Letter

Influence of the gas phase on doping in diamond chemical vapor deposition

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Abstract

A series of calculations has been carried out to examine the relationship between gas phase composition and film composition in diamond chemical vapor deposition. It is predicted that the ability to carry out in situ doping of films with N and S, and the inability to dope with O, can be explained from a simple thermodynamic perspective. Probable precursor dopant species are identified as ·CN and ·SH for the $CH_4/H_2/N_2$ and $CH_4/H_2/H_2S$ systems, although it is expected that these are the most likely precursors regardless of the initial forms of nitrogen and sulfur. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Undoped polycrystalline films of diamond grown by chemical vapor deposition (CVD) have been successfully inserted into cutting tool and thermal management markets [1], as well optical transmission applications, most notably, the use of diamond for CO_2 laser windows [2]. The use of diamond in semiconductor applications has lagged, in part due to the perceived expense of the material, but mainly because of the difficulty in producing low-defect *p*-type and *n*-type diamond with the required thermal, optical, or mechanical properties. There are important applications for which it has been shown that doped diamond is ideally suited, and moreover, that high quality diamond can be synthesized with the required electrical properties. Examples include electrochemistry [3,4] and field emission [5,6], and to date have involved the use of boron-doped diamond to form an acceptor level. P-type diamond films doped in situ, that is, films grown in the presence

of a reactive boron precursor such as B_2H_6, exhibit high carrier mobility, good crystal structure, low sp^2 content, and reasonable thermal conductivity [7–9].

There has been much less success reported in producing high quality *n*-type diamond films. The elements N, P, and O have been shown to form donor levels in diamond [10–14], and S is known to form deep donor levels in silicon [15] and germanium [16]. Nitrogen, which is ubiquitous as an impurity in sub-atmospheric deposition systems, readily incorporates itself into the diamond lattice and forms a deep donor level. One problem is the donor level is so deep, with an ionization level of 1.7 eV, that N-doped films are insulating at room temperature [10]. Another significant issue is that the presence of small amounts of nitrogen in the gas phase, 20–50 ppm, yield films with poor thermal and microstructural properties; the latter may be associated with the higher growth rates observed when nitrogen is present in small concentration [17–19]. The successful growth of diamond using a CS_2 precursor [20] recently led other investigators to explore the feasibility of using a $CH_4/H_2/H_2S$ mixture to grow semiconducting films [21]. N-type behavior was re-

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ported for the S-doped films, with an ionization energy of 0.38 eV and a room temperature Hall mobility of 600 cm^2 V^{-1} s^{-1}, but a more recent study has indicated that these films may actually be *p*-type rather than *n*-type [22]. In situ doping with PH_3 and $P(C_2H_5)_3$ precursors have yielded films with *n*-type characteristics, but very low, temperature dependent mobilities [23,24]. An alternative, ex situ approach using P^+ ion implantation has been demonstrated to produce films with reasonable donor levels (0.6 eV), but this may come at the cost of deleterious lattice damage that eliminates any *n*-type behavior [14,25].

The ion-induced lattice damage resulting from the relatively large P atom has led investigators to examine the feasibility of implanting O or S as alternative donors [26,27]. Furthermore, it has been proposed that ion implantation is the only possible method for phosphorous, oxygen, or sulfur doping because of a lack of chemical affinity between these elements and the carbon atoms in the diamond lattice [25,28]. In other words, ex situ implantation methods are needed because neither P, O, nor S readily adsorb onto the diamond surface and become incorporated into the bulk during CVD.

However, it will be shown here that this interpretation is not necessarily true, and there may a very simple gas-phase explanation for the facility of in situ doping with N, the potential for doping with S, and the lack of success with O doping. It has been reported in a number of separate investigations that the carbon-containing species, particularly the C_1 species, rapidly undergo reactions to reach a near-equilibrium state based on the local H and H_2 concentrations [29–32]. These investigations focused on systems containing only hydrogen and carbon but, as will be discussed below, the same conclusion can be drawn when there are small amounts of an impurity present. And finally, it is the stable equilibrium distribution of species that may indeed dictate which elements can be successfully incorporated as dopants into the lattice of the growing diamond film. To illustrate the connection in a typical diamond CVD process between the gas phase state and the film composition, three dopant species have been chosen: N, O, and S. Calculations have been carried out to demonstrate that the equilibrium distributions of gaseous species in the different systems are consistent with the observed ability or inability to obtain a doped film.

2. Results and discussion

For the three dopant systems considered equilibrium calculations were performed at temperatures ranging from 1200 to 2000 K, and with one exception, at a pressure of 115 torr. These conditions are representative of gas-phase temperatures and pressures found in hot-filament or microwave deposition chambers, and because of the moderate pressure it may be assumed that all gas transport and chemical processes are thermal. It is possible that, adjacent to a filament array or at the center of a plasma ball, the gas temperature will be somewhat higher than the upper limit of 2000 K considered here. However, as will be shown in the figures below, the asymptotic nature of the species' distributions at higher temperatures supports the basic conclusions drawn from this work. In all of the calculations specified amounts of CH_4, H_2, and dopant precursor (N_2, O_2, or H_2S) were introduced, and the system was allowed to come to chemical equilibrium at a fixed temperature and pressure. For each system all possible stable and free radical species have been included, up to C_3, but only the major, i.e. most prevalent, species are shown in the figures. Due to the thermal nature of the systems considered, only neutral species have been included in the calculations. The equilibrium state was determined through standard Gibbs energy minimization techniques, and the thermodynamic properties of all species were calculated using polynomial fits to published data [33].

The major hydrocarbon species distribute themselves in a very consistent manner, as illustrated in Fig. 1. The equilibrium data in that figure correspond to two different chemistries: the first system contains an initial mixture of 29 ppm N_2 in 1.7 mol% CH_4 and 98.3 mol% H_2 (open symbols) and the second system consists of an initial mixture of 50 ppm H_2S in 4 mol% CH_4 and 96 mol% H_2. These dopant concentrations were chosen because they are representative of values appearing in the literature [17,21]. Although the absolute amounts of the hydrocarbons in Fig. 1 differ due to the initial CH_4 concentrations chosen, the general trend is the same, and in fact it is the same as would be observed if no dopant was present. Most of the CH_4 is converted to C_2H_2 at temperatures above 1450 K because the atomic hydrogen formed by H_2 dissociation reacts quickly with CH_4 to create CH_3, and the equilibrium constant for the reaction transforming CH_3 to C_2H_2 is on the order of 10^7 at 1500 K. Thus, there is a strong driving force for the conversion of CH_4 to C_2H_2 in these systems.

When the mixture of 29 ppm N_2 in 1.7 mol% CH_4 and 98.3 mol% H_2 comes to equilibrium, the nitrogen is distributed primarily between the three species shown in Fig. 2. The N≡N bond is very strong, 226 kcal mol^{-1}, but homogeneous kinetics calculations indicate that, when there are sufficient concentrations of H and CH_3 present to attack this molecule the bond can be broken at relatively high rates; for temperatures above 1400 K, virtually all of the nitrogen in N_2 is converted to HCN at equilibrium. The HCN molecule is stable and probably does not react with radical sites on the diamond surface, but the H–CN bond is only 120 kcal
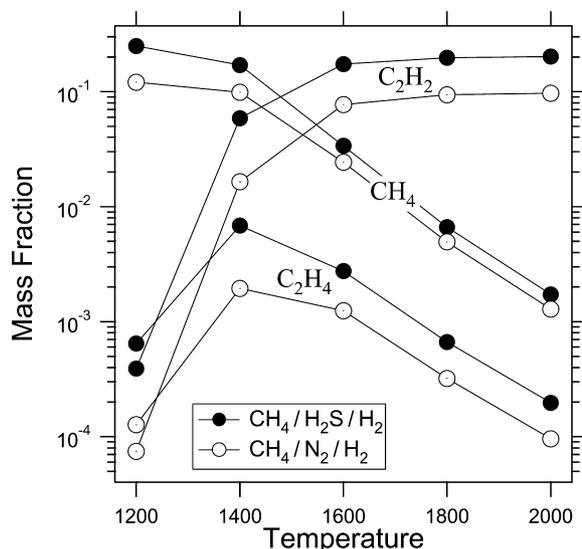
Fig. 1. A representative equilibrium distribution of the major hydrocarbon species at 115 torr and different temperatures for characteristic in situ sulfur and nitrogen doping conditions. The closed symbols correspond to 50 ppm (0.066 wt.%) H_2S in 4 mol% CH_4 and 96 mol% H_2, and the open symbols denote 29 ppm (0.036 wt.%) N_2 in 1.7 mol% CH_4 and 98.3 mol% H_2.

mol^{-1} — not significantly greater than the bond strength of a surface-terminated hydrogen — and atomic hydrogen can attack this bond to form H_2 and a reactive ·CN radical species. Therefore it is likely that investigators can routinely grow N-doped films because sufficient inlet nitrogen is converted to HCN and then to ·CN, which in turn adsorbs onto the diamond surface before undergoing subsequent incorporation reactions.

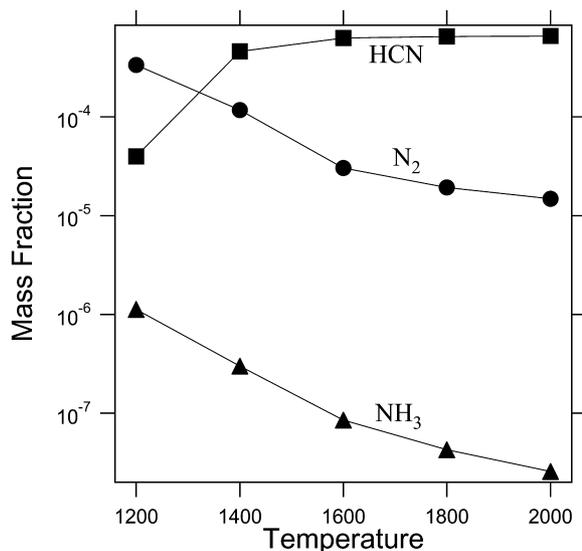When oxygen is present in the CH_4/H_2 system

Fig. 2. The equilibrium distribution of the major nitrogen-containing species at 115 torr and different temperatures, for an initial mixture of 29 ppm (0.036 wt.%) N_2 in 1.7 mol% CH_4 and 98.3 mol% H_2.
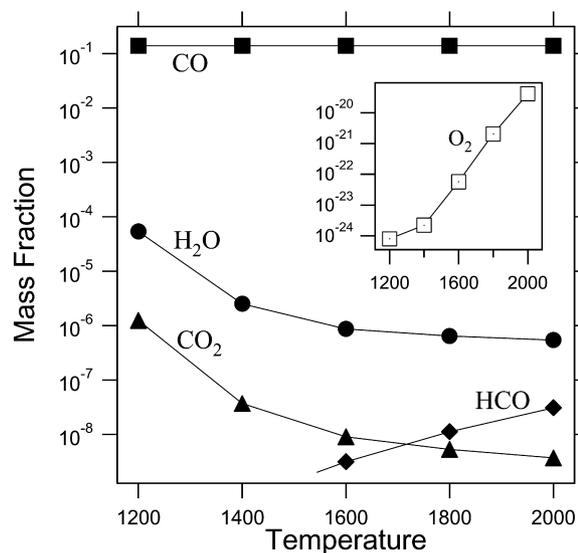

Fig. 3. The equilibrium distribution of the major oxygen-containing species at 115 torr and different temperatures, for an initial mixture of 6400 ppm (7.9 wt.%) O_2 in 2.8 mol% CH_4 and 96.6 mol% H_2.

instead of nitrogen or sulfur, the equilibrium hydrocarbon distribution looks qualitatively similar to that shown in Fig. 1. One difference, however, between O_2 addition and N_2 or H_2S addition, is that oxygen is typically present in higher concentrations — up to 1 mol%, as opposed to 20–100 ppm. As illustrated in Fig. 3, for an initial mixture of 6400 ppm O_2 in 2.8 mol% CH_4 and 96.6 mol% H_2, the oxygen is converted to CO with an efficiency no less than 99.9% at all temperatures; the percent conversion increases with temperature, and regardless of the temperature, essentially none of the oxygen leaves the system as O_2. The behavior reported in Fig. 3 is independent of initial O_2 concentrations ranging from 5 ppm (the lowest considered) to 1 mol%. Oxygen is often added at concentrations of up to 0.5 mol% because it is recognized that this element does not get incorporated into the diamond film, and it somehow contributes to the growth of higher quality films. The improvement in quality may be due, at least in part, to the ppb-to-ppm levels of sp^2-scavenging hydroxyl radical adjacent to the surface. However, as will be discussed below, the results shown in Fig. 3 may also account for both the lack of O incorporation and the improved film quality.

As indicated earlier, at temperatures above 1450 K there is a strong driving force for the transformation of CH_4 to C_2H_2. Once C_2H_2 forms, in the presence of O_2 there is an even stronger driving force for the conversion of this species to CO and H_2. For example, at 1500 K the equilibrium constant for the oxidation of C_2H_2 to CO is 10^{22}. After the oxygen is bound to carbon as CO, it remains there: homogeneous kinetics calculations indicate that, for a wide range of temperatures, pressures, and compositions representative of

diamond growth, the 257 kcal mol^{-1} C≡O bond is not broken once it forms. This molecule is extremely stable, and there is no evidence that it reacts with the diamond surface. Therefore, essentially all oxygen introduced into a diamond CVD system will be quickly converted to CO, and it will leave the system in that species. Introducing oxygen in other forms does not appear to alleviate this problem, because these species are also converted to CO. For example, at 1500 K the equilibrium constants for the oxidation of CH_3OH and CH_2O to CO are 10^9 and 10^6, respectively. At this point it is difficult to determine whether oxygen can be incorporated into a diamond film under CVD conditions because it is always converted to a form, i.e. CO, not amenable to chemisorption. However, it is for this reason that oxygen addition may improve film quality. For each oxygen molecule fed to the reactor two carbon atoms are irreversibly tied up; this lowers the effective gas-phase hydrocarbon population, which in turn tends to yield higher quality films.

The addition of H_2S to the CH_4/H_2 system results in the equilibrium compositions shown in Figs. 4 and 5. Fig. 4 illustrates the dependence of the distribution of the major sulfur-containing species on system pressure. The initial mixture is the same in both cases and is the same as in Fig. 1, that is, 50 ppm H_2S in 4 mol% CH_4 and 96 mol% H_2. Atomic hydrogen readily attacks the 90 kcal mol^{-1} H−S bond in H_2S to form the more stable H_2 and the reactive ·SH radical. When this radical is present with hydrocarbon radical species at temperatures greater than 1600 K, the system is driven

Fig. 5. The effect of initial H_2S concentration on the equilibrium distribution of gas species at 115 torr and different temperatures. The closed symbols correspond to an initial H_2S concentration of 84 ppm (0.12 wt.%) and the open symbols denote an initial concentration of 50 ppm (0.066 wt.%).

towards the production of the stable species CS. Because the C≡S bond strength is 167 kcal mol^{-1}, relatively weak for a triple bond, it may be possible in a kinetic process for available atomic hydrogen or ·CH_x radicals to attack this molecule to form a reactive sulfur species. However, it is more likely that most of the sulfur remains bound in the stable CS molecule, and it is the equilibrium ·SH concentration, which can account for up to 3% of total sulfur, that adsorbs onto the diamond surface and undergoes subsequent incorporation reactions. This is supported by SIMS data taken from 50 ppm H_2S doping experiments in which it was found that the sulfur content in the films was approximately 0.5 ppm [21]. Fig. 5 illustrates the effect of initial H_2S concentration on equilibrium distribution. In general, additional sulfur leads to enhanced levels of ·SH and CS, but the increase in CS only occurs for temperatures above 1600 K. If ·SH is, indeed, the precursor species for sulfur incorporation, then Fig. 5 would imply that a higher inlet H_2S concentration is better. However, CS is known to readily undergo polymerization reactions when its concentration is sufficiently high, and this may offset any benefits associated with enhanced ·SH.
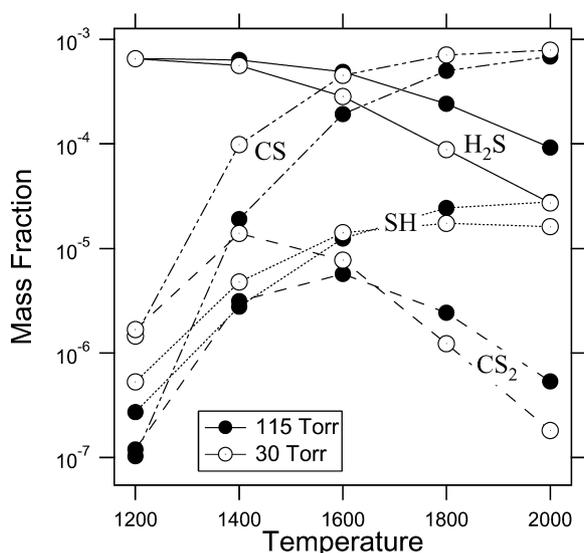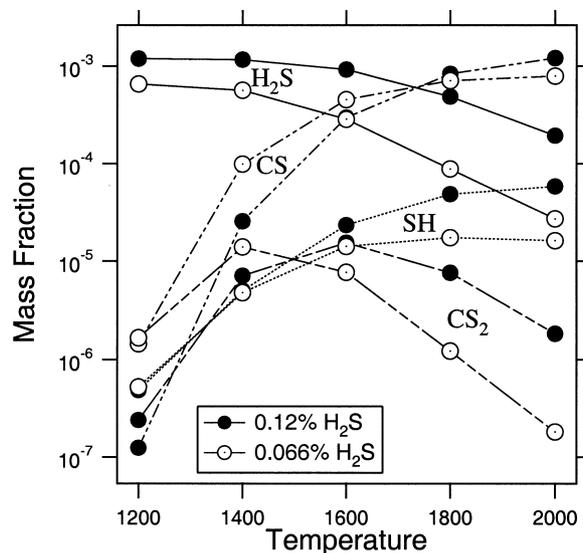
Acknowledgements

Fig. 4. The effect of system pressure on the equilibrium distribution of sulfur-containing species at different temperatures, for an initial mixture of 50 ppm (0.066 wt.%) H_2S in 4 mol% CH_4 and 96 mol% H_2. The solid symbols correspond to 115 torr and the open symbols denote 30 torr.

References

[1] J.E. Butler, H. Windischmann, MRS Bull. 23 (1998) 22.

[2] C.J. Brierley, C.M. Beck, G.R. Kennedy, J. Metcalfe, D. Wheatley, Diamond Relat. Mater. 8 (1999) 1759.

[3] M.C. Granger, G.M. Swain, J. Electrochem. Soc. 146 (1999) 4551.

[4] P.A. Michaud, E. Mahe, W. Haenni, A. Perret, C. Comninellis, Electrochem. Solid State Lett. 3 (2000) 77.

[5] A. Wisitsora-at, W.P. Kang, J.L. Davidson, Y. Gurbuz, D.V. Kerns, Diamond Relat. Mater. 8 (1999) 1220.

[6] A. Wisitsora-at, W.P. Kang, J.L. Davidson, Q. Li, J.F. Xu, D.V. Kerns, Appl. Surf. Sci. 146 (1999) 280.

[7] S. Yamanaka, H. Watanabe, S. Masai, D. Takeuchi, H. Okushi, K. Kajimura, Jpn. J. Appl. Phys. 37 (1998) L1129.

[8] X. Jiang, P. Willich, M. Paul, C.P. Klages, J. Mater. Res. 14 (1999) 3211.

[9] A. Hatta, S. Sonoda, T. Ito, Diamond Relat. Mater. 8 (1999) 1470.

[10] R.G. Farrer, Solid State Commun. 7 (1969) 685.

[11] T. Yamada, K.S. Chang, K. Okano, A. Hiraki, Electron. Commun. Jpn. Pt. II-Electron. 81 (1998) 54.

[12] A.E. Alexenko, B.V. Spitsyn, Diamond Relat. Mater. 1 (1992) 705.

[13] N. Fujimori, T. Imai, H. Nakahata, H. Shiomi, Y. Nishibayashi, Mater. Res. Soc. Symp. Proc. 162 (1990) 23.

[14] G. Popovici, M.A. Prelas, T. Sung, S. Khasawinah, A.A. Melnikov, V.S. Varichenko, A.M. Zaitsev, A.V. Denisenko, W.R. Fahrner, Diamond Relat. Mater. 4 (1995) 877.

[15] G.W. Ludwig, Phys. Rev. 137 (1959) A1520.

[16] W.W. Tyler, J. Phys. Chem. Solids 8 (1959) 59.

[17] W. Müller-Sebert, E. Worner, F. Fuchs, C. Wild, P. Koidl, Appl. Phys. Lett. 68 (1996) 759.

[18] J. Stiegler, A. Bergmaier, J. Michler, S. Laufer, G. Dollinger, E. Blank, Thin Solid Films 352 (1999) 29.

[19] J.J. Schermer, F.K. de Theije, Diamond Relat. Mater. 8 (1999) 2127.

[20] G.D. Barber, W.A. Yarbrough, J. Am. Ceram. Soc. 80 (1997) 1560.

[21] I. Sakaguchi, M.N. Gamo, Y. Kikuchi, E. Yasu, H. Haneda, T. Suzuki, T. Ando, Phys. Rev. B 60 (1999) R2139.

[22] R. Kalish, A. Reznik, C. Uzan-Saguy, C. Cytermann, Appl. Phys. Lett. 76 (2000) 757.

[23] S. Koizumi, M. Kamo, Y. Sato, H. Ozaki, T. Inuzuka, Appl. Phys. Lett. 71 (1997) 1065.

[24] T. Saito, M. Kameta, K. Kusakabe, S. Morooka, H. Maeda1, Y. Hayashi, T. Asano, Jpn. J. Appl. Phys. 37 (1998) L543.

[25] J.F. Prins, Diamond Relat. Mater. 8 (1999) 1635.

[26] J.F. Prins, Ind. Diamond Rev. 56 (1996) 22.

[27] M. Hasegawa, D. Takeuchi, S. Yamanaka, M. Ogura, H. Watanabe, N. Kobayashi, H. Okushi, K. Kajimura, Jpn. J. Appl. Phys. 38 (1999) L1519.

[28] J.F. Prins, Diamond Films Technol. 8 (1998) 181.

[29] D.S. Dandy, M.E. Coltrin, J. Mater. Res. 10 (1995) 1993.

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

[31] D.G. Goodwin, Appl. Phys. Lett. 59 (1991) 277.

[32] J.E. Butler, F.G. Celii, in: A.J. Purdes, K.E. Spear, B.S. Meyerson, K.V. Ravi, T.D. Moustakis, M. Yoder (Eds.), Proc. 1st Intl. Symp. Diamond and Related Materials, The Electrochemical Society, 1989, p. 317.

[33] NIST-JANAF Thermochemical Tables, 4th ed., J. Phys. and Chem. Ref. Data, Monograph 9 (1998).