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Investigation of the addition of nitrogen-containing gases to a hot filament diamond chemical vapour deposition reactor

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Abstract

We have investigated the effect that addition of various nitrogen-containing gases, such as ammonia, methylamine and HCN, has on the composition of the films deposited in a standard hot filament diamond chemical vapour deposition reactor. Total process gas concentration (C + N) was maintained at 1% in H_2 throughout the experiments. When using a feedstock of methane and ammonia, we generally find that for methane-rich mixtures diamond films are formed; for ammonia-rich mixtures, silicon nitride is formed by reaction of the ammonia with the Si substrate; for approximately equal ratios of CH_4 to NH_3, little film deposition occurs. Other gases, such as CH_3NH_2 and HCN, behave similarly to 1:1 mixtures of CH_4 and NH_3. Results are explained in terms of a simple chemical model of the gas phase chemistry and surface interactions.

Keywords: Diamond CVD; Nitrogen; Carbon nitride; Ammonia

1. Introduction

The theoretical compound carbon nitride (β-C_3N_4) has been predicted to have a hardness similar to, or even greater than, that of diamond [1,2]. As such, there have recently been a number of reported attempts to make β-C_3N_4 using a variety of methods [3–14] including sputtering a carbon target in a nitrogen atmosphere [3], laser ablation of a graphite rod with simultaneous N^+ ion bombardment of a substrate [4,5], and pyrolytic decomposition of C–N–H organics [6]. These attempts have met with only limited success, with mainly amorphous films being produced. Although some of these films had up to 40% nitrogen content, they were still a long way from the 53% required for crystalline β-C_3N_4. Such nitrogen-doped diamond-like carbon films are interesting in themselves [15,16], since they have many useful electronic properties which may lead to semiconducting device applications. The most reliable reports of crystalline carbon nitride to date [5,10,14] are from groups who claim to have produced nanocrystals of β-C_3N_4 in an amorphous CN_x matrix. These findings have still to be convincingly confirmed, and meanwhile the search continues for an easier route to form carbon nitride.

Most of the techniques used have been mainly physical in nature, with the carbon and nitrogen being created as reactive atoms or ions by "brute force" methods and then made to strike a surface at high impact energies. Compare this with the mainly chemical nature of diamond chemical vapour deposition (CVD) where the reactive carbon species are created by thermal or plasma means and simply diffuse to the substrate surface. This gentler approach allows the delicate crystalline lattice to self-assemble, without the danger of amorphization due to ion bombardment. In this paper, we report the results of our investigations into whether it is possible to make carbon nitride by adding nitrogen-containing gases into the methane–hydrogen gas mixture normally used for diamond CVD. The idea is that C and N, in the presence of H atoms, might self-assemble into C_3N_4 in the same way as diamond self-assembles from the mixture of hydrocarbons and radicals present during normal hot filament CVD. Previous attempts at similar work involved additions of N_2 gas to CVD systems [17,18], but these were largely unsuccessful in producing either highly N-doped diamond or carbon nitride. Small amounts (tens of parts per million) of N_2 added to the process gas mixture have been shown to affect the deposition characteristics dramatically [19], stabilizing

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the ⟨100⟩ surface with respect to other surfaces, but again did not result in significant N incorporation. This may reflect the relative unreactivity of N_2, and so we have chosen more reactive precursor gases, based on ammonia. Ammonia has been used as precursor gas in previous studies [20]; however, the aim there was to produce N-doped diamond films rather than carbon nitride and so the ammonia concentration used in these experiments was very low (around 0.05%).

2. Experimental details

The apparatus used was a typical hot filament CVD reactor. Standard operating conditions were as follows: substrate, Si(100), pre-abraded with 1–3 μm diamond grit, maintained at a temperature of about 900 °C; Ta filament at a temperature of 2300 °C placed about 6 mm from the substrate; pressure, 20 Torr; H_2 flow, 200 standard cm^3 min^{-1}; percentage of C- and/or N-containing gases, around 1%.

Three types of C–N precursor gases were used:

- the C and N present in different, small molecules, such as methane + ammonia;
- the C and N bonded together in the same molecule, such as methylamine (CH_3NH_2);
- the C and N present as C≡N in hydrogen cyanide gas.

Methane, ammonia and methylamine were obtained as commercial products, but HCN was synthesized in house by reaction between NaCN and phosphoric acid (dried by the addition of P_2O_5, in vacuo). This produced enough HCN for a 6 h deposition run.

Experiments performed included variation of gas flow rates, mixing ratios, total pressure, and substrate and filament temperatures. Film composition was determined by transmission electron microscopy (TEM), X-ray diffraction (XRD), laser Raman and scanning Auger analysis. Determination of the major gas phase species present during CVD was performed using molecular beam mass spectrometry (MBMS) [21,22], and the resulting concentration profiles for the various gaseous nitrogen- and carbon-containing species under different deposition conditions were measured.

3. Results

3.1. Methane + ammonia mixtures

Experiments were performed varying several of the process conditions, such as pressure and filament temperature. The total CH_4 and NH_3 was maintained at around 1% in H_2 for all the experiments; only the CH_4:NH_3 ratio was varied. The results are summarized in Fig. 1, with the composition of the resulting film being determined by XRD and TEM analysis and laser Raman spectroscopy.

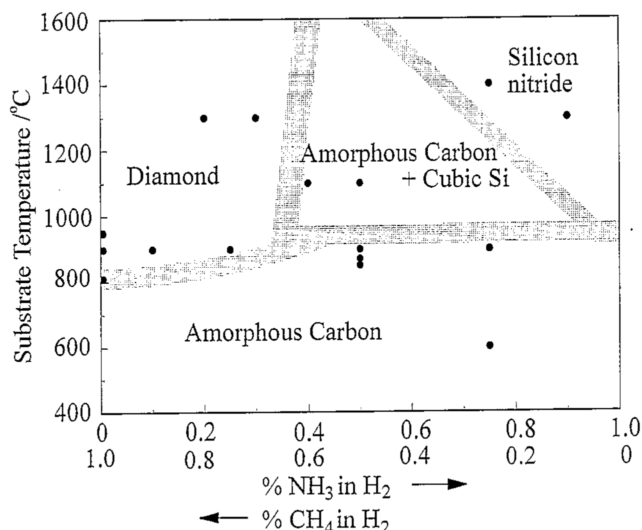
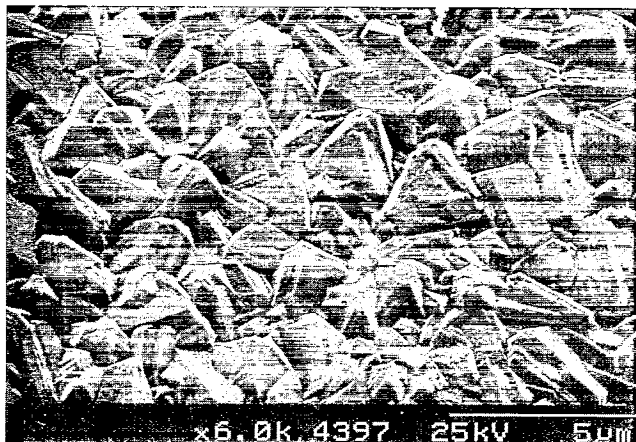


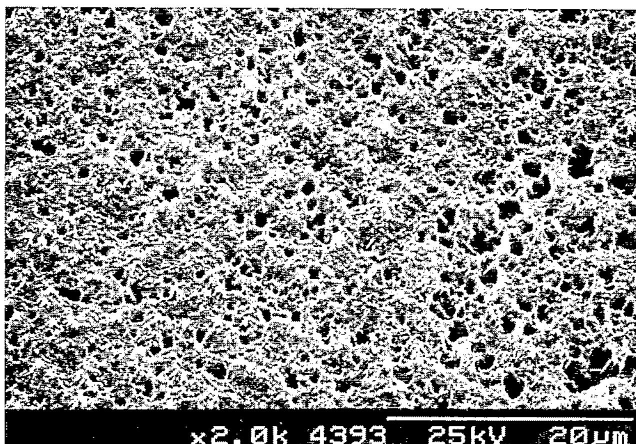
Fig. 1. Diagram showing the types of films produced on Si substrates after CVD as a function of different substrate temperatures and methane: ammonia ratios. Approximate phase boundaries are included to guide the eye.

At substrate temperatures lower than about 800 °C only amorphous carbon films were produced, with little or no N content. At higher temperatures, the film composition depended strongly on the ammonia-to-methane ratio. With methane-rich gas mixtures, as expected, diamond was grown (Fig. 2(a)), the morphology of which was similar to that seen in standard CVD processes, although as the fraction of ammonia increased the films became more nanocrystalline and the growth rate decreased. Scanning Auger analysis combined with Ar^+ ion depth profiling showed that the nitrogen content of these films was less than 3%, with all the nitrogen being found within the top 10 nm of the surface. With ammonia-rich gas mixtures, the Si substrate preferentially reacted with the ammonia to produce an Si_3N_4 coating, with no carbon content (see Fig. 2(b)). If a CVD diamond-coated Si substrate was used with ammonia-rich gas mixtures, the diamond was found slowly to etch back to the Si surface, at which point Si_3N_4 was again formed. The deposition rate for gas mixtures with C:N ratios approaching 1:1 was very small (less than 50 nm h^{-1}), and any deposit consisted mainly of amorphous carbon containing occasional small cubic Si crystals. The latter were presumably redeposited after transitory etching, or resulted from recrystallization of damaged surface sites catalysed by the chemisorption and desorption of N-containing species. Laser Raman analysis of selected samples did not show peaks that could be easily assigned to known or predicted [14] C–N modes, confirming that β-C_3N_4 was not produced using any of the above deposition conditions and gas mixing ratios.

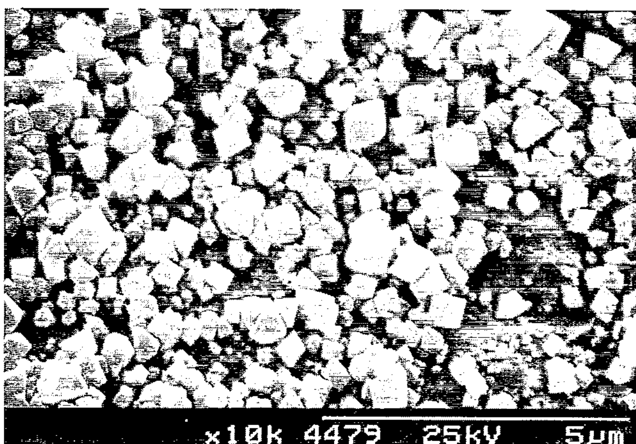
These results can be explained if the dominant reac-



(a)



(b)



(c)

Fig. 2. (a) Scanning electron micrograph of film produced after 6 h growth using methane-rich gas mixtures (0.2% NH_3–0.8% CH_4) and otherwise standard conditions. Analysis showed this film to be diamond with around 3% N incorporation into the top 10 nm. (b) Scanning electron micrograph of a film produced after 6 h growth using ammonia-rich gas mixtures (0.7% NH_3–0.3% CH_4) and otherwise standard conditions. The film was confirmed to be silicon nitride by TEM, laser Raman and scanning Auger analysis. (c) Scanning electron micrograph of a diamond film produced after 6 h growth using 0.5% CH_3NH_2 in H_2 and standard conditions. Similar films resulted when using 0.5% HCN or 1:1 mixtures of CH_4 and NH_3.

tions occurring in the process chamber are gas phase reactions between the carbon-containing and the nitrogen-containing species, to produce stable molecules, such as HCN. In such a scheme, where the stoichiometry of the C–N reaction is 1:1, the only way net deposition can occur is when one of the species is in excess. Excess carbon species result in diamond; excess nitrogen species result in silicon nitride (or etching of any exposed diamond layers). For gas ratios approaching 1:1, deposition onto the surface is hindered by the tendency for the newly chemisorbed species to be etched back into the gas phase by reaction to form highly stable cyanide species. Some deposition does still occur since not all the carbon is removed from the surface, but the nucleation rate on non-diamond areas is very small. This results in a slow growth rate and low nucleation density, leading eventually to large numbers of small, but well-faceted, crystals (see Fig. 2(c)).

Further evidence for this mechanism is obtained from studies using an in situ molecular beam mass spectrometer [21,22]. In this system we are able to measure simultaneously the concentrations of a number of important gas phase species close to the hot filament during CVD. The results will be presented in more detail elsewhere [23], but a summary is given in Fig. 3. This

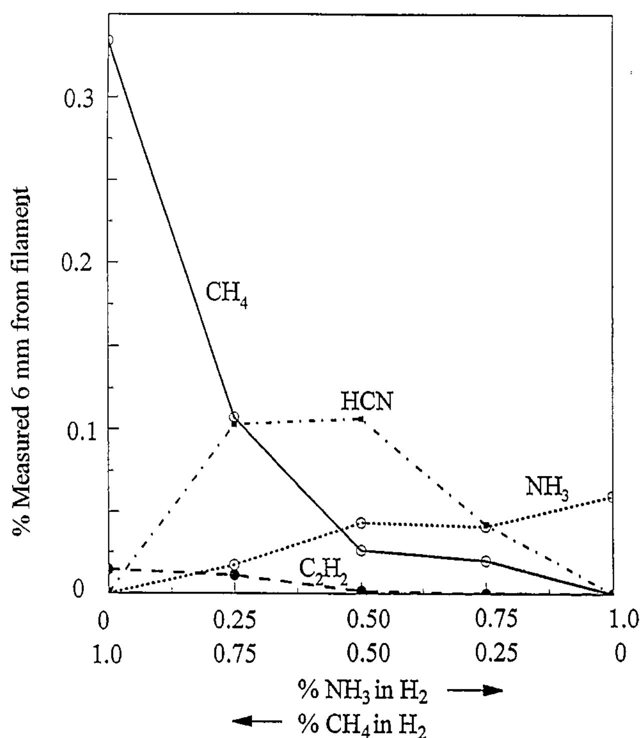
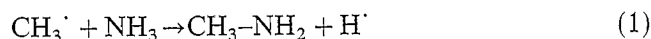


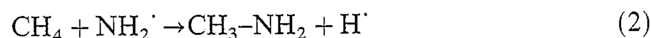
Fig. 3. The concentration of various species within the hot filament reactor as a function of methane and ammonia mole fraction, with the total concentration of methane+ammonia in the feedstock being kept constant at 1% in H_2 with otherwise standard conditions. The gases were sampled at the same distance from the filament as the substrate (around 6 mm). Note that the total C and N concentrations measured at this position are less than the input concentrations owing to thermal diffusion effects [21,22].

shows the concentrations of various species with varying methane: ammonia input gas ratio measured with the filament temperature maintained at 2300 °C. HCN is detected in high concentrations, and at gas ratios close to 1:1 the HCN concentration is significantly higher than that of either of the two precursor gases. Also, it is interesting to note that, at these filament temperatures, very little N_2 is observed. The N is locked up as either unreacted NH_3 or HCN (the most stable N-containing species at this temperature).

A suggested reaction scheme first of all requires the formation of a C–N bond. A prerequisite to this is the creation of reactive radical species, such as $CH_3^{\cdot}$ or $NH_2^{\cdot}$. These will be formed by H abstraction reactions initiated by H atoms produced from the thermal dissociation of H_2. The radicals can then react, i.e.

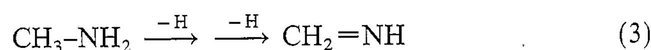


$$CH_3^{\cdot} + NH_3 \rightarrow CH_3\text{–}NH_2 + H^{\cdot} \quad (1)$$

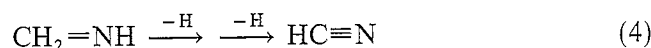


$$CH_4 + NH_2^{\cdot} \rightarrow CH_3\text{–}NH_2 + H^{\cdot} \quad (2)$$

and produce methylamine, which can then either redissociate or, more probably, undergo successive H abstractions to produce HCN:



$$CH_3\text{–}NH_2 \xrightarrow{-H} \xrightarrow{-H} CH_2{=}NH \quad (3)$$



$$CH_2{=}NH \xrightarrow{-H} \xrightarrow{-H} HC{\equiv}N \quad (4)$$

Reactions (3) and (4) are the most likely on thermodynamic grounds, owing to the stability of the C≡N bond. In fact, MBMS measurements at different filament temperatures suggest that $NH_2^{\cdot}$ is formed at lower temperature than $CH_3^{\cdot}$, implying that reaction (2) is the preferred route to methylamine formation. Methylamine and $CH_2{=}NH$ are not observed directly by MBMS, presumably because reactions (3) and (4) are so fast that the steady state concentration of these species is low. There will also be competing reactions, such as formation of C_2 and C_3 species by combination of two smaller hydrocarbons, which will reduce the effective concentration of C_1 species available to take part in reactions (1) and (2). These only play any real part in the overall reaction scheme when the concentration of C_1 species is sufficiently high, i.e. when using methane-rich mixtures.

3.2. *Methylamine mixtures*

The concentration of methylamine (CH_3NH_2) was maintained at 0.5% in H_2 (to make the total concentration of C + N species 1%) and the usual process parameters were varied. It was found that growth using standard conditions produced diamond films (see Fig. 2(c)), although at a much reduced growth rate (about 0.05 μm h^{-1}) compared with that obtained when using 1% methane in H_2 (typically 0.5 μm h^{-1}). MBMS analysis showed that HCN was again a major product of the gas phase reaction, with similar amounts being produced as with NH_3–CH_4 mixtures. In this case, however, HCN was produced at much lower filament temperatures (e.g. about 1500 °C compared with above 1900 °C when using NH_3–CH_4 mixtures). This probably reflects the fact that a C–N bond already exists in methylamine, which can be readily converted to the C≡N triple bond by the successive H abstraction reactions (3) and (4). We no longer require high filament temperatures to produce $CH_3^{\cdot}$ or $NH_2^{\cdot}$ radicals or the relatively low probability step of the two precursor species meeting and reacting together, reactions (1) and (2). Also, competing reactions, such as acetylene formation are much reduced. In effect, methylamine as a process gas simply behaves like a 1:1 mixture of NH_3 and CH_4, except that it lowers the gas temperatures at which reactions occur. As before, however, the reactions are unfavourable, promoting gas phase production of HCN rather than deposition.

3.3. *Hydrogen Cyanide mixtures*

Using 0.5% HCN in H_2 under standard process conditions produced amorphous films containing both diamond and SiC crystals, but again the deposition rate was low (below 0.1 μm h^{-1}). There was no evidence of nitrogen in these films. The fact that diamond and SiC could be produced from HCN shows that some cycling of the carbon must be occurring, with the HCN breaking up to form C- and N-containing species, which then either recombine to form HCN or deposit onto the surface. Evidence for the break-up of HCN was again given by the MBMS which confirmed formation of ammonia, methane and acetylene, although most (75%–85%) of the C and N were still locked up as HCN.

4. Conclusions

One conclusion from this work is that addition of nitrogen-containing species into the process gas mixture normally used in diamond CVD does not readily produce carbon nitride films. The formation of gaseous HCN seems to be the dominant chemical reaction occurring in the chamber, and the stability and volatility of this species inhibit the formation of solid films containing carbon and nitrogen. Thermodynamic equilibrium calculations [24] confirm that HCN production is highly favoured in H–C–N gas mixtures at high gas processing temperatures, but unfortunately it seems that this does not lead to significant incorporation of N into the diamond lattice. This is in agreement with the conclusions of Jin and Moustakas [17] who calculated a theoretical value for the doping efficiency of nitrogen in diamond of around 10^{-4}. In this work, we have only

been able to study a small fraction of the possible parameter space available in CVD reactors. The "gentle" approach appears to have been unsuccessful, so perhaps some degree of brute force is necessary to force C and N to form a solid film. This is confirmed by the very recent results of Yen and Chou [14], who reported the growth of nanophase crystalline carbon nitride using a plasma jet deposition method. They suggest that the high concentration of atomic nitrogen produced in their plasma jet, combined with intensive mixing of evaporated carbon species, significantly aids the preferential formation of carbon nitride. High concentrations of atomic nitrogen may well be the key to producing carbon nitride, which might explain why the hot filament method proved unsuccessful. Alternative sources of atomic N, e.g. microwave plasma CVD, combined with in situ ion bombardment may therefore be an avenue worth pursuing. Use of much higher concentrations (10%, 50%, maybe even 100%) of the C–N precursor gases may be another.

Acknowledgements

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