ELSEVIER

Diamond and Related Materials 8 (1999) 1383–1387

DIAMOND AND RELATED MATERIALS

www.elsevier.com/locate/diamond

H atom production in a hot filament chemical vapour deposition reactor

S.A. Redman, C. Chung, M.N.R. Ashfold *

School of Chemistry, University of Bristol, Bristol BS8 1TS, UK

Accepted 30 November 1998

Abstract

Multiphoton ionisation spectroscopy of atomic hydrogen, resonance enhanced at the two photon energy by the $2s^1;^2S_{1/2}$ state, and subsequent analysis of the resulting Doppler broadened lineshapes, has been used to provide direct, spatially resolved relative H atom number densities and gas temperature profiles in the vicinity of a coiled Ta hot filament (HF) in a reactor used for diamond chemical vapour deposition. The effects of filament temperature and H_2 pressure on the relative H atom number densities and the gas temperature profiles have been investigated, as have the effects of small amounts of added CH_4. The effective activation energy for H atom production so obtained ($E_a = 237 \pm 22$ kJ mol^{-1}) suggests that the HF provides a particularly efficient means of heating (and thus promoting the dissociation of) H_2 molecules that adsorb onto its surface. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Chemical vapour deposition; Diamond; Atomic hydrogen; Case diagnostics

---

1. Introduction

Diamond chemical vapour deposition (CVD) using a hot filament (HF) reactor continues to attract much attention because of its inherent simplicity and its ease of implementation [1]. However, the precise role of the filament remains a matter of some debate. Atomic hydrogen is produced heterogeneously by thermal decomposition of H_2 on the HF surface, and then rapidly diffuses into the bulk gas; radial profiles of H atom number density as a function of d, the distance from the filament, have been quite widely reported [2–7]. Several groups have also noted that the H atom number density, [H], measured in the immediate vicinity of the filament scales with the filament temperature, T_{fil}, in a manner broadly consistent with expectations based on the assumption that the chemical reaction:

$$H_2 \rightleftarrows 2H, \qquad (1)$$

is in thermal equilibrium at the temperature of the filament surface [1–5,8], but whether the filament surface is merely playing the role of a convenient heat bath or is actually catalysing the decomposition remains unclear. The absolute H atom concentration close to the filament is generally accepted to be lower than the chemical equilibrium value (at T_{fil}). The apparent sub-equilibrium concentrations measured very close to the filament can be attributed to the H atoms diffusing into the cooler bulk of the gas. H atom recombination reactions are sufficiently slow at the typical process pressures (~20 Torr) that most of the H atoms diffuse to, and are destroyed at, the reactor walls; when viewed from the perspective of the local gas temperatures, H atoms are present at super-equilibrium concentrations throughout most of the reactor. Adding trace amounts of hydrocarbon causes a reduction in the H number density measured close to the filament [1,8], to an extent that increases non-linearly with hydrocarbon partial pressure. This has been explained in terms of progressive carburisation and the eventual development of a graphitic layer on the filament surface, which poisons its catalytic activity for H production [1,9].

Here we report the use of multiphoton ionisation (MPI) spectroscopy, resonance enhanced at the two photon energy by the $2s^1;^2S_{1/2}$ state, to provide relative H atom number densities (and local gas temperatures) at various user selected distances d from the lower edge of a coiled hot Ta filament, as a function of H_2 pressure, gas flow rate and T_{fil}. The effect of adding a small

---

* Corresponding author. Tel: (117)-9288312; Fax: (117)-9251295.
E-mail address: mike.ashfold@bris.ac.uk (M.N.R. Ashfold)

PII: S0925-9635(99)00015-1

amount of CH_4 was also investigated. The results serve to reinforce those previous suggestions that the HF is best regarded as an efficient means of heating H_2 molecules that adsorb onto its surface, rather than as a true catalyst (i.e. an entity that lowers the effective activation energy) for H_2 dissociation. Similarly, the results suggest that the principal effect of trace hydrocarbon addition is best viewed as reducing the number (or efficiency) of the active surface sites on the HF surface.

2. Experimental

The experimental arrangement and procedures are reported elsewhere [7], and are only summarised here. The HFCVD reactor consists of a six-way cross with pumping, gas and electrical power inlets, and observation and laser entrance and exit ports. The reactor is typically maintained at a pressure of 20 Torr H_2, with or without added CH_4, flowing at 100 sccm. Activation of the process gas is by a coiled tantalum filament (seven turns, $\sim$11 mm long, 3 mm i.d. coil, 250 μm wire). H atoms are detected by 2+1 resonance enhanced multiphoton ionisation (REMPI) on the 2s←1s transition using 243.1 nm radiation generated using a Nd-YAG pumped dye laser operating with the dye coumarin 480 and subsequent frequency doubling (in β-barium borate (BBO)), that is focused into the centre of the reactor using a 20 cm f.l. lens. The laser focal volume and the negatively biased Pt probe wire that collects the resulting H^+ ions are maintained fixed in the laboratory frame and the entire filament and substrate assembly may be translated vertically by symbol $\leq$25 mm, with sub-millimetre precision, around the detection volume. The intensity of the frequency doubled light exiting the reactor is also monitored for power normalisation of the measured REMPI signals. Translational temperatures and relative concentrations both derive from measurement and analysis of the Doppler broadened H(2s←1s) two photon lineshapes. The transmission of a portion of the fundamental dye laser output through an etalon, monitored concurrently with the profiles, allows calibration of the spectral frequency dispersion and thus the linewidths of the profiles, which in turn provide the measure of the local gas temperature. The areas under the Doppler envelopes give a relative measure of H atom number density.

3. Results and discussion

Fig. 1 shows plots of [H] measured at $d=1$ and 5 mm from the filament, at a constant H_2 flow rate 100 sccm), as a function of H_2 pressure (P_{H_2}) in the range of 10.6–41.5 Torr. The power supplied to the filament remained almost constant throughout these measurements, but T_{fil} (measured with a two colour optical pyrometer) was observed to fall slightly with increasing P_{H_2}. Both T_{fil} and the local gas temperatures deduced from Doppler lineshape analysis at each d and P_{H_2} are also included in Fig. 1. The gas temperatures measured at both d first increase and then decline with increasing P_{H_2}. Such trends accord well with the calculated temperature profiles of Meier et al. [10], for a similar range of pressures, and are broadly consistent with the expectation that the thermal conductivity of the gas improves with increasing P_{H_2}. Thus the gentle increase at low P_{H_2} is attributable to the improved heat transport from the filament, whilst the subsequent decrease at higher pressures probably reflects both the observed decrease in T_{fil} and increased heat loss to the cold reactor walls. Fig. 1 also shows [H] to be almost invariant to P_{H_2}throughout the pressure range investigated, in accord with the conclusions reached in earlier two photon laser induced fluorescence (LIF) studies [2,10], and with measurements of the pressure dependence of the power consumption by hot

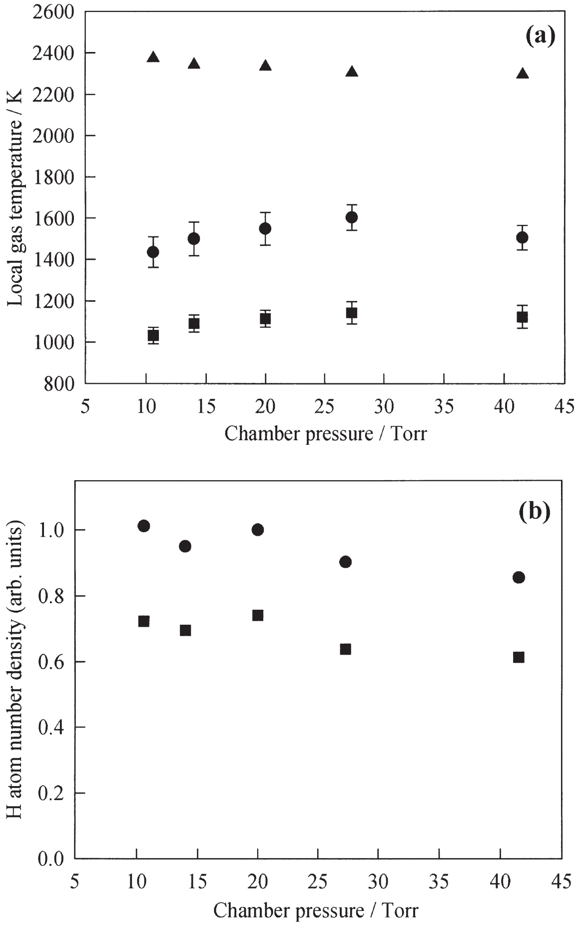

Fig. 1. (a) H atom translational temperatures and (b) relative number densities as deduced from analysis of the 2s←1s two photon Doppler lineshapes recorded at $d=1$ (●) and 5 mm (■), plotted as a function of P_{H_2}. T_{fil} (▲, from optical pyrometry) varies weakly with P_{H_2} as shown in (a).

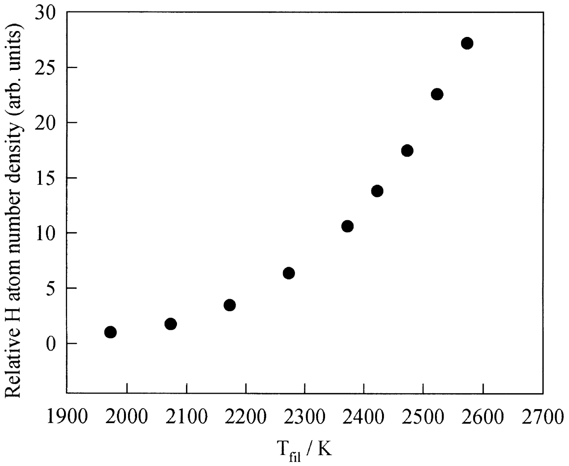

Fig. 2. Relative H atom number densities as deduced from analysis of the 2s←1s two photon Doppler lineshapes measured at $d=1$ mm, plotted as a function of T_{fil}.

Ta and W filaments when used to dissociate H_2 [11]. All are consistent with the assumption that, at the prevailing pressures and temperatures, H atoms are formed solely by H_2 bond fission on the surface of the HF and thus exhibit kinetics that are zero order with respect to P_{H_2}. The very gradual decrease in [H] observed at higher P_{H_2} probably reflects the increasing contribution from three body homogenous recombination [11]:

$$H+H+M(H_2)\rightarrow H_2+M(H_2). \quad (2)$$

Measurements using 20 Torr of H_2 feed gas and a flow rate of 50 sccm yielded local gas temperatures and relative [H] signals that were indistinguishable from those shown in Fig. 1. Such observations serve to reinforce the consensus view that diffusion is the dominant transport mechanism in low pressure (e.g. HFCVD) reactors [11–14].

Fig. 2 shows the a plot of [H] versus T_{fil} measured at $d=1$ mm using 20 Torr of pure H_2 and a flow rate of 100 sccm. The local gas temperature (as revealed by the Doppler linewidths) increases almost linearly with increasing T_{fil}, but even 1 mm from the filament is ca 800 K cooler than the filament surface as measured by optical pyrometry. Temperature discontinuities of this magnitude have been reported previously [4,5,15], and accord with expectations based on the original work of Langmuir [16]. The measured [H] increases near exponentially in the temperature range investigated; we observe similar dependencies at $d=4$ mm, as did Celii and Butler [8] when using 3+1 REMPI to monitor H atoms in a HFCVD reactor. Very similar [H] versus T_{fil} trends have been extracted from measurements (at three different d values) of the development of [H] upon addition of 0.5% CH_4 [7]. T_{fil} was not raised high enough in the present work to observe any plateau in H atom production such as has been reported in previous studies of H_2 decomposition on a hot metal surface [17].

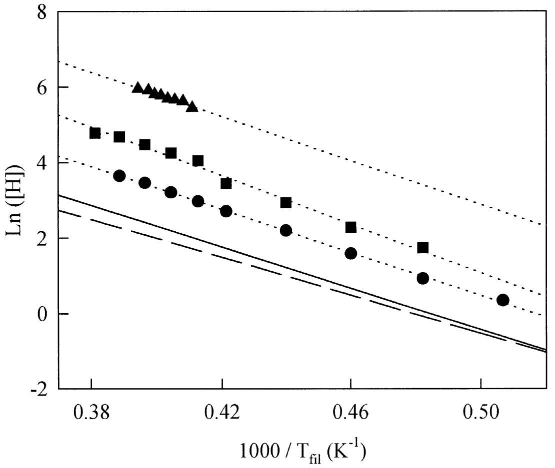

Fig. 3. Van't Hoff plot illustrating the good linear correlation between ln[H] and $(T_{fil})^{-1}$ using 20 Torr pure H_2 and measuring at $d=1$ mm (●) and 4 mm (■), and at $d=0.5$ mm with 0.5% CH_4 added (▲). The results of linear regression analysis of each data set are shown by dotted lines in the graph and, for clarity of presentation, the various data sets are offset from one another. Interpreting the gradients in terms of $-E_a/R$ yields effective activation energies of, respectively, 237, 268 and 244 kJ mol^{-1}. The solid line shows the dependence expected on the basis of the tabulated temperature dependence of K_f for Reaction (1), while the dashed line shows how this would be modified if gas phase H_2 was heated homogeneously to temperatures in the same range while maintaining the pressure constant.

Fig. 3 shows that a Van't Hoff type plot of ln[H] measured at $d=1$ mm against $(T_{fil})^{-1}$ yields a straight line, the gradient of which can be interpreted in terms of $-E_a/R$, where E_a (237 kJ mol^{-1}) is an effective activation energy for H_2 decomposition on the surface of the HF. The biggest source of uncertainty in this measurement is likely to be the absolute accuracy of the pyrometer calibration; at these temperatures a systematic error of ±100 K translates into a ±22 kJ mol^{-1} uncertainty in E_a. The data taken in pure H_2 at $d=4$ mm yields a slightly steeper gradient, whilst E_a values extracted from measurements in the presence of 0.5% CH_4 gave $E_a=244$ kJ mol^{-1} at $d=0.5$ mm. As Fig. 4 shows, these values and trends compare well with those that result from similar analyses of the data from the earlier direct REMPI measurements of Celii and Butler [8], probing at $d=8$ mm both in pure H_2 and in dilute CH_4/H_2 mixtures. They are also in reasonable accord with the less direct estimates of [H] versus T_{fil} derived by Childs et al. [18] from vacuum ultraviolet absorption measurements of the column densities of C atoms and CH radicals in a 1% CH_4 in H_2 mixture at $d=3$ mm. All of these spectroscopic studies yield E_a values somewhat lower than that which may be deduced from the data of Harris and Weiner [19], who monitored the temperature rise attributable to H atom recombination

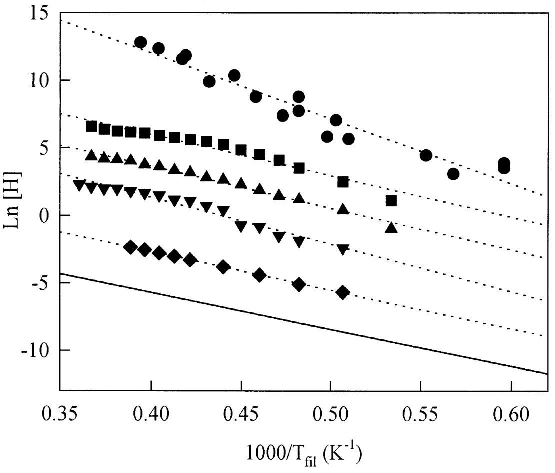

Fig. 4. Comparisons of the present measurements of [H] versus T_{fil} [$d=1$ mm, 20 Torr pure H_2 (◆)] with the previous 3+1 REMPI measurements of Celii and Butler [8] [$d=8$ mm, 20 Torr H_2 plus 0 (■), 0.5 (▲) and 1% CH_4 (▼)] and the recombination enthalpy measurements of Harris and Weiner [19] (●). Again, the results of linear regression analysis of each data set are shown by dashed lines and the various data sets are offset from each other for clarity. Also shown for reference is the gradient corresponding to thermodynamic equilibrium between H and H_2 at T_{fil} (solid line, as in Fig. 3).

on a thermocouple probe situated ~4 mm from a W filament in a 1% CH_4/H_2 gas mixture.

How should we interpret these E_a values? H atom production in HFCVD reactors is normally visualised in terms of reversible elementary steps of the type:

$$H_2+S^* \rightleftarrows H+SH \tag{3}$$

$$SH \rightleftarrows H+S^*, \tag{4}$$

where Reactions (3) and (−3) represent dissociative adsorption of H_2 on an active site (S^*) on the metal surface and H atom recombination on a hydrogen terminated surface site, respectively, and Reactions (4) and (−4) involve desorption and adsorption of an H atom. Increasing T_{fil} will affect the local H atom number density through its possible effect on all backward and forward reaction rates — not just by helping to overcome any energy barriers associated with the various processes as written, but also by affecting the mean lifetime of any chemisorbed species on the filament surface, the balance between non-dissociative (not shown) and dissociative adsorption (3), the fraction of surface sites that are 'active' (i.e. S^* versus SH), and the local gas phase [H] — which affects the extent of contributions from Reaction (4).

Notwithstanding this complexity, we note that the sum of these two reactions is simply Reaction (1) at the surface. Fig. 3 also shows (solid line) the ln[H] versus T^{-1} dependence we should expect on the basis of the tabulated temperature dependence of K_f for Reaction (1) [20], and use of the relationship:

$$[H]=\left(\frac{4K_f^2}{4+K_f^2}\right)^{1/2}. \tag{5}$$

The resulting gradient gives $E_a=228\ \mathrm{kJ\ mol^{-1}}$. The similarity between this and the measured dependencies in pure H_2 is striking, and encourages the view that the main role of the filament surface is to provide an efficient means by which H_2 molecules can attain T_{fil}. Of course, were it possible to heat H_2 purely in the gas phase to the same temperature (at constant pressure) the measured [H] yield should be expected to show a slightly shallower temperature dependence ($E_a=207\ \mathrm{kJ\ mol^{-1}}$) because of the inverse dependence between total number density and temperature that follows if we assume ideal gas behaviour. This is shown by the dashed line in Fig. 3. Addition of CH_4 leads to carburisation of the filament and further complicates the problem by introducing a wider range of possible surface sites — the reactivity and stability of each of which will exhibit their own characteristic temperature dependence — and offers a new and efficient reactive loss mechanism for H atoms. Small CH_4 additions cause some reduction in [H] at any given T_{fil}; this becomes more dramatic if some critical hydrocarbon fraction is exceeded [8,9]. Both observations are consistent with progressive loss of 'active' sites on the filament surface as the extent of carburisation increases.

The literature contains at least two further plots of H atom concentrations versus T_{fil}, in which the H atoms have been measured after passage through a small orifice in a substrate upon which diamond CVD is occurring. The data of Hsu et al. [21] gives a comparable E_a value (186 kJ mol^{-1}), but the more recent study by Zumbach et al. [6] gives a much lower number. The steady state [H] is much reduced in the immediate vicinity of a heated CVD diamond surface [1,7], mainly because of H atom loss through surface abstraction reactions. [H] depends on the substrate surface temperature (which is itself affected by direct heating from the HF), and by the local H atom flux and the extent of H atom recombination at the surface (which liberates energy to the surface). Clearly, given these additional complicatory factors, the interpretation of [H] versus T_{fil} measurements made at or through the substrate surface, simply in terms of an effective E_a for dissociation on the filament surface, is fraught with potential ambiguity.

4. Conclusions

This report demonstrates the applicability of 2+1 REMPI spectroscopy, and subsequent analysis of the Doppler broadened lineshapes so obtained, as a viable route to determining relative H atom number densities and local gas temperature profiles in a purpose designed HFCVD reactor. Measurements of the way in which [H] depends on T_{fil}, and on the H_2 pressure and flow rate, yields an effective activation energy $E_a = 237 \pm 22$ kJ mol^{-1} for H atom formation, and suggests that the 'catalytic' role often ascribed to the HF in HFCVD reactors is largely a reflection of the fact that it provides a particularly efficient means of heating (and thus promoting the dissociation of) H_2 molecules that adsorb onto its surface.

Acknowledgements

The authors are grateful to EPSRC for equipment grants and for the award of a Senior Research Fellowship (MNRA) and studentship (SAR), and to Drs J.E. Butler (Naval Research Laboratory, Washington, D.C.), S.H. Ashworth, S.R. Langford, P.W. May, A.J. Orr-Ewing and C.M. Western for their help and interest in this work.

References

[1] D.G. Goodwin, J.E. Butler, in: M.A. Prelas, G. Popovici, L.K. Bigelow (Eds.), Handbook of Industrial Diamonds and Diamond Films, Marcel Dekker, New York, 1998, pp. 527–581.

[2] L. Schafer, C.-P. Klages, U. Meier, K. Kohse-Hoinghaus, Appl. Phys. Lett. 58 (1991) 571.

[3] M. Chenevier, J.C. Cubertafon, A. Campargue, J.P. Booth, Diamond Relat. Mater. 3 (1994) 587.

[4] K.-H. Chen, M.-C. Chuang, C.M. Penney, W.F. Banholzer, J. Appl. Phys. 71 (1992) 1485.

[5] L.L. Connell, J.W. Fleming, H.-N. Chu, D.J. Vesteck Jr,, E. Jensen, J.E. Butler, J. Appl. Phys. 78 (1995) 3622.

[6] V. Zumbach, J. Schafer, J. Tobai, M. Ridder, T. Dreier, B. Ruf, F. Behrendt, O. Deutschmann, J. Warnatz, J. Chem. Phys. 107 (1997) 5918.

[7] S.A. Redman, C. Chung, K.N. Rosser, M.N.R. Ashfold, Phys. Chem. Chem. Phys. (in press).

[8] F.G. Celii, J.E. Butler, Appl. Phys. Lett. 54 (1989) 1031.

[9] M. Sommer, F.W. Smith, J. Mater. Res. 5 (1990) 2433.

[10] U. Meier, K.. Kohse-Hoinghaus, L. Schafer, C.-P. Klages, Appl. Opt. 29 (1990) 4993.

[11] T. Otsuka, M. Ihara, H. Komiyama, J. Appl. Phys. 77 (1995) 893.

[12] D.G. Goodwin, G.G. Gavillet, J. Appl. Phys. 68 (1990) 6393.

[13] D.S. Dandy, M.E. Coltrin, J. Appl. Phys. 76 (1994) 3102.

[14] K. Tankala, T. DebRoy, J. Appl. Phys. 72 (1992) 712.

[15] K.L. Menningen, M.A. Childs, L.W. Anderson, J.E. Lawler, Rev. Sci. Instrum. 67 (1996) 1546.

[16] I. Langmuir, J. Am. Chem. Soc. 37 (1915) 417.

[17] J.N. Smith, W.L. Fite, J. Chem. Phys. 37 (1962) 898.

[18] M.A. Childs, K.L. Menningen, L.W. Anderson, J.E. Lawler, J. Chem. Phys. 104 (1996) 9111.

[19] S.J. Harris, A.M. Weiner, J. Appl. Phys. 74 (1993) 1022.

[20] M.W. Chase Jr., C.A. Davies, J.R. Downey Jr., D.J. Frurip, R.A. McDonald, A.N. Syverud, J. Phys. Chem. Ref. Data 14 (Suppl.) (1985) 1.

[21] W.L. Hsu, M.C. McMaster, M.E. Coltrin, D.S. Dandy, Jpn. J. Appl. Phys. 33 (1994) 2231.