Sulfur addition to microwave activated CH4/CO2 gas mixtures used for diamond CVD: growth studies and gas phase investigations

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Microwave plasma chemical vapour deposition (MPCVD) has been used to deposit diamond films with H2S additions of 0–5000 ppm to a 51% CH4/49% CO2 plasma, with growth carried out for two different substrate temperatures (620 and 900 °C). Film morphology, growth rate and quality are all observed to deteriorate with increased H2S addition, as investigated by scanning electron microscopy (SEM) and laser Raman spectroscopy (LRS). H2S addition also appears to alter the resistivity of films, as measured by the four-point probe method, however X-ray photoelectron spectroscopy (XPS) revealed little incorporation of sulfur. The plasma chemistry leading to film deposition has been investigated using optical emission spectroscopy (OES), in which H2S addition leads to a reduction in C2H and CH intensities. Molecular beam mass spectrometry (MBMS) measurements have detected a build-up in CS, CS2, SO and SO2 concentrations with addition of H2S. Experimental results have been compared to CHEMKIN simulations of plasma chemistry and S-incorporation within the diamond lattice.

I. Introduction

The many extreme physical and mechanical properties1,2 of thin diamond films grown by chemical vapour deposition (CVD) have prompted interest in such films for use in electronic devices. CVD diamond films exhibiting p-type semiconductor properties are routinely grown by addition of B-containing gases to the standard CVD gas mixture (1% CH4/H2).3,4 However, obtaining n-type semiconducting diamond films by CVD has proved more challenging, mainly due to the fact that potential donor atoms (e.g. N, P, O and As) are larger than carbon, discouraging incorporation into the diamond lattice. However, n-type conductivity has been reported by the method of sulfur ion implantation into CVD homoepitaxial diamond (100) films.5 Furthermore, Sakaguchi et al.5–8 have reported that H2S addition to a 1% CH4/H2 gas mixture during microwave plasma enhanced CVD (MPCVD) leads to the growth of semiconducting, homoepitaxial diamond films exhibiting n-type behaviour. Film growth rates were observed to decline with increased H2S addition, however the quality of the films (as assessed via Raman spectroscopy) was found to be comparatively insensitive to changes in H2S addition. Relatively high Hall mobilities (597 cm2 V−1 s−1) were measured8 for films produced using H2S doping levels of 50–100 ppm. Subsequent re-analysis of these samples5 has raised some uncertainties with these results, however.

Experimental measurements of gas phase species concentrations present during the growth of sulfur doped CVD diamond films from H2S have been reported by both our group9–11 and others.12 In the work of Sternschulte et al.,12 gas was sampled via a glass capillary tube at a point downstream from the microwave (MW) plasma, and was analysed by a quadrupole mass spectrometer. They showed that H2S addition to a 1% CH4/H2 MW plasma caused a decrease in CH4 concentrations leading to a decrease in diamond film growth rate, with the conclusion being that CH4 and H2S were reacting in the gas phase to form CS.

Studies within our own group10,11 used molecular beam mass spectrometry (MBMS) to sample gas directly from the plasma, thus probing the gas phase chemistry with minimum perturbation from gas-surface reactions. We have used this powerful technique previously to obtain absolute mole fractions of the gas phase species present in both hot filament13–16 and microwave systems10,17,18 for a variety of gas mixtures and dopant gas additions. Our conclusions from measurements made of H2S/1% CH4/H2 MW plasmas were in good agreement with those of Sternschulte et al.,12 and led us to propose a mechanism, based on the overall Reaction 1, for the coupling of C and S-containing species in the gas phase to form CS and CS2. This proposal was supported by simple thermodynamic arguments, while CS was suggested as a possible species responsible for S incorporation within the diamond lattice.

\[
\text{CH}_4 + 2\text{H}_2\text{S} \rightarrow \text{CS}_2 + 4\text{H}_2 \quad \text{(Reaction 1)}
\]

Computer simulations of the gas phase chemistry of H/C/S containing CVD gas mixtures have been carried out by Barber and Yarborough.19 They concluded that addition of CS2 to the 1% CH4/H2 mixture caused a reduction in the gas phase concentration of hydrocarbons, leading (in conjunction with other proposed mechanisms) to the reduction in diamond film growth rates observed experimentally. Dandy20 presented equilibrium calculations for H2S/CH4/H2 gas mixtures and concluded that sulfur incorporation into the diamond lattice in such systems was via the SH radical. However, both of these studies were confined to equilibrium thermodynamic calculations, with the kinetics relevant to a CVD environment neglected. Our proposed S–C coupling mechanism (i.e. Reaction 1) has been validated by comparing the results of SEN-KIN kinetics calculations to previously published MBMS experimental measurements of species mole fractions, for H2S/1% CH4/H2 gas mixtures.19
Sternschulte et al have suggested that a substrate temperature, $T_{\text{sub}}$, lower than that used during standard diamond CVD (900°C), may influence the growth of S-doped diamond films.\(^1\) Gas mixtures in the region of 50% CH$_4$/50% CO$_2$ have been shown to enable diamond growth at significantly lower temperatures than those required by the orthodox 1% CH$_4$/H$_2$ gas mixture.\(^2\)-\(^4\) No previous studies have investigated the effect of H$_2$S addition to a 5% CH$_4$/49% CO$_2$ gas mixture at various $T_{\text{sub}}$, from the perspective of either the deposited films or the gas phase chemistry. Here, we present such a study for additions of 0–5000 ppm H$_2$S, with deposition carried out at $T_{\text{sub}} = 900$ and 620°C. Experimental MBMS measurements of plasma species are also compared with SENKIN predicted species mole fractions.

II. Experimental

(a) Growth experiments

Diamond deposition was performed using a 1.5 kW ASTEx-style 2.45 GHz microwave plasma CVD reactor.\(^1\) The double-walled chamber was water cooled and contained a water-cooled Mo substrate holder. Experiments were carried out at two substrate temperatures, $T_{\text{sub}}$, 620 and 900°C. For the 900°C experiments, the Mo substrate holder was covered using a blank Si wafer, since it has been reported that Mo at such high temperatures possibly acts as a sink for gas phase S species, scavenging them and reacting to form solid MoS$_2$.\(^2\) Substrates were placed on an alumina plate on top of this Si cover wafer, and were thus elevated about 1 mm into the plasma, enabling automatic heating of the substrate to ~900°C (as measured by a two color optical pyrometer, emissivity setting = 1.0). Such substrate mounting was used in previous work using H$_2$S/1% CH$_4$/H$_2$ gas mixtures,\(^5\) thus enabling direct comparisons of results obtained using both this, and the CH$_4$/CO$_2$ gas mixture used in the present work. Experiments using the lower substrate temperature were carried out with the substrate placed directly on the Mo substrate holder, thus allowing $T_{\text{sub}}$ to be maintained at 620°C using a substrate holder cooling system as reported previously.\(^6\) The surface of the substrate holder not covered by the substrate was covered with Si wafers to prevent possible scavenging of sulfur as described above.

Films were deposited on undoped single crystal (100) silicon wafers (resistivity ~2.3 x 10$^{12}$ Ω cm), and had been manually pre-abraded with 1–3 μm diamond grit. The duration of deposition was 8 h at a pressure of 40 Torr with 1 kW applied microwave power. The feedstock gases used were CH$_4$ (99.999% purity), CO$_2$ (99.99% purity) and H$_2$S (99.5% purity). To obtain gas phase H$_2$S levels below 1000 ppm, a cylinder of 1% H$_2$S in CH$_4$ was employed, and further diluted by use of appropriate flow rate ratios regulated by mass flow controllers. Total gas flow was maintained at 100 sccm. At the conclusion of deposition the plasma was switched off, H$_2$S and CH$_4$ flows were shut off, and the substrate was cooled in a CO$_2$ atmosphere.

Films were examined by scanning electron microscopy (SEM, JEOL 5600LV instrument) to determine crystal morphology and thickness, and by 514.5 nm (Ar+) laser Raman spectroscopy (LRS, Renishaw system 2000) to assess film quality. Film growth rates were calculated by dividing the SEM measured cross-sectional thickness by the deposition time of 8 h. Raman spectra were fitted using the Grams/32 computer program.\(^2\) The procedure used a quadratic function to fit the underlying spectral background and Gaussian lineshapes to fit to the bands. The film quality, i.e. diamond content, was investigated by calculating a quality factor, $Q$. This is defined in terms of the integrated area of the diamond line, $A_D$, and the combined integrated areas of all the non-diamond Raman bands, $A_a$. If it is assumed that these non-diamond components are all amorphous carbon (which has a reported Raman cross section ~233 times larger than diamond at 514 nm), then $Q$ can be defined as a percentage\(^2\) as shown below:

$$Q = \frac{A_D}{A_D + (A_a/233)} \times 100$$  \((1)\)

Sulfur content was investigated by X-ray photoelectron spectroscopy using Mg K$_\alpha$ excitation. Charging of insulating films was minimised by use of an electron flood gun, and any remaining charging effects were counteracted by offsetting the energy scale with respect to the known values for carbon peaks. The absolute values for the sulfur content (i.e. S:C ratio) of the films were calculated by comparison of the areas of selected S peak(s) and C peak(s), following calibration using the sensitivity factors\(^2\) appropriate for each element.

The resistivity of the films was determined by four-point probe\(^2\) measurements. Being a technique that relies upon surface contacts, this will measure the surface conductivity of diamond, rather than the conductivity through the bulk. Care was therefore taken to ensure that the surface properties of each of the diamond samples were treated identically both during and after deposition.

(b) Optical emission spectroscopy

Optical emission spectra were obtained using an Oriel Insta-Spec IV spectrometer to disperse emission from the plasma after exiting through a quartz view port, focusing and passage through a quartz fibre-optic bundle. Light was sampled from the center of the plasma ball with a spatial resolution of ~3 mm, and a spectral resolution ~0.9 nm, over the wavelength range of 200–520 nm.

(c) Molecular beam mass spectrometry. A full description of the MBMS system and gas sampling technique has been published previously,\(^1\) but a brief outline will be given here. A two stage differential pumping system was used to sample gas (at 20 Torr) from the side of the microwave plasma ball via an orifice (~100 μm diameter) in a sampling cone. Although such an intrusive method is bound to perturb the plasma, the fact that the position of the plasma ball and the reflected microwave power level are insensitive to the presence of the probe, suggests that this perturbation is minimal. However, the presence of the probe does reduce the size of the plasma ball at pressures above 20 Torr, thus making measurements at the growth pressure of 40 Torr unreliable. Therefore MBMS measurements were carried out at the lower pressure of 40 Torr. Gas passing through this orifice experienced a pressure differential (20 – 10$^{-3}$ Torr) and underwent adiabatic expansion, forming a molecular beam in which chemical reactions were effectively frozen out. The molecular beam then passed through a collimating skimmer into a quadrupole mass spectrometer (Hiden Analytical) maintained at ~10$^{-6}$ Torr, whereupon gas phase species were ionized by electron impact.

The electron ionisation energy is user-selectable in the range 4–70 eV. The electron ioniser energies used to detect each species were: CH$_4$, CO, C$_2$H$_2$, SO and SO$_2$ 16.0 eV, C$_2$H$_4$ 13.2 eV (to minimise contributions to the m/z = 26 signal due to the cracking of C$_2$H$_4$ occurring above 13.5 eV), H$_2$S 13.2 eV, CS$_2$ 13.6 eV (to minimise signal from CO$_2$ occurring above 13.8 eV), CH$_3$ 13.6 eV (to reduce signal from cracking of CH$_4$ above 14.3 eV), S$_2$ 12.0 eV (to minimise contributions to the m/z = 64 signal due to ionisation of SO$_2$ occurring above 12.35 eV) and S 13.2 eV (to reduce cracking of S$_2$ and CS$_2$ which occurs above 14.0 eV).

As stated previously,\(^2\) it has proved impossible to convert the counts measured by the MBMS into absolute mole fractions when using CH$_4$/CO$_2$ plasmas. In order to obtain such
a calibration, information is required about: (i) the thermal diffusion coefficients for species of different masses within the plasma bulk; (ii) the relative transmission efficiency of the sampling orifice for heavy and light particles; and (iii) the detector sensitivity factors for different species. Although estimates for some of these data can be obtained, we lack sufficient information about all of the important species to make conversion of counts into absolute mole fractions reliable. Therefore, no correction has been attempted for these effects, which may result in the experiment being more sensitive to lighter species (e.g. CH₄) than heavier species (e.g. CS₂).

As a consequence of the experimental considerations made above, no quantitative comparisons of species counts will be made, and the quoted magnitude of signal counts should be treated with caution. Instead, this work will concentrate on comparisons of the trends observed in measured species counts over the range of plasma gas mixtures investigated.

(d) Computer simulation. Computer simulations of the gas phase reactions occurring in the microwave plasma were carried out using the SENKIN code, which is part of the CHEMKIN package. All of the C, H and O containing species reactions and temperature dependent rate constants used in these calculations were obtained from the GRI-Mech 3.0 reaction mechanism database, as used for previous studies of H/C/O gas mixtures. Information regarding reactions involving C, H and S containing species was obtained from the literature, with rate data for analogous O containing species reactions used when none for S were available. A more detailed description of the H/C/S reaction mechanism, its implementation and validation, is presented elsewhere. The remaining H, C and O containing species reactions were obtained from the Leeds University combined methane and SO₂ combustion mechanism, which, although being the least reliable aspect of the reaction mechanism used during the present SENKIN simulations, has been tested against a wide variety of data.

Mole fractions of the 53 gas phase species (H₂, H, CH₄, CH₂, CH₃, CH₂, CH₃, OH, H₂O, CO, CO₂, CH₂O, CH₃OH, CH₂O, CH₄, CH₂, OH, CH₃CO, CH₂HCO, C, HCO, HCCO, HCOH, Si₂, S, SH, H₂S, H₂S₂, H₂SO, SO₂, SO₃, HSO, HSO₂, HSO₃, HOSO₂, CS, CS₂, COS, HOSHO, CH₃SH, CH₃S, CH₂S and HCS) involved in this reaction scheme were calculated, for a chosen input gas mixture (e.g. 1% H₂S/51% CH₄/49% CO₂), at a fixed gas temperature, Tgas, and pressure (20 Torr). Limitations inherent in this approach include:

1. The adoption of a single temperature, e.g. 2000 K, which is considered to be representative of the gas temperature of a 51% CH₄/49% CO₂ plasma in low power (<3 kW) microwave CVD chambers at ~20 Torr, within the region from which gas was sampled during MBMS measurements.

2. The neglect of any electron impact dissociation, ionic reactions or surface chemistry. The modelling assumes that reaction is initiated solely by thermal dissociation.

3. Transport into and out of the reaction volume neglected also. To mimic experiment, therefore, it is necessary to run the simulation for a finite (user selected) time, t. The calculations reported here employ t = 5 s. This time was previously found to give the best agreement with MBMS measured trends in CO₂/CH₄ plasma species counts.

Calculations were run repeatedly in order to determine plots of species mole fraction as functions of gas mixing ratio.

III. Results and discussion

(a) Film growth

Fig. 1 presents SEM images of diamond films grown at substrate temperatures of (a)–(c) 620 °C and (d)–(f) 900 °C, at various H₂S additions. The film grown at the lower Tsub, using an H₂S addition of 100 ppm (Fig. 1(a)) exhibits a continuous coating of predominantly triangular facets ~5 μm in size. Increasing H₂S input levels to 2000 ppm decreases the facet size to <2.5 μm (Fig. 1(b)), while 5000 ppm H₂S additions produce a film primarily composed of small (<1 μm) facets (Fig. 1(c)) with the occasional larger crystallite. In contrast, there is little change in the surface morphology of films grown at Tsub = 900 °C for H₂S additions of 100, 2000 and 5000 ppm, as illustrated by Figs. 1(d), (e) and (f), respectively. Here, all three films are continuous and display crystalline facets ~5 μm in size.

Fig. 2 shows that the growth rates of films grown at Tsub = 900 °C are approximately one order of magnitude greater than those grown at Tsub = 620 °C. As a consequence of the experimental considerations made above, no quantitative comparisons of species counts will be made, and the quoted magnitude of signal counts should be treated with caution. Instead, this work will concentrate on comparisons of the trends observed in measured species counts over the range of plasma gas mixtures investigated.
additional peaks may correspond with nanoscale sp\textsuperscript{3} phases of 5000 ppm at (a) 620°C, resulting from the small sized crystallites grown at this low T (sub).

51% CH\textsubscript{4}/49% CO\textsubscript{2} gas mixtures for (a) line, two Gaussian peaks centered at C24 and (b). Both spectra can be fitted using a quadratic base line shape curve fits. Fig. 3(c) presents a plot of the diamond film quality factor, Q, vs. H\textsubscript{2}S addition (Q having been defined in eqn. (1)). Key: (■) T\textsubscript{sub} = 620°C, (○) T\textsubscript{sub} = 900°C, with other process conditions as for Fig. 1. The lines are linear least squares fits to the two data sets (as labeled).

Fig. 3 Laser Raman spectra of films deposited using 5000 ppm H\textsubscript{2}S/51% CH\textsubscript{4}/49% CO\textsubscript{2} gas mixtures for (a) T\textsubscript{sub} = 620°C and (b) T\textsubscript{sub} = 900°C. Each spectrum includes a fitted baseline and Gaussian line shape curve fits. Fig. 3(c) presents a plot of the diamond film quality factor, Q, vs. H\textsubscript{2}S addition (Q having been defined in eqn. (1)). Key: (■) T\textsubscript{sub} = 620°C, (○) T\textsubscript{sub} = 900°C, with other process conditions as for Fig. 1. The lines are linear least squares fits to the two data sets (as labeled).

greater than for those grown at 620°C. However, despite this difference, the observed growth rate trend, i.e. a fall of ∼66% when H\textsubscript{2}S addition is increased from 0 to 5000 ppm, is similar for both temperatures.

Raman spectra of diamond films grown at an H\textsubscript{2}S addition of 5000 ppm at (a) 620°C and (b) 900°C are presented in Figs. 3(a) and (b). Both spectra can be fitted using a quadratic base line, two Gaussian peaks centered at ∼1332 cm\textsuperscript{-1} (sharp diamond Raman line and a broader D band), a peak at ∼1530 cm\textsuperscript{-1} (the G band) and a broad band at ∼1450 cm\textsuperscript{-1} (polyacetylene\textsuperscript{37} or a diamond precursor\textsuperscript{38}). However, a number of additional features are evident in the spectrum of the sample grown at the lower T\textsubscript{sub}, including the presence of peaks at ∼1172 cm\textsuperscript{-1} (nanofase diamond\textsuperscript{39} or polyacetylene present in grain boundaries\textsuperscript{40}) and 876, 967 and 1088 cm\textsuperscript{-1}. These additional peaks may correspond with nanoscale sp\textsuperscript{3} phases resulting from the small sized crystallites grown at this low T\textsubscript{sub}.

In order to gain a measure of film quality (i.e. the ratio of sp\textsuperscript{3}:sp\textsuperscript{2} carbon bonding) the quality factor, Q (as defined in eqn. (1)) is presented in Fig. 3(c). Somewhat surprisingly, Q for films grown at the lower T\textsubscript{sub} is generally slightly higher than those deposited at 900°C. In both cases there is a slight fall in film quality with increased H\textsubscript{2}S addition for both sets of data.

XPS analysis has afforded S/C ratios of high temperature films grown with input gas mixture H\textsubscript{2}S concentrations of 3500 ppm (S/C ∼0.07%) and 5000 ppm (S/C ∼0.08%). We note that XPS yields an average signal over the whole area of the substrate (1 cm\textsuperscript{2}), and so the position of the S (i.e. grain boundaries versus crystallites) cannot be determined. S/C ratios for all other deposited films were below the detection limit of the apparatus (∼0.05%). It should be noted that these measured film S/C ratios are generally an order of magnitude lower than that of the input gas mixture (e.g. input S/C ratio = 0.5% in the case of an H\textsubscript{2}S addition level of 5000 ppm).

There is a general fall in resistivities with increased H\textsubscript{2}S addition, for the films grown at both high and low T\textsubscript{sub} (Fig. 4). The scatter seen for samples grown with low H\textsubscript{2}S additions and at high T\textsubscript{sub} is due to the measurements being made at the limit of the apparatus capabilities. There is also a large offset of ∼3 orders of magnitude between resistivity measurements of high and low T\textsubscript{sub} grown films. Apart from this offset, the trend in film resistivities for H\textsubscript{2}S additions over 1000 ppm is similar for both datasets. Both show a ∼100-fold reduction in resistivity when H\textsubscript{2}S additions are increased from 1000 to 5000 ppm.

(b) Optical emission spectroscopy

An optical emission spectrum of a 1% H\textsubscript{2}S/51% CH\textsubscript{4}/49% CO\textsubscript{2} MW plasma is presented in Fig. 5(a). Emissions due to C\textsubscript{2} Swan bands are clearly present at ∼470, 516 and 860 nm. Also evident are emissions of the 3rd Positive and 5B bands (260–370 nm) and Angstrom bands (451, 484, 520 and 561 nm) of CO. Emissions due to CH (431 nm) and H (483 nm) are also seen. Emission spectra taken of plasmas containing 0% and 1% H\textsubscript{2}S were almost identical. Therefore, six emission wavelengths were chosen and their relative intensities were plotted vs. H\textsubscript{2}S addition, as presented in Fig. 5(b). It is clear that the intensities of the CO and H emission features stay relatively constant or even increase slightly over the range of H\textsubscript{2}S additions, while those of C\textsubscript{2} and CH are seen to reduce by ∼18 and 20%, respectively, over the same range. This suggests that increased H\textsubscript{2}S addition to the 51% CH\textsubscript{4}/49% CO\textsubscript{2} gas mixture causes a reduction in hydrocarbon concentrations.

(c) Computer simulation and MBMS.

Fig. 6 shows combined plots of MBMS measured species counts and SENKIN predicted species mole fractions, against added H\textsubscript{2}S. The respective vertical scales in each plot have been arranged so as to aid comparison. The plots of C\textsubscript{2}H\textsubscript{2}, CH\textsubscript{4} and CH\textsubscript{3} show good agreement between the measured and predicted species trends, with H\textsubscript{2}S addition resulting in a decrease in species

Fig. 4 Four point probe resistivity vs. H\textsubscript{2}S addition for films deposited using H\textsubscript{2}S/51% CH\textsubscript{4}/49% CO\textsubscript{2} gas mixtures. Key: (■) T\textsubscript{sub} = 620°C, (○) T\textsubscript{sub} = 900°C, with other process conditions as for Fig. 1.
mole fraction and measured counts. Similarly, experiment and simulation are in agreement in the case of H$_2$S, CS and C$_2$S, with species mole fraction and measured counts increasing upon increased H$_2$S addition. There is, again, good agreement between MBMS and SENKIN results in the case of SO. However, the predicted mole fraction, $X$, of SO is $\sim 10^{-7}$, which is $\sim 100$ times below the estimated detection limit of the MBMS apparatus. This suggests that SO is present within the microwave plasma at concentrations much greater than predicted by SENKIN. A similar conclusion can be drawn from the SENKIN and MBMS results for SO$_2$. Here, the scatter in SO$_2$ measured species counts data suggests SO$_2$ concentrations are near the MBMS detection limit ($X \sim 10^{-5}$), whereas the predicted SO$_2$ mole fractions are below this, i.e. $\sim 10^{-11}$. On the other hand, the MBMS measured counts of S and S$_2$ appear to be at or below the MBMS detection limit, suggesting that the predicted mole fractions of S ($\sim 10^{-7}$) and S$_2$ ($\sim 10^{-7}$) may be overestimates.

IV. Discussion

H$_2$S addition to 51% CH$_4$/49% CO$_2$ MW plasmas during diamond CVD is seen to have a considerable impact upon the growth rates, quality and resistivities of the resulting films. S addition also induces changes in film morphology, particularly in the case of low temperature deposition, e.g. $T_{\text{sub}} = 620$ °C. Reduction of $T_{\text{sub}}$ from 900 to 620 °C results in a ~10-fold drop in film growth rate. Such reduction in growth rates upon lowering of $T_{\text{sub}}$ is consistent with previous observations, but the increased substrate-plasma separation used during low $T_{\text{sub}}$ deposition in the present studies may also contribute to the observed variation. However, the fact that we observe very similar downward trends in film growth rate for increased H$_2$S additions at both deposition temperatures suggests that the trend is primarily due to gas phase reaction instigated by H$_2$S, rather than gas–surface interactions.

A large offset was observed between the measured film resistivities of samples grown at high (900 °C) and low (620 °C) $T_{\text{sub}}$. We suggest that the lower resistivity of the low temperature grown samples is probably due to H-induced surface conduction. This effect is reported to be annealed out of films at temperatures above ~700 °C in vacuum and ~190 °C in air. The resistivity of such annealed films is several orders of magnitude greater than the H-terminated samples, pre-annealing. We therefore suspect that the growing diamond surface is (at least partially) H-terminated at $T_{\text{sub}} = 900$ °C. However, at the end of a deposition run the plasma is shut off and the film is left to cool down in a 100% CO$_2$ atmosphere. During cooling from 900–700 °C, we envisage that the H-induced surface conductivity is annealed out, thereby resulting in the highly resistive film observed. $T_{\text{sub}} = 620$ °C is below the temperature for such annealing. In this scenario, therefore, films grown at this lower substrate temperature would retain their H-induced surface conductivity intact when cooled in a CO$_2$ atmosphere. Previously films have been deposited at $T_{\text{sub}} = 900$ °C using a MW reactor (identical to that used in the present study) and H$_2$S/1% CH$_3$/H$_2$ gas mixtures. After growth, these films were cooled in a H$_2$ atmosphere and the measured film resistivities were comparable with those obtained for the low temperature deposited films in the present work. This observation lends further credence to the scenario outlined above.

Increased H$_2$S additions (>1000 ppm) appear to cause a reduction in film resistivities, regardless of $T_{\text{sub}}$. It is important to note that the reduction in film resistivities observed between high $T_{\text{sub}}$ grown films with 0 and 5000 ppm H$_2$S additions is much greater than the ~3-fold reduction seen for H$_2$S doping of 1% CH$_3$/H$_2$ gas mixtures (~3 times reduction), using similar process conditions. However, it remains unclear whether this reduction is a result of S-incorporation into the diamond films or due to an increase in graphitic phases within the film (as indicated by a parallel reduction in the quality factor). OES measurements of C$_2$ and CH emission features suggest that increased H$_2$S additions caused a drop in gas phase hydrocarbon concentrations. This conclusion is reinforced by the observed trends in MBMS measured counts and SENKIN predicted mole fractions for C$_2$H$_2$, CH$_4$, and CH$_3$. The methyl radical is generally believed to be the major diamond growth precursor in most low pressure CVD reactors. Therefore, it seems reasonable to associate the measured drop in CH$_3$ MBMS counts with the observed drop in film growth rates upon increased H$_2$S addition.

A reaction scheme for the chemistry of H$_2$S addition to 51% CH$_4$/49% CO$_2$ gas mixtures is presented in Table 1. It should be noted that all except Reaction 4 are composite conversions composed of many elementary reactions. Reaction 1 is the dominant reaction involving S containing species. This is shown by the large SENKIN predicted mole fractions and MBMS measured counts of CS$_2$ and CS. Previous investigations of 50% CH$_4$/50% CO$_2$ gas mixtures concluded that the majority of the input carbon is transformed to CO via Reaction 2. Any excess CH$_4$ not destroyed by this reaction is able to undergo further conversions to produce CH$_2$ and CH$_3$, via Reactions 3 and 4, respectively. However, Reaction 1 is able to compete with these reactions, with the result that increased H$_2$S additions leading to a reduction in the CH$_4$ available for production of CH$_2$, CH$_3$ and H$_2$O. This is analogous to the situation seen for H$_2$S addition to 1% CH$_3$/H$_2$. 

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Fig. 5 Plot of (a) optical emission spectrum of a 1% H$_2$S/51% CH$_4$/49% CO$_2$ MW plasma and (b) peak intensity vs. H$_2$S addition to a 51% CH$_4$/49% CO$_2$ gas mixture. Emission features are as labeled and percentages given indicate the drop in intensity of the indicated feature over the range of H$_2$S addition shown. Conditions: applied microwave power 1 kW, pressure 40 Torr.
Fig. 6  Plots of MBMS measured species counts (right hand scale) and SENKIN predicted species mole fractions (left hand scale) vs. H$_2$S addition to a 51% CH$_4$/49% CO$_2$ gas mixture, for the following species: (i) C$_2$H$_2$; (ii) CH$_4$; (iii) CH$_3$; (iv) H$_2$S; (v) CS; (vi) CS$_2$; (vii) SO; (viii) SO$_2$; (ix) S and (x) S$_2$. Conditions are as given in Fig. 2, except that the pressure was reduced to 20 Torr to improve plasma stability in the presence of the sampling probe. SENKIN computer simulation results are for a H$_2$S/51% CH$_4$/49% CO$_2$ gas mixture at a temperature of 2000 K and a pressure of 20 Torr. Key: ○ MBMS species counts, (●) SENKIN computer simulation mole fractions. The two data sets in each panel have been vertically scaled to illustrate the degree of consistency between the experimental and modeled trends.
Table 1 Proposed reaction scheme for the gas phase chemistry of H2S/51% CH4/49% CO2 diamond CVD gas mixtures at 2000 K and ~20 Torr. ΔG_{eq} values were calculated using species Gibbs free energies of formation obtained from ref. 48 and were also used to calculate reaction equilibrium constants, K_{eq}.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>ΔG_{eq}/kJ mol^{-1}</th>
<th>K_{eq}</th>
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<tbody>
<tr>
<td>1 CH4 + 2H2S ≡ CS2 + 4H2</td>
<td>-172.1</td>
<td>3.124 × 10^6</td>
</tr>
<tr>
<td>2 CO2 + CH4 ≡ 2CO + 2H2</td>
<td>-306.0</td>
<td>1.014 × 10^1</td>
</tr>
<tr>
<td>3 2CH4 = C2H2 + 2H2</td>
<td>-144.4</td>
<td>5.916 × 10^3</td>
</tr>
<tr>
<td>4 CH4 + H ≡ CH3 + H2</td>
<td>-53.30</td>
<td>24.67</td>
</tr>
<tr>
<td>5 CO2 + H2 = CO + H2O</td>
<td>-25.00</td>
<td>5.477</td>
</tr>
<tr>
<td>6 CO2 + H2S = CO + H2 + SO</td>
<td>32.45</td>
<td>1.420 × 10^{-1}</td>
</tr>
<tr>
<td>7 H2O + H2S = SO + 2H2</td>
<td>60.74</td>
<td>2.592 × 10^{-2}</td>
</tr>
<tr>
<td>8 CO2 + SO = CO + SO2</td>
<td>-36.34</td>
<td>8.893</td>
</tr>
</tbody>
</table>

*a Reaction taken from ref. 10. b Reaction taken from ref. 21.

As stated above, the reduction in CH3 concentrations caused by increased H2S addition leads to a reduction in deposited film growth rates. In addition, we recall that there is a large (~2 mm) separation between the visible edge of the plasma and the substrate in the case of films grown at low T_{sub} grown films, whereas the growth surface of samples deposited at high T_{sub} are in direct contact with the visible edge of the plasma. The larger substrate–plasma separation for low T_{sub} grown films clearly causes a further reduction in the CH3 flux reaching the substrate surface, as a result of radical recombination reactions (e.g. involving CH3 and H radicals). Of greater significance, the reduced diffusion of species across the growing film surface at low T_{sub} is proposed as a reasonable predictor of the ability of a gas mixture to produce diamond films with high S-incorporation. The numbers present the S/C ratio (as measured by XPS) for films deposited at the H2S additions indicated. Key: (—) H2S/1% CH4/H2 gas mixture, (■) H2S/51% CH4/49% CO2 gas mixture (scaled up by a factor of 5).

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V. Conclusions

Diamond films have been grown from 51% CH4/49% CO2 gas mixtures, with H2S additions of up to 5000 ppm, and at substrate temperatures of 900 and 620 °C. The texture of films grown at the higher T_{sub} is seen to be independent of the level of H2S addition while the morphology of films deposited at the lower T_{sub} are greatly influenced by increased H2S additions. The growth rate, quality and resistivity of deposited films are all reduced by increased H2S additions. Gas phase experimental species number density measurements and companion SENKIN computer simulations allow construction of a plausible reaction scheme for the chemistry of H2S/51% CH4/49% CO2 gas mixtures.

Acknowledgements
References