

25 August 2000

Chemical Physics Letters 326 (2000) 400-406



www.elsevier.nl/locate/cplett

Cavity ring down detection of SiH₃ on the broadband $\tilde{A}^{2}A'_{1} \leftarrow \tilde{X}^{2}A_{1}$ transition in a remote Ar-H₂-SiH₄ plasma

M.G.H. Boogaarts ¹, P.J. Böcker, W.M.M. Kessels, D.C. Schram, M.C.M. van de Sanden*

Centre for Plasma Physics and Radiation Technology (CPS), Department of Applied Physics, Eindhoven University of Technology, P.O. box 513, 5600 MB Eindhoven, The Netherlands

Received 26 April 2000; in final form 26 June 2000

Abstract

Here we report on the use of the cavity ring down (CRD) technique for the detection of the silyl radical SiH₃ on the broadband $\tilde{A}^{2}A'_{1} \leftarrow \tilde{X}^{2}A_{1}$ transition around 215 nm. SiH₃ has been detected in a remote Ar-H₂-SiH₄ plasma during hydrogenated amorphous silicon (a-Si:H) thin film growth. The measurements demonstrate the capability of CRD to measure small broadband absorptions in the deep UV in the hostile environment of a deposition plasma. The SiH₃ absorption shows an expected dependence on the SiH₄ precursor flow and correlates well with the a-Si:H growth rate. The observed absorptions correspond with SiH₃ densities in the range $2-13 \times 10^{18} \text{ m}^{-3}$, which is at least two orders of magnitude above the estimated SiH₃ detection limit. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

In many low-temperature plasma applications, low density (i.e. short lived) species play a key role, but often their role is not established in detail. The study of these species in plasmas calls for a sensitive technique that is applicable in the hostile plasma environment. The technique should be non-intrusive and preferably also in situ and remote at the same time. In the plasma enhanced chemical vapour deposition of hydrogenated amorphous silicon (a-Si:H) for instance, an in situ measurement of the silyl

¹ E-mail: M.G.H.Boogaarts@tue.nl

radical SiH₃ in the plasma could elucidate the crucial plasma chemistry and the assumed dominant role of SiH₃ in the growth mechanism of a-Si:H thin films, but not many direct observations of this species under real plasma deposition conditions exist. Most detailed studies on SiH₃ in a plasma reactor are performed with mass spectrometry where state of the art techniques are used to enable neutral radical detection [1,2]. The sensitivity of mass spectrometry is very high (SiH₃ detection limit < 10^{16} m⁻³) but the technique has no spatial resolution and calibration is laborious. Furthermore, when in situ it is not non-intrusive and vice versa, unless an extraction orifice is used at the position of the substrate.

Optical/spectroscopic techniques generally are non-intrusive, remote, and in situ, but very few

^{*} Corresponding author. Fax: +31-(0)40-2456442; e-mail: M.C.M.v.d.Sanden@phys.tue.nl

^{0009-2614/00/\$ -} see front matter © 2000 Elsevier Science B.V. All rights reserved. PII: \$0009-2614(00)00795-8

studies on SiH₂ in plasmas are reported that apply such techniques. Most of the experimental data on the electronic spectroscopy of SiH_2 (and SiD_2) currently available results from resonance enhanced multi-photon ionization (REMPI) studies in a flow reactor [3–5]. However, like mass spectrometry, the REMPI technique is very sensitive, but generally not in situ. The first electronic transition of SiH₃ is the $\tilde{A}^{2}A'_{1} \leftarrow \tilde{X}^{2}A_{1}$ transition, which is optically accessible in the deep UV around 215 nm [5]. The upper electronic A state is predicted to be predissociative [6] and thus short-lived and non-radiative. Therefore, unless higher electronic states are probed [3-5], only direct absorption techniques can be applied that generally lack sensitivity. Nevertheless, the first experimental observation of the $\tilde{A} \leftarrow \tilde{X}$ transition of SiH₃ resulted from direct UV absorption measurements in a flash photolysis cell [7], and meanwhile this technique has even been successfully applied for the detection of SiH₃ in a radio frequency (RF) generated H_2 -SiH₄ plasma under high silvl production conditions [8].

Optical/spectroscopic techniques for the detection of silyl also have been applied in the infrared region. Infrared diode-laser spectroscopy has been applied in a silane glow discharge to study the spectroscopy and the structure of SiH₃ in the electronic ground-state [9]. A further study employed infrared diode-laser absorption spectroscopy (IRLAS) for the measurement of SiH₃ in an RF silane plasma [10], yielding among other things the rotational temperature of the silyl radical. However, even with this sophisticated (and complex) technique, in situ optical detection limits for SiH₃ can not be pushed below 10^{17} m⁻³.

The availability of the 'cavity ring down (CRD)' technique in the last decade [11], enables an important step forward in the in situ detection of key radicals in low-temperature plasma processing [12– 16]. The highly sensitive CRD technique (first demonstrated by O'Keefe and Deacon in 1988 [17]), is based on the measurement of the rate of absorption of a light pulse confined in a closed optical cavity. The cavity usually consists of two highly reflective mirrors with a reflectivity R and a separation d around the sample medium with density n, absorption cross section σ , and absorption pathlength L. With monochromatic light, the rate of absorption, which is characterized by the decay time τ of the light intensity in the cavity, is related to the absolute absorption per pass $n\sigma L$, via the expression $1/c\tau = (1 - R + n\sigma L)/d$, where *c* is the speed of light. A measurement of the decay time, which is commonly referred to as the 'ring-down time', therefore directly provides the absolute absorption in the cavity, independent of the peak intensity of the light pulse.

In this Letter we report on the use of the cavity ring down technique for the detection of the silyl radical on the broadband $\tilde{A}^2A'_1 \leftarrow \tilde{X}^2A_1$ transition around 215 nm in a remote Ar-H₂-SiH₄ plasma that is used for the fast deposition of a-Si:H thin films. The measurement of broadband absorptions with CRD is discussed, in which special attention is given to the implication of the hostile plasma environment for the broadband measurement procedure. Also, the problem of identifying the broadband signal carrier is discussed.

2. Experimental

A scheme of the experimental set-up is depicted in Fig. 1. The method and the set-up for fast a-Si:H



Fig. 1. Scheme of the experimental set-up for the CRD measurements in a remote $Ar-H_2-SiH_4$ plasma. The cascaded arc plasma source is operated on a 45 A DC current, a 55 sccs Ar flow, and a 10 sccs H_2 flow. The downstream injected SiH₄ flow is varied. The distance between plasma source and substrate is 35 cm. The ring-down cavity samples the plasma beam 11 cm from the substrate. The cavity length is 1.02 m.

deposition using an expanding thermal plasma generated by a cascaded arc have already been described in detail elsewhere [18–20]. In the experiments reported here the plasma is generated by a 45 A DC discharge in a premixed argon-hydrogen flow (55 standard cubic centimeter per second (sccs) Ar, 10 sccs H₂). The plasma expands from a nozzle into a low-pressure (0.20 mbar) vessel. The chemical activity in the plasma beam emanating from the nozzle comes mainly from atomic hydrogen. The silane precursor is injected into the plasma beam via a ring that is mounted 5 cm downstream from the nozzle. At this point, silane is dissociated and the silyl radical is mainly produced by hydrogen abstraction [21]:

H + SiH₄ → SiH₃ + H₂
(
$$k \approx 5 \cdot 10^{-17} \text{ m}^3 \text{s}^{-1}$$
 at 1000 K). (1)

The distance between plasma source and substrate is 35 cm. The chosen experimental conditions correspond to the optimum conditions for which device quality a-Si:H is deposited at rates up to 10 nm/s [22].

The ring-down cavity samples the plasma beam 11 cm from the substrate. The stable optical cavity is set up by two plano-concave highly reflective dielectric mirrors (Laseroptik GmbH), that are a distance d = 1.02 m apart. The mirrors have a 1 inch diameter, a radius of curvature r = -1 m, and a specified minimum transmittivity T = 0.2% around 218 nm (implying a maximum reflectivity R = 0.998). The mirrors are mounted on flexible bellows and directly seal the plasma reactor. To protect the mirrors from the hostile plasma environment, a small Ar flow can be maintained from the mirrors into the vessel through 5 mm diameter diaphragms that are positioned in front of the mirrors on the axis of the cavity [14].

The light pulse, that is coupled into the cavity via the lower mirror, is generated by a pulsed tunable dye-laser (Sirah Laser- und Plasmatechnik GmbH, Precisionscan-D) that is pumped with a 10 Hz Nd:YAG-laser (Spectra-Physics/ Quanta-Ray DCR-11) at 355 nm. The dye-laser has a bandwidth of 1.7 pm ($\approx 0.1 \text{ cm}^{-1}$ at 430 nm) and is operated on a coumarin dye around 430 nm. The dye-laser output

is frequency-doubled in a BBO-crystal, resulting in a light pulse around 215 nm with an estimated bandwidth of 0.2 cm^{-1} . The light leaking out from the second mirror (on the top), is detected with a PMT (Hamamatsu R928). An interference bandpass filter with a central transmission wavelength close to the light pulse wavelength is used behind the second mirror to reduce the exposure of the PMT to continuous plasma and background light. A similar filter is used in front of the first mirror to suppress the residual fundamental 430 nm dye-laser light and to assure a low light intensity level in the ring-down cavity. The PMT signal is sampled by a digital 500 Ms/s, 100 MHz oscilloscope (Tektronix TDS340A), averaged on board over several laser pulses, and the resulting transient is processed by a PC, where the characteristic 'ring-down time' τ is determined from a weighed least-squares fitting of the logarithm of the data.

3. Results and discussion

In order to identify the absorbing species, we first performed a spectral scan. Fig. 2 shows the absorption of SiH₃ on the $\tilde{A}^2A'_1 \leftarrow \tilde{X}^2A_1$ transition as it



Fig. 2. The absorption of SiH₃ on the $\tilde{A}^2 A'_1 \leftarrow \tilde{X}^2 A_1$ transition around 220 nm as measured with cavity ring down in an expanding Ar-H₂-SiH₄ plasma (10 sccs SiH₄ flow, \blacktriangle). The absorption data are the net result of CRD measurements with and without SiH₄ flow at each wavelength value. The data are compared to those reported by Lightfoot et al. (\circ , scaled vertically) [7].

is measured in the expanding $Ar-H_2-SiH_4$ plasma with a 10 sccs silane flow. For clarity, we plotted a reduced data set. The complete data set covers the full range of our optical set-up (≈ 13 nm, mainly limited by the cavity mirrors) with a resolution of at least 0.1 nm without revealing any structure. This is consistent with the observations by other groups who also found a very broad absorption feature [7.8]. For comparison, Fig. 2 also shows the data reported by Lightfoot et al. [7]. Measuring the SiH₃ $\tilde{A} \leftarrow \tilde{X}$ spectrum for different plasma conditions, had no influence on the shape of the spectrum. Since these different conditions correspond to different kinetic temperatures in the plasma, we conclude that, over the temperature range encountered upon changing these conditions, the shape of the spectrum is mainly determined by the predissociation lifetime broadening and not by the temperature.

Notice that in CRD absolute absorptions are always determined by measuring the difference in 'cavity loss' $1/c\tau$ of the cavity with $(1/c\tau = (1 - R))$ $(1/c\tau_0 = (1-R)/d)$ and without $(1/c\tau_0 = (1-R)/d)$ the absorbing species. In the case of a narrowband absorption, this is automatically accounted for by recording a spectral scan, in which the cavity loss of the 'empty' cavity determines the baseline in the spectrum. Due to the broadband nature of the SiH₃ $\tilde{A} \leftarrow \tilde{X}$ transition, the net absolute absorption had to be determined for each data point separately. This was accomplished by measuring the cavity loss at each wavelength setting both with and without silane precursor flow. After switching the SiH₄ flow, enough time (several seconds) was allowed for the plasma reactor to stabilize.

The observed cavity loss without silane flow (the 'baseline absorption') between 215 and 218 nm corresponds to an effective mirror reflectivity $R \approx 0.96$. On a short time scale (a few minutes), no significant change in this baseline absorption was observed when switching off the plasma or switching off both the plasma and all gas flows. This reflectivity value is dramatically less than the above mentioned maximum reflectivity of 0.998. The difference can partly be explained by the fact that the minimum transmission value overestimates the maximum reflectivity when additional refractive mirror losses are not taken into account. More importantly, despite the protecting measures we took, the plasma seems to have an

effect on the mirror reflectivity. In nearly all measurements we found the ring-down time τ_0 of the 'empty' cavity to decrease on a longer time scale (half an hour), and when the mirrors were kept under high vacuum conditions for a prolonged time (a day) the reflectivity was found to improve again, sometimes up to 0.985. This effect has also been observed by other groups that applied CRD detection in a plasma [15]. As a direct consequence, a procedure for determining the baseline cavity loss in a broadband absorption spectrum, as proposed by Romanini et al. [23], where the 'zero absorption baseline' is measured afterwards by repeating the same scan without absorbing medium, is not possible in our case. The ability to separately determine the baseline in a broadband (or congested) CRD spectrum that is recorded in a plasma does not only depend on the mechanical stiffness of the set-up or on the proper mode matching of the laser beam to the cavity, but mainly on the durability of the mirrors in a plasma environment. We therefore think that extreme care has to be taken when this procedure is followed in the case of application of CRD in a reactive environment, such as a plasma.

Unfortunately, the absorbing species cannot be unambiguously identified from a broadband spectrum. The absence of structure in the observed spectrum at least excludes the interfering absorption of species that exhibit a line spectrum. It does not rule out, however, the broadband absorption by other species that are produced in the Ar-H₂-SiH₄ plasma. More in particular, it does not rule out the cavity loss due to light scattering from large clusters that are commonly produced in silane plasmas. The feasibility of CRD detection of dust has already been demonstrated in an industrial-scale RF plasma reactor [15]. In that case, powder formation was identified from the time behaviour of the measured cavity loss. In our case, the absorption by dust is excluded by the observation that the ring-down time τ decreases and increases instantly when the silane flow is switched on and off, respectively. The topic of dust formation and its possible influence on the observed absorption will be more extensively discussed in a subsequent paper.

Additional evidence that the observed absorption is due to SiH_3 is obtained from a measurement of the dependence of the absorption on the silane pre-



Fig. 3. SiH₃ absorption and corresponding SiH₃ density as a function of SiH₄ precursor gas flow. The measurements are performed at 215 nm.

cursor flow (Fig. 3). The absorption (measured at 215 nm) increases monotonically with increasing SiH_4 flow, as expected for the SiH_3 density that is produced via reaction (1). The reproducibility of the measurement can be estimated from the spread in absorption values for the SiH_4 flow settings for which we performed the measurement twice. The shape of the silane flow dependence convincingly agrees with independent SiH_3 measurements that are performed with threshold ionization mass spectrometry (TIMS) at the position of the substrate [2]. This shape and the conclusions that can be drawn from it regarding the SiH_3 production mechanism are discussed in Ref. [2].

In order to know whether the above mentioned TIMS measurements and the here presented CRD results also agree quantitatively, we need to correlate the measured absorptions with SiH₃ densities. Since radial density profiles of the silvl radical are not available yet, we assume a homogeneous distribution of SiH_2 over a 30 cm absorption path length, which is based on the structure of the flow pattern as it appears from for instance Phoenics-CVD model calculations. Using in addition the absorption cross section $\sigma = 2.4 \cdot 10^{-21}$ m² at 215 nm [7], results in SiH_3 densities (given by the right scale in Fig. 3) that lie in the range $2-13 \cdot 10^{18}$ m⁻³. These values are in agreement with the TIMS measurements within a factor of two. When comparing the results of the two techniques, it should be noticed that TIMS has been performed at the position of the substrate, while the CRD results are obtained at 11 cm from the substrate. In addition, the TIMS measurements are local, while the CRD technique yields line-integrated results. Considering the complex and laborious calibration of the TIMS technique and the uncertainty in the radial SiH_3 distribution in the CRD measurements, the agreement is quite satisfactory. As mentioned before, the effective absorption cross section is independent of the temperature in the range associated with the range of operating conditions in our plasma reactor, since in this range the shape of the spectrum is mainly determined by predissociation lifetime broadening.

The observed high SiH₃ densities are strongly related to the high a-Si:H growth rate in our plasma reactor. In the end, SiH₃ is a short lived radical that has a much lower density in more conventional plasma reactors like those used in RF PECVD [1,10], and its detection therefore generally requires a high sensitivity. Based on the measurements presented in this Letter we estimate our current SiH₃ detection limit to be $\approx 10^{17}$ m⁻³, which is mainly determined by the effective reflectivity of the cavity mirrors. As mentioned above, we feel that we can improve on the reflectivity, which would immediately benefit our current SiH₃ detection limit.

At this point we could try to correlate the observed SiH_3 densities in the remote plasma, via the corresponding plasma conditions, with the a-Si:H growth rates that have been established in earlier experiments [22]. In Fig. 4 the silicon growth flux, which is the film growth rate corrected for the Si atomic density of the film, is plotted against the



Fig. 4. Correlation between silicon growth flux (from previous studies [22]) and SiH_3 density (this study).

 SiH_3 density that is measured with CRD at 215 nm. The error in the density is estimated from the reproducibility of the CRD measurements. The figure shows a clear correlation, which is a minimum requirement when silyl would be a dominant contributor to a-Si:H film growth.

Besides the correlation, a more quantitative argument can be obtained to prove the dominance of the silyl contribution to a-Si:H growth. The silicon growth flux $\Gamma_{\rm g}$ can be directly related to the silyl density $n_{\rm SiH_3}$ in front of the surface via the Chantry expression [1]:

$$\Gamma_{\rm g} = \frac{n v_{\rm th}}{4} \cdot \frac{s}{1 - \beta/2} \,, \tag{2}$$

that uses the thermal flux $nv_{\rm th}/4$ of particles arriving at a surface, where *s* is the sticking probability and β the total loss probability of SiH₃ at the a-Si:H surface. From the slope in Fig. 4 we obtain the ratio $\Gamma_{\rm g}/n_{\rm SiH_3} \approx 61$ m/s. Then, using a thermal velocity at 1500 K of $v_{\rm th} \approx 10^3$ m/s and a loss probability $\beta = 0.3$ that has been determined in a previous study [24], we obtain $s \approx 0.2$, which is a plausible value for the sticking probability [24,25]. This shows that the present silyl density can fully account for the observed silicon growth flux for the conditions that are used in this study.

4. Conclusions

We demonstrated the applicability of the cavity ring down technique for the measurement of small broadband absorptions at deep UV wavelengths. The CRD technique is found to be well suited for the detection of small amounts of the short lived silyl radical SiH₂ in a low-temperature processing plasma. To the best of our knowledge, this is the first reported use of CRD for the detection of the silvl radical. We detected SiH₃ in a remote Ar-H₂-SiH₄ plasma on the $\tilde{A}^{2}A_{1} \leftarrow \tilde{X}^{2}A_{1}$ transition to the predissociative A state around 215 nm, during a-Si:H thin film growth. The silicon growth flux of the a-Si:H film correlates with the observed absorption due to the silvl radical in the plasma, and we showed that the corresponding high SiH₃ densities in the range $2-13 \cdot 10^{18}$ m⁻³ can fully explain the high a-Si:H growth rates in our plasma reactor.

Acknowledgements

We acknowledge H.M.M. de Jong, A.B.M. Hüsken, M.J.F. van de Sande, and J.F.C. Jansen for their skillful technical assistance. This work is part of the research programme of the 'Netherlands Foundation for Fundamental Research on Matter' (FOM: 98PR1781 and 99PSI03) and it is also financially supported by the 'Netherlands Organization for Scientific Research' (NWO).

References

- P. Kae-Nune, J. Perrin, J. Guillon, J. Jolly, Plasma Sources Sci. Technol. 4 (1995) 250.
- [2] W.M.M. Kessels, M.C.M. van de Sanden, D.C. Schram, to appear in J. Vac. Sci. Technol. 18 (2000) issue 5 (Sep./Oct.)
- [3] R.D. Johnson III, J.W. Hudgens, Chem. Phys. Lett. 141 (1987) 163.
- [4] R.D. Johnson III, B.P. Tsai, J.W. Hudgens, J. Chem. Phys. 91 (1989) 3340.
- [5] R.D. Johnson III, J.W. Hudgens, J. Chem. Phys. 94 (1991) 5331.
- [6] G. Olbrich, Chem. Phys. 101 (1986) 381.
- [7] P.D. Lightfoot, R. Becerra, A.A. Jemi-Alade, R. Lesclaux, Chem. Phys. Lett. 180 (1991) 441.
- [8] H. Toyoda, M. Goto, M. Kitagawa, T. Hirao, H. Sugai, Jpn. J. Appl. Phys. 34 (1995) L448.
- [9] C. Yamada, E. Hirota, Phys. Rev. Lett. 56 (1986) 923.
- [10] N. Itabashi, N. Nishiwaki, M. Magane, S. Naito, T. Goto, A. Matsuda, C. Yamada, E. Hirota, Jpn. J. Appl. Phys. 29 (1990) L505.
- [11] A full account of the CRD literature will not be given here. For further reading about CRD one is referred to: Cavity-Ringdown Spectroscopy: An Ultratrace-Absorption Measurement Technique, K.W. Busch, M.A. Busch (Eds.), American Chemical Society, Washington, DC, 1999.
- [12] A. Campargue, D. Romanini, N. Sadeghi, J. Phys. D: Appl. Phys. 31 (1998) 1168.
- [13] E. Quandt, I. Kraemer, H.F. Döbele, Europhys. Lett. 45 (1998) 32.
- [14] R. Engeln, K.G.Y. Letourneur, M.G.H. Boogaarts, M.C.M. van de Sanden, D.C. Schram, Chem. Phys. Lett. 310 (1999) 405.
- [15] F. Grangeon, C. Monard, J.-L. Dorier, A.A. Howling, Ch. Hollenstein, D. Romanini, N. Sadeghi, Plasma Sources Sci. Technol. 8 (1999) 448.
- [16] J.P. Booth, G. Cunge, L. Biennier, D. Romanini, A. Kachanov, Chem. Phys. Lett. 317 (2000) 631.
- [17] A. O'Keefe, D.A.G. Deacon, Rev. Sci. Instrum. 59 (1988) 2544.
- [18] M.C.M. van de Sanden, R.J. Severens, W.M.M. Kessels,

R.F.G. Meulenbroeks, D.C. Schram, J. Appl. Phys. 84 (1998) 2426.

- [19] M.C.M. van de Sanden, R.J. Severens, W.M.M. Kessels, R.F.G. Meulenbroeks, D.C. Schram, J. Appl. Phys. 85 (1999) 1243.
- [20] M.C.M. van de Sanden, W.M.M. Kessels, R.J. Severens, D.C. Schram, Plasma Phys. Control. Fusion 41 (1999) A365.
- [21] A. Goumri, W.-J. Yuan, L. Ding, Y. Shi, P. Marshall, Chem. Phys. 177 (1993) 233.
- [22] W.M.M. Kessels, A.H.M. Smets, B.A. Korevaar, G.J. Adriaenssens, M.C.M. van de Sanden, D.C. Schram, Mat. Res. Soc. Symp. Proc. 557 (1999) 25.
- [23] D. Romanini, A.A. Kachanov, F. Stoeckel, Chem. Phys. Lett. 270 (1997) 546.
- [24] W.M.M. Kessels, M.C.M. van de Sanden, R.J. Severens, D.C. Schram, J. Appl. Phys. 87 (2000) 3313.
- [25] A. Matsuda, K. Nomoto, Y. Takeuchi, A. Suzuki, A. Yuuki, J. Perrin, Surf. Sci. 227 (1990) 50.