acquisition. This work was supported by the U.S. Department of Energy.

[1]See, for example, the Biannual Series, *Chemical Vapor Deposition*, Vols. I–VIII, International Conference Proceedings (The Electrochemical Society, Pennington, New Jersey, 1968–1981).
[2]V. S. Ban, J. Electrochem. Soc. **118**, 1475 (1971); **119**, 761 (1972); **122**, 1389 (1975); S. Lin, J. Electrochem. Soc. **124**, 1945 (1977); **125**, 1877 (1978).
[3]G. Cochet, H. Mellottee, and R. Delbourgo, J. Electrochem. Soc. **125**, 487 (1978).
[4]J. Nishizawa and M. Saito,J. Cryst. Growth **52**, 213 (1981); J. Nishizawa and H. Nihira, J. Cryst. Growth **45**, 82 (1978).
[5]T. O. Sedgwick, J. E. Smith, Jr., R. Ghez, and M. E. Cowher, J. Cryst. Growth **31**, 264 (1975).
[6]J. E. Smith, Jr. and T. O. Sedgwick, Thin Solid Films **40**, 1 (1977).
[7]T. O. Sedgwick and J. E. Smith, Jr., J. Electrochem. Soc. **123**, 254 (1976).
[8]P. J. Hargis, Jr., Appl. Opt. **20**, 149 (1981).
[9]L. Talbot, R. K. Cheng, R. W. Schefer, and D. R. Willis, J. Fluid Mech. **101**, 737 (1980).

Downloaded 27 Mar 2003 to 128.174.115.149. Redistribution subject to AIP license or copyright, see http://ojps.aip.org/aplo/aplcr.jsp