H atom production in a hot filament chemical vapour deposition reactor

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Abstract

Multiphoton ionisation spectroscopy of atomic hydrogen, resonance enhanced at the two photon energy by the \(2s^1S_{1/2} \rightarrow 2p^1P_{1/2}\) 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 CH4. The effective activation energy for H atom production so obtained (\(E_a = 237 \pm 22 \text{ kJ mol}^{-1}\)) 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.

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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:

\[ H_2 \rightarrow 2H, \tag{1} \]

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 spectroscopy, resonance enhanced at the two photon energy by the \(2s^1S_{1/2} \rightarrow 2p^1P_{1/2}\) 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...
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, ~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 densities as deduced from analysis of the 2s–1s two photon Doppler lineshapes recorded at $d=1$ (MOOTH) and $d=5$ mm, plotted as a function of the laboratory frame and the entire filament and substrate assembly may be translated vertically by symbol ≤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.

The transmission of a portion of the fundamental dye laser output through an etalon, monitored concurrently with the profiles, allows calibration of the spectral 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 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
The addition of 0.5% Taccord with expectations based on the original work of [8], probing at optical pyrometry. Temperature discontinuities of this type result from similar analyses of the data from the transport mechanism in low pressure (e.g. HFCVD) reactors [11–14]. The data taken in pure H2 at d=4 mm yields a slightly steeper gradient, whilst Ee values extracted from measurements in the presence of 0.5% CH4 [7] were 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 H2 decomposition on a hot metal surface [17].

Fig. 3 shows that a Van’t Hoff type plot of ln[H] measured at d=1 mm against (TaH2)−1 yields a straight line, the gradient of which can be interpreted in terms of −Ef/R, where Ef (237 kJ mol−1) is an effective activation energy for H2 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 Ef. The data taken in pure H2 at d=4 mm yields a slightly steeper gradient, whilst Ee values extracted from measurements in the presence of 0.5% CH4 gave Ee=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 H2 and in dilute CH4/H2 mixtures. They are also in reasonable accord with the less direct estimates of [H] versus TaH2 derived by Childs et al. [18] from vacuum ultraviolet absorption measurements of the column densities of C atoms and CH radicals in a 1% CH4 in H2 mixture at d=3 mm. All of these spectroscopic studies yield Ee 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.
on a thermocouple probe situated ~4 mm from a W filament in a 1% CH₂H₂/H₂ 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:

$$\text{H}_2 + S' \rightarrow \text{H} + \text{SH} \tag{3}$$
$$\text{SH} \rightarrow \text{H} + S' \tag{4}$$

where Reactions (3) and (−3) represent dissociative adsorption of H₂ 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 In[H] versus $T^{-1}$ dependence we should expect on the basis of the tabulated temperature dependence of $K_T$ for Reaction (1) [20], and use of the relationship:

$$[\text{H}] = \frac{4K_T^2}{(4 + K_T^2)^{1/2}}$$

The resulting gradient gives $E_a = 228$ kJ mol$^{-1}$. The similarity between this and the measured dependencies in pure H₂ is striking, and encourages the view that the main role of the filament surface is to provide an efficient means by which H₂ molecules can attain $T_{fil}$. Of course, were it possible to heat H₂ 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 ($E_a = 207$ 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 CH₄ 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 CH₄ 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 Zumback et al. [6] gives a much lower number. The steady state [H] is much reduced in the immediate vicinity of a filament surface as the extent of carburisation increases.

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 $T_{\text{gas}}$ 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.

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