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Boron doping: B/H/C/O gas-phase chemistry; H atom density dependences on pressure and wire temperature; puzzles regarding the gas-surface mechanism

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ABSTRACT

Experimental and modeling studies of the gas-phase chemistry occurring in dilute, hot filament (HF) activated $B_2H_6/CH_4/H_2$ gas mixtures appropriate for growth of boron-doped diamond are reported. The results of two-dimensional modeling of heat and mass transfer processes and the B/H/C chemistry prevailing in such HF activated gas mixtures (supplemented by reactions involving trace O_2 present as air impurity in the process gas mixture) are discussed and compared with measurements of B atom densities as functions of the hot wire temperature T_w and distance from the wire. Most of the B_2H_6 molecules that diffuse from the cool, near-wall regions into the hot, near wire region are thermally decomposed (yielding two BH_3 molecules as primary products) and then converted into various 'active' B-containing species like B, BH and BH_2 — some of which are able to accommodate into the growing diamond film. H-shifting reactions $BH_x + H \leftrightarrow BH_{x-1} + H_2$ enable rapid inter-conversion between the various BH_x ($x = 0$–3) species and the BH_x source is limited by diffusional transfer of B_2H_6. H atoms play several key roles — *e.g.* activating the process gas mixture, and driving inter-conversions between the various $H_xB_yC_zO_{z'}$ species. We show that the T_w and gas pressure dependences of the H atom production rate (by H_2 dissociation on the HF surface) can be accommodated by a simple gas-surface reaction model.

1. Introduction

Hot-filament (HF) activation of dilute hydrocarbon/H_2 (*e.g.* CH_4/H_2) gas mixtures is an established low-cost route for diamond chemical vapour deposition (CVD) [1–3]. Addition of trace amounts of a boron containing precursor (*e.g.* 10–1000 ppm of B_2H_6) during diamond CVD is of considerable interest, as incorporated B atoms act as acceptors ($E_a \sim 0.37$ eV) and impart p-type semiconductivity to the as-grown B-doped diamond [4]. B-doped diamond is attracting interest for its potential application in electronic and optical devices [5,6], bio-sensing [7], and as a result of its more recently discovered superconductivity [8,9]. All such applications require reliable recipes for forming high quality B-doped diamond, with controllable doping levels; hence the emerging need for a much fuller understanding of the doping processes and of the B/H/C chemistry. However, the details of the gas-phase and gas-surface chemistry involved in the growth of B-doped CVD diamond are still poorly understood. The literature contains only a handful of papers reporting diagnostics relevant to B-containing microwave (MW) plasmas, though several studies have sought to establish relationships between diamond film quality, dopant concentration and reactor parameters such as the B_2H_6 flow rate (or the input [B]/[C] ratio), substrate temperature, *etc.* [10–12]. We have embarked on combined experimental and theoretical studies of the B/H/C chemistry prevailing in both HFCVD [13] and MW plasma enhanced (PE) CVD reactors [14,15]. The experimental part of the HFCVD project has involved use of resonance enhanced multiphoton ionization (REMPI) techniques to measure spatially resolved relative number densities of B (and H) atoms – henceforth represented as [B], [H], *etc.* – as functions of process conditions (*e.g.* the hot wire material, and its temperature T_w, gas pressure p, the B_2H_6/H_2 mixing ratio, and the presence (or not) of added CH_4) [13]. The complementary modeling builds on previous analyses of CH_4/H_2 [3,16–18], $CH_4/NH_3/H_2$ [19], B_2H_6/H_2 and $CH_4/B_2H_6/H_2$ [13] gas-phase and gas-surface chemistry in HFCVD reactors. One of the challenges of the present study is to determine the important reaction pathways (with known and/or assumed rate coefficients) in B/C/H gas mixtures under typical HFCVD reactor conditions. Our recent studies of B/H/C chemistry in a MW PECVD reactor [14,15] showed that trace amounts of O_2 impurity (air leakage, impurity in source gas) present at concentrations comparable to the B_2H_6 concentrations typically used in B-doped diamond CVD can have a major effect on the BH_x concentrations — hence the need to establish the much more complex, four component, B/H/C/O chemical mechanism.

2. Modeling of HFCVD reactor processes in B/H/C/O mixtures

To start the study of B/H/C/(O) chemistry in HFCVD reactors one first needs to be able to describe the processes involved in diamond

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deposition from conventional (*e.g.* 1%CH_4/H_2) mixtures, *i.e.* proper treatments of the catalytic dissociation of H_2 on the HF surface, the H/C gas-phase chemistry, the gas temperature (T_{gas}) and species concentration distributions, diamond growth models, *etc*. Then one needs to collect and analyze scarce data on B/H/O chemical kinetics and thermochemistry from previous studies under conditions that, as a rule, are far from the typical HFCVD conditions. These include combustion studies of boranes (B_xH_y) in the search for high-energy fuels [20–22], studies of MW PECVD reactors [14,15,23,24], theoretical studies of various B_xH_y, $B_xH_yO_z$ species, their structures and reactions with H, H_2, H_xO_y and C_xH_y species [20–22,25,26], and B_2H_6 dissociation studies (in B_2H_6 and B_2H_6/H_2 mixtures) [27]. Below we describe the main stages of our model development.

2.1. Catalytic H_2 dissociation on HF surface

H atoms play a crucial role in activating the process gas mixtures and initiating the various inter-conversions within and between the CH_x and C_2H_y families (and $H_xB_yC_zO_{z'}$ species in B/H/C/O mixtures). Previous theoretical [16,18,28,29] and experimental studies have explored H atom densities (as functions of process parameters) by, for example, REMPI [3,13], laser induced fluorescence [30], third-harmonic generation [31], and calorimetric studies of the filament power balance in order to establish the fractions of supplied electrical power expended through radiation, conduction and catalytic H_2 dissociation [18,32,33]. Such studies have shown that the distribution of H atom densities under typical HFCVD reactor conditions (*e.g.* p ~ 10–50 Torr, T_w ~ 2300–2700 K) is largely established by the balance of production (H_2 catalytic dissociation on the HF surface), loss (both recombination on the cold reactor walls, substrate, substrate holder, and consumption in gas-phase reactions) and diffusional transfer. The H atom source term should be well described as a function of process parameters like p and T_w, but various aspects of the dissociation mechanism and measured dependences remain unclear. For example, the input powers required to maintain the hot wire at a given T_w appear to saturate at $p(H_2)$ ~10–20 Torr, as do the measured H atom concentrations (which thereafter remain flat or even decline slightly upon increasing p ~ 100 Torr) — in marked contradiction with expectations based on the ~5-fold increase of the number of collisions between H_2 molecules and the HF surface and the ~5-fold decrease in the diffusional coefficient ($D \sim 1/p$) [18]. In addition, T_w dependent measurements of the effective enthalpy for forming H atoms return a value, $\Delta H \sim 2.45$ eV, that is much lower than the H_2 bond strength [18]. In an attempt to explain such apparent paradoxes, we recently proposed a self-consistent approach based on analytical distributions of T_{gas} and H atom concentrations in the immediate proximity of the HF, and a simple gas-surface model based on two effective (and reversible) chemisorption/desorption reactions:

$$S^* + H_2 \leftrightarrow SH + H, \quad k_1\left[\mathrm{cm^3/s}\right] = 2.8\times10^{-12}T_{nw}^{0.5}\exp(-10440/T_w), \quad k_{-1} = 1.5\times10^{-11}\left[\mathrm{cm^3/s}\right] \qquad (1)$$

$$SH \leftrightarrow S^* + H, \quad k_2\left[\mathrm{s^{-1}}\right] = 10^{13}\exp(-41780/T_w), \quad k_{-2} = 2.85\times10^{-11}\left[\mathrm{cm^3/s}\right]. \qquad (2)$$

S* and SH are the active (free) and H-terminated sites on the HF surface, respectively, $[S_0] = [SH] + [S^*]$ is the total surface site density per unit area, $T_{nw} = T_{gas}(d=0)$ is the gas temperature adjacent to the hot wire surface, d is the distance from the HF, and k_i are the rate coefficients adopted in [18] for a bare Ta wire. This approach affords a consistent description of all of the experimental observations, and the measured trends upon varying p and T_w. In particular, the saturation of the catalytic source term Q [cm^{-2} s^{-1}] (where Q is the number of H atoms produced per second per unit area of hot surface, *i.e.* $Q = 2(R_1 - R_{-1}) = 2(R_2 - R_{-2})$ in terms of reaction rates R_i ($i = 1, 2$) [18]) and of the H atom densities measured a few mm from the HF surface are explained by the appropriate drop of the free site fraction $[S^*]/[S_0]$ — as can be seen in Fig. 1, which illustrates results from [18] for the case of a bare Ta wire at $T_w = 2440$ K in H_2 gas. This plot also highlights the sensitivity of the $[H](d=2\text{ mm})/[H](d=0)$ ratio to $p(H_2)$: the observed saturation of the H atom density measured a few mm from the HF surface does not imply a similar saturation for the H atom concentration at $d = 0$. This effect, which is induced by the very steep gradients in T_{gas} and [H] near the HF [18] and the decline in the diffusion coefficient with p ($D_H \sim 1/p$), illustrates a limitation of using H atom concentrations measured near the HF as a proxy for the H atom densities at the HF surface itself when varying $p(H_2)$: such an assumption introduces a >200% error in the $[H](d=2\text{ mm})/[H](d=0)$ ratio across the range $20 < p(H_2) < 100$ Torr. The catalytic source term Q is an important parameter for the 2D/3D models discussed below.

2.2. 2D/3D models of HFCVD reactor processes

Another important element in our theoretical studies is the development of 2D(r,z) and 3D(x,y,z) models to describe (i) activation of the reactive mixture (*e.g.* gas heating, catalytic H atom production on the HF and, in the present case, loss of gas-phase boron by incorporation at the HF surface), (ii) gas-phase processes (heat and mass transfer, and chemical kinetics), and (iii) gas-surface processes at the substrate. The models involve the conservation equations for mass, momentum, energy, and species concentrations, together with appropriate initial and boundary conditions, thermal and caloric equations of state. These equations are integrated numerically to yield spatial distributions of T_{gas} and, in the case of H/C gas mixtures, the various H_xC_y species (H, H_2, CH_x ($x = 0$–4), C_2H_y($y = 0$–6)) densities. The calculated results for different reactor parameters succeed in reproducing a wealth of data and trends observed experimentally [3,16–19]. For the present study of B-doped diamond deposition, the chemical mechanism was necessarily expanded to incorporate the B/H/C/O mechanism described below.

Most of the calculations in the present study employed the computationally less time consuming 2D(r,z) model and base conditions as follows: $p = 20$ Torr, substrate temperature $T_{sub} = 1073$ K, flow rates $F(CH_4) = 1$ standard cm^3 per minute (sccm), $F(H_2) = 99$ sccm, $F(B_2H_6) = 0.0475$ sccm, and T_w values of 2073, 2300 and 2573 K. The reactor is represented in cylindrical coordinates, with z parallel to the direction of gas flow. The modeling considers a part of the Bristol HFCVD reactor (a chamber based on a six-way cross). The model reactor volume was bounded in the radial and vertical directions by, respectively, $0 < r < 25$ mm and $-10\text{ mm} < z < 30$ mm, with the point (0,0) defining

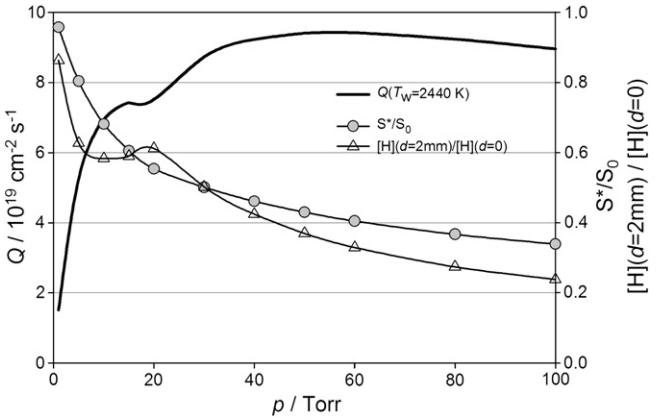

Fig. 1. Plot illustrating the calculated $p(H_2)$ dependences of the catalytic H atom production rate Q, the free site fraction $[S^*]/[S_0]$ and the $[H](d=2\text{ mm})/[H](d=0)$ ratio for a bare Ta HW at $T_w = 2440$ K.