ELSEVIER

3 July 2002



Chemical Physics Letters 360 (2002) 189–193 www.elsevier.com/locate/cplett

Time-resolved cavity ring-down spectroscopic study of the gas phase and surface loss rates of Si and SiH₃ plasma radicals

J.P.M. Hoefnagels, A.A.E. Stevens, M.G.H. Boogaarts, W.M.M. Kessels, M.C.M. van de Sanden *

Department of Applied Physics, Center for Plasma Physics and Radiation Technology, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

Received 22 March 2002; in final form 13 May 2002

Abstract

Time-resolved cavity ring-down spectroscopy (CRDS) has been applied to determine gas phase and surface loss rates of Si and SiH₃ radicals during plasma deposition of hydrogenated amorphous silicon. This has been done by monitoring the temporal decay of the radicals densities as initiated by a minor periodic modulation applied to a remote SiH₄ plasma. From pressure dependence, it is shown that Si is reactive with SiH₄ [$(1.4 \pm 0.6) \times 10^{-16} \text{ m}^{-3} \text{ s}^{-1}$ reaction rate constant], while SiH₃ is unreactive in the gas phase. A surface reaction probability β of $0.9 < \beta \le 1$ and $\beta = 0.30 \pm 0.05$ has been obtained for Si and SiH₃, respectively. © 2002 Elsevier Science B.V. All rights reserved.

For basic understanding and modeling of plasma deposition processes, information on the density as well as the surface reactivity of the plasma species is essential. The surface reaction probability β of the species has often been obtained indirectly, e.g., from measurements of a macroscopic compound value of β [1], or under process conditions different from the actual plasma deposition process, e.g., by measurements in an afterglow plasma [2–4] or from a molecular beam scattering experiment [5]. In this Letter, we will present a technique to obtain the gas phase and surface loss rates of radicals during plasma deposition, here particularly in the case of high rate deposition of hydrogenated amorphous silicon [6]. In this technique, the highly sensitive cavity ring-down spectroscopy (CRDS) method [7] is used to map the temporal decay of an increased radical density by means of time-resolved absorption measurements. This so-called 'additional radical density' is created in a continuously operated remote silane plasma by applying a *minor* periodic modulation to the applied plasma power. Although time-resolved CRDS has been employed previously to obtain gas phase loss rates of radicals [8], in this work we apply the technique also to determine surface loss rates of the radicals. This yields simultaneous information on the surface reaction probability β and the density of the radicals under the specific plasma conditions. Using this method, it is shown that Si is mainly lost in the gas phase to

^{*}Corresponding author. Fax: +31-40-2456442.

E-mail address: m.c.m.v.d.sanden@tue.nl (M.C.M. van de Sanden).

 SiH_4 , whereas SiH_3 is only lost via diffusion to and reactions at the surface.

In the expanding thermal plasma technique (ETP) (Fig. 1a) a remote expanding Ar-H₂ plasma is created in which SiH₄ precursor gas is injected downstream. To detect (low-density) radicals such as SiH₃ and Si in this highly-diluted SiH₄ plasma the CRDS technique has previously been employed; SiH₃ has been identified at the $A^2A'_1 \leftarrow$ $\tilde{\mathbf{X}}^2 \mathbf{A}_1$ broadband transition ranging from ~ 200 to \sim 260 nm [9], whereas Si radicals have been probed at the $4s^{3}P_{0,1,2} \leftarrow 3p^{23}P_{0,1,2}$ transition around 251 nm [10]. This has yielded typical densities of SiH₃ and Si of $\sim 5 \times 10^{18}$ m⁻³ [11] and $\sim 10^{15}$ m⁻³ [12], respectively. In the time-resolved CRDS (τ -CRDS) measurements, a minor periodic modulation of the radical densities is produced by applying 5 Hz, 2.5% duty cycle rf pulses to the substrate in addition to the continuously operating ETP. The power in the rf pulse is 63 W and the bias voltage is between -40 and -120 V with a fall off time of less then 20 μ s. The additional absorption $A_{\rm rf}$ due to



Fig. 1. (a) The ETP setup equipped with the cavity ring-down spectroscopy system, which is aligned at 5 mm in front of the substrate. A pulsed rf bias can be applied to the substrate holder. (b) A timing scheme illustrating the modulation of the radical density and the synchronization of the CRDS laser pulses.

the radicals generated by the rf pulse is obtained from the difference in absorption at some point Δt in the rf afterglow and at a point long after the influence of the rf pulse has extinguished (see Fig. 1b). Every CRDS trace is handled separately by means of a new 'state-of-the-art' 100 MHz, 12 bit data acquisition system [13] and an averaged $A_{\rm rf}$ is obtained as a function of the time Δt in the afterglow of the rf pulse.

A typical τ -CRDS measurement for Si and SiH₃ is shown in Fig. 2. A duty cycle of 2.5% has been used in order to obtain a good signal-to-noise ratio in the additional Si and SiH₃ absorption, while possible powder formation due to the 'anion confining' rf plasma sheath is suppressed [14]. Fig. 2 shows that both Si and SiH₃ decrease single exponentially, which is expected from the radicals' mass balance when the loss term is linear in the radical density [15]. The corresponding loss rate τ^{-1} depends linearly on the gas phase loss on one hand and the loss due to diffusion to and reactions at the surface on the other hand [15]:

$$\tau^{-1} = k_{\rm r} n_x + \frac{D}{\Lambda^2}.\tag{1}$$

In this equation, k_r is the gas phase reaction rate with species x with density n_x , D is the diffusion



Fig. 2. A typical measurement during the rf afterglow of the additional absorption $A_{\rm rf}$ of Si and SiH₃ generated by the rf pulse during the continuously operating ETP plasma. Every data point is an average of 128 CRDS traces and the statistical error in the decay time obtained from least-squares analysis of the Si and SiH₃ decay curves is less then 5%. In the rf pulse (i.e., at $\Delta t < 0$), the densities of Si and SiH₃ have reached a saturated value of 2×10^{15} and 3×10^{18} m⁻³, respectively.



Fig. 3. The Si and SiH₃ loss rate as a function of the SiH₄ density at constant total pressure of 0.27 mbar. The error bars represent the statistical error in the decay time as shown in Fig. 2.

coefficient for the specific radical in the Ar–H₂–SiH₄ mixture [16], and Λ is the effective diffusion length of the radical. The latter depends on diffusion geometry and on the radical's surface reaction probability β [15].

As revealed by Fig. 2, Si is lost typically a factor of 10 faster than SiH₃ in the Ar-H₂-SiH₄ plasma. As will be shown below, this is mainly due to the difference in the gas phase loss processes that need to be considered first before surface loss rates of the radicals can be deduced. For Si and SiH₃ in the ETP plasma the only candidate for a significant gas phase loss is SiH₄ [16]. To investigate this reaction channel, the loss rate of Si and SiH₃ has been obtained as a function of the SiH₄ density (Fig. 3) keeping the total pressure and thus the diffusion term in Eq. (1) nearly constant. The SiH₄ density has been calculated from the SiH₄ partial pressure using a kinetic gas temperature of 700 K and including a correction for the local SiH₄ consumption¹. The loss rate of SiH₃ in Fig. 3 is independent of SiH₄ density, which indicates no gas phase loss of SiH₃, while the loss rate of Si increases linear with the SiH₄ density. The slope

reveals a reaction rate constant of Si(³P) with SiH₄ of $k_{\rm r} = (1.4 \pm 0.6) \times 10^{-16} \text{ m}^{-3} \text{s}^{-1}$. In the error analysis of this reaction rate the small statistical error in the loss rates as well as the following systematic uncertainties have been considered: The variation in the diffusion term in Eq. (1) can be neglected for the small SiH₄ dilutions used in Fig. 3, while the local SiH₄ density correction affects k_r only slightly. The uncertainty in k_r is mainly determined by the gas temperature, which has been estimated to be (700 \pm 200) K from plasma model calculations [11]. The value of k_r is somewhat lower than the value of $k_{\rm r} = (3.5 \pm 1.0) \times 10^{-16}$ $m^{-3}s^{-1}$ and $k_r = (4.4 \pm 1.0) \times 10^{-16} m^{-3} s^{-1}$ as obtained, respectively, by Tanaka et al. [3] at \sim 350 K in an rf plasma and Takahara et al. [17] at 295 K in a photolysis experiment. The value of Tanaka et al. is in relatively good agreement with our value considering the assumptions made (in both cases) on, e.g., the gas temperature and thermalization of Si, while the unaccounted presence of disilane in continuous rf plasmas could also easily account for the discrepancy. The comparison with the value of Takahara et al. which has been determined in a somewhat indirect way using a pre-assumed chemistry model, might not be so straightforward since it was obtained under a \sim 50 times higher He background pressure.

In order to deduce the surface reaction probability β of Si and SiH₃ from the diffusion term in Eq. (1), a semi-empirical expression for the cylinder symmetrical geometry has been assumed to determine the effective diffusion length Λ as has been proposed by Chantry [15]. However, the diffusion geometry in the ETP reactor, although cylinder symmetric, is not as well defined as for example in an rf parallel plate reactor. In our approach we have assumed that the diffusion of the radicals in radial direction can be neglected in respect to the diffusion in axial direction. Although this assumption introduces the main uncertainty in β , larger than the uncertainty due to the radical's temperature, the assumption is validated by the fact that within the 5 ms duration of the rf pulse the additional radicals do not have sufficient time to reach the outer reactor wall, while the additional density saturates due to axial diffusion to the substrate (see Fig. 2). Moreover, on the basis of

¹ From the mass balance it follows that the production term of a radical (proportional to the local SiH₄ density and the electron density) in the rf pulse under steady state conditions is equal to the radical density over its loss rate (i.e., n/τ). The electron density remains fairly constant for the conditions used yielding therefore information on the local SiH₄ density.

arguments such as plasma model calculations [11] and light emission measurements, it is assumed that the additional radicals are produced and confined close to the substrate and that the transport to the substrate is diffusion dominated. Consequently, from the pressure dependence of the decay time of SiH₃ (Fig. 4) and the SiH₃ diffusion coefficient [16] the parameters describing the axial diffusion geometry can be obtained: Fig. 4 reveals a good linear dependence of the decay time of SiH₃ on the total pressure and therefore Eq. (1) has been fitted to the data points setting the gas phase loss term to zero. The surface reaction probability follows from the offset in Fig. 4 yielding a value of $\beta = 0.30 \pm 0.05$ for SiH₃ in the ETP plasma. This value is in good agreement with the estimated β for SiH₃ from indirect measurements as obtained previously with the 'aperture-well assembly' method applied under similar conditions in the same setup [1]. The value is also in good agreement with β of SiH₃ of $\beta = 0.28 \pm 0.03$ as determined by Perrin et al. [2] by time-resolved threshold ionization mass spectrometry in an rf plasma with a 100% on-off modulation. Furthermore, by applying the same axial diffusion geometry to the measurements of Si (while taking into account the gas phase loss to SiH₄), a lower limit of 0.9 has been obtained for β of Si, yielding therefore $0.9 < \beta \le 1$. Although this is the first direct experimental evidence for a nearly unity surface reaction probability of Si, a β of ~ 1 is



Fig. 4. The SiH₃ decay time as a function of the total pressure for a constant SiH₄ density of 3.7×10^{19} m⁻³.

generally assumed for the Si radical on the basis of its hydrogen deficiency [4].

In conclusion, it has been shown that the timeresolved cavity ring-down experiment applied on a remote plasma is capable of obtaining radical loss rates during the actual plasma deposition process. From partial and total pressure series, it has been shown that Si is highly reactive in the gas phase with SiH₄ whereas its surface reaction probability β is $0.9 < \beta \le 1$. SiH₃ on the other hand is unreactive with SiH₄ and has a surface reaction probability of $\beta = 0.30 \pm 0.05$ which is in good agreement with previously reported values. In the future, the geometrical model will be refined such that the β values of these and other silane radicals can be determined at very high accuracy and as a function of plasma and surface conditions.

Acknowledgements

The authors gratefully acknowledge the contribution of D.C. Schram as well as the Technical Laboratory Automation group of the Eindhoven University of Technology, the technical assistance by M.J.F. van de Sande, J.F.C. Jansen, H.M.M. de Jong, and A.B.M. Hüsken and the experimental work performed by Y. Barrell. This research was supported by The Netherlands Foundation for Fundamental Research on Matter (FOM: 98PR1781 and 99PSI03) and the Royal Netherlands Academy of Sciences and Arts (KNAW) by the fellowship of one of the authors (W.K.).

References

- See e.g., W.M.M. Kessels, M.C.M. van de Sanden, R.J. Severens, D.C. Schram, J. Appl. Phys. 87 (2000) 3313, and references therein.
- [2] J. Perrin, M. Shiratani, P. Kae-Nune, H. Videlot, J. Jolly, J. Guillon, J. Vac. Sci. Technol. A 16 (1998) 278.
- [3] T. Tanaka, M. Hiramatsu, M. Nawata, A. Kono, T. Goto, J. Phys. D 27 (1994) 1660.
- [4] P. Kae-Nune, J. Perrin, J. Guillon, J. Jolly, Plasma Sources Sci. Technol. 4 (1995) 250.
- [5] P.R. McCurdy, K.H.A. Bogart, N.F. Dalleska, E.R. Fisher, Rev. Sci. Instrum. 68 (1997) 1684.
- [6] W.M.M. Kessels, R.J. Severens, A.H.M. Smets, B.A. Korevaar, G.J. Adriaenssens, D.C. Schram, M.C.M. van de Sanden, J. Appl. Phys. 89 (2001) 2404.

- [7] K.W. Busch, M.A. Busch (Eds.), Cavity-Ringdown Spectroscopy: An Ultratrace-Absorption Measurement Technique, ACS, Washington DC, 1999.
- [8] D.B. Atkinson, J.W. Hudgens, J. Phys. Chem. A 101 (1997) 3901, and references therein.
- [9] P.D. Lightfoot, R. Becerra, A.A. Jemi-Alade, R. Lesclaux, Chem. Phys. Lett. 180 (1991) 441.
- [10] A.A. Radzig, B.M. Smirnov, References Data on Atoms, Molecules and Ions, Springer, Berlin-Heidelberg, 1985.
- [11] W.M.M. Kessels, A. Leroux, M.G.H. Boogaarts, J.P.M. Hoefnagels, M.C.M. van de Sanden, D.C. Schram, J. Vac. Sci. Technol. A. 19 (2001) 467.

- [12] W.M.M. Kessels, J.P.M. Hoefnagels, M.G.H. Boogaarts, D.C. Schram, M.C.M. van de Sanden, J. Appl. Phys. 89 (2001) 2065.
- [13] Technical Laboratory Automation Group, Eindhoven University of Technology, Den Dolech 2, 5600 MB Eindhoven, The Netherlands.
- [14] C. Courteille, J.L. Dorier, C. Hollenstein, L. Sansonnens, A.A. Howling, Plasma Sources Sci. Technol. 5 (1996) 210.
- [15] P.J. Chantry, J. Appl. Phys. 62 (1987) 1141.
- [16] J. Perrin, O. Leroy, M.C. Bordage, Contrib. Plasma Phys. 36 (1996) 1.
- [17] A. Takahara, A. Tezaki, H. Matsui, J. Phys. Chem. 103 (1999) 11315.