

GAS PHASE DIAGNOSTICS FOR CVD DIAMOND GROWTH FROM $\text{CCl}_4/\text{H}_2/\text{O}_2$ MIXTURES

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ABSTRACT

Optical emission spectroscopy (OES) and exhaust gas mass spectrometry (MS) were used in a microwave plasma assisted chemical vapour deposition (MWPACVD) reactor. The dissociation mechanism of CCl_4 associated with O_2 addition in the gas phase for diamond growth have been analysed. OES was used to observe the H_α line intensity as a function of CCl_4 and O_2 concentration in the feed gas. The results have shown an increase of atomic hydrogen concentration over 200% for addition of 3% CCl_4 . It was also observed an additional increase in the H generation when O_2 is added in the H_2/CCl_4 mixtures. The films grown in different concentrations of CCl_4 and O_2 were analysed by scanning electron microscopy and Raman spectroscopy.

1. INTRODUCTION

The use of halogens in the regular mixtures for CVD diamond growth has demonstrated as a novel method of producing atomic hydrogen. Diagnostic techniques such as optical emission spectroscopy (OES) and mass spectrometry (MS) are very important for the gas phase study. OES is one of the simplest and most effective methods, inexpensive and nonintrusive for studying plasma chemical process in a gas volume. MS permits to analyse the stable species formed in the reactor for different mixtures. The control of these species may be connected with good quality diamond growth and may play important roles in the study of gas-surface process.

Diamond growth from mixtures with O_2 addition or halogenated precursor have been studied by many authors [1-7]. Harris and Weiner [8,9] have studied the O_2 addition in H_2/CH_4 mixtures by mass spectrometry. The O_2 addition reduces the hydrocarbon mole fractions with conversion into mainly CO and H_2O . They have concluded that the more important oxygen effect is reduce the effective concentration of carbon with CO formation. In addition, the OH radicals formed in the gas phase helps to remove non-diamond carbon on the growth surface. Bachmann et al. [10] have studied the ternary diagrams using C/H/Cl- gas mixtures for CVD diamond growth. They concluded that high chlorine

concentrations seem to foster the deposition of non-diamond carbon phases. They have shown that in the C-H-Cl system the diamond growth domain is determined by the limits of this carbon solubility, that is restrict to carbon percentage lower than 0.5 vol %.

Recently we have shown some aspects of halogen addition in the gas phase. Corat et al. [4] have proposed that CF_4 addition in a hot filament reactor may create excess atomic hydrogen. Mendes de Barros et al. [11] have extended this study to CCl_4/H_2 mixtures in this same reactor. Ferreira et al. [12,13] have effectively identified by actinometry technique an expressive increase of atomic hydrogen concentration in microwave plasma CVD (MWPACVD) for halogenated mixtures.

In this work we continue the study of atomic hydrogen increase with the use of halogen based mixtures. In particular, we study the effect of oxygen addition to CCl_4 gas mixtures. We use actinometry of the H_α line to evaluate the relative atomic hydrogen concentration and mass spectrometry to analyse the stable species formed in the reactor. We confirmed the increase of apparent H atom concentration in the halogenated mixtures and observed an additional increase of 100% with O_2 addition for mixtures of 1% CCl_4 . Mass spectrometry shows that CCl_4 is completely dissociated with the halogen atoms entirely converted into HCl, and the carbon atoms divided among hydrocarbons and, mainly, CO. Our study also shows the possibility of growing diamond films with high concentration of CCl_4 when O_2 is present in the regular mixtures. The O_2 addition reduces the hydrocarbon mole fractions with conversion into mainly CO and H_2O . Due to its high stability CO works as a trap of carbon, increasing the carbon solubility in the gas phase.

2. EXPERIMENTAL

Experimental details of the deposition system were given in a previous paper [12]. MWPACVD reactor consists of 700 W magnetron at 2.45 GHz and was used associated with four mass flow meters so that the total rate of flow of feed gas was around 100 sccm. The CCl_4 and O_2 concentrations ranged from 0 to 3% in volume. The gas feed apparatus is formed of two hydrogen lines. Part of the

hydrogen flux was derived to pass through a bubbler containing the CCl_4 . The CCl_4 content in the gas mixtures was varied by controlling the flow rates of both hydrogen lines, the pressure and temperature in the bubbler. The correct concentration of CCl_4 in the feed gas was measured by mass spectrometry. A small flow of argon (3 sccm) was added to act as an actinometer. The experiments were carried out in 7.0×10^3 Pa in the substrate temperature of 1000 K. The system used for optical emission measurements consists of a monochromator (HRS type Jobin Yvon) and a photomultiplier (60R type RCA). Relative concentrations of atomic hydrogen were recorded as the ratio of the Balmer line H_α (656.3 nm) to the Ar 750.4 nm line. The (100) silicon wafer was polished in ultrasonic bath of 0.25 μm diamond powder dissolved in hexane medium and cleaned by acetone. The measurements of the exhaust gas were made using a quadrupole mass spectrometer (Balzers QMG model 421 C). Raman spectra were recorded using a Renishaw microscopic system 2000 and the film structure were analysed by scanning electron microscopy.

3. RESULTS AND DISCUSSION

3.1. OES and MS

A complete series of OES experiments were made to study the effect of halogenated mixtures, such as $\text{H}_2/\text{Ar}/\text{CCl}_4$ and $\text{H}_2/\text{Ar}/\text{CCl}_4/\text{O}_2$, in the generation of atomic hydrogen in our plasma reactor. Results with CCl_4 addition are shown in Fig. 1a. For these mixtures the increase of atomic hydrogen generation is much higher than the increase observed for CF_4 and CCl_2F_2 mixtures for the same system in previous works [12]. This increase is also much higher than observed by Mucha et al. [14] for the addition of O_2 in $\text{H}_2/\text{Ar}/\text{CH}_4$ mixture.

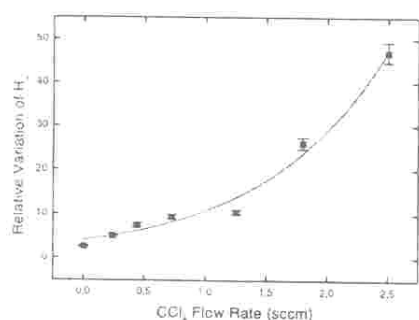


Fig. 1a. Relative variation of H_α as a function of CCl_4 concentration. The line is only a guide for the eyes.

Experiments made for $\text{H}_2/\text{Ar}/\text{CCl}_4$ mixtures with O_2 addition are shown in Fig. 1b. For 1% of CCl_4 in the feed gas we have observed in Fig. 1b an increase of around 100% in the atomic hydrogen concentration for the addition of 2% O_2 . Considering the result shown in Fig. 1a and similar results obtained for $\text{H}_2/\text{Ar}/\text{CF}_4$ and $\text{H}_2/\text{Ar}/\text{CCl}_2\text{F}_2$, we concluded that O_2 addition promoted an additional increase of H atom generation

for all halogenated mixtures studied. The bars error of around 5% is mainly attributed to the peak intensity measurements for the ratio evaluation H_α/Ar .

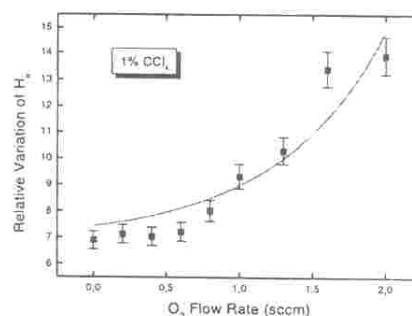


Fig. 1b. Relative variation of H_α as a function of O_2 concentrations. The line is only a guide for the eyes.

The mass spectrometry for mixtures with CCl_4 and O_2 additions are shown in Fig. 2a and Fig. 2b. The objective was to observe the difference on chemical paths in the reactor for the two mixtures studied. The measurements were normalised by hydrogen concentration and the results are shown as the relative concentration of the species studied. Fig. 2a presents the main species observed for H_2/Ar mixture with addition of 2% CCl_4 . The analysis has shown an increase of C_2H_2 and CH_4 concentration, indicating a mechanism of complete CCl_4 dissociation with a conversion into hydrocarbons and HCl , that is the main final reaction product formed in near stoichiometric proportions. Fig. 2b shows the results for O_2 addition in the mixtures with 1% CCl_4 . It was observed basically the formations of CO , HCl and H_2O . The hydrocarbon concentration reduces while CO concentration increases. As in the case of CH_4/H_2 , CF_4/H_2 and CCl_2F_2 mixtures, the extreme thermodynamic stability of CO at high temperatures accounts for its activity as a carbon trap product in this system and it is likely that the carbon involved in the formation of CO is not readily available for deposition.

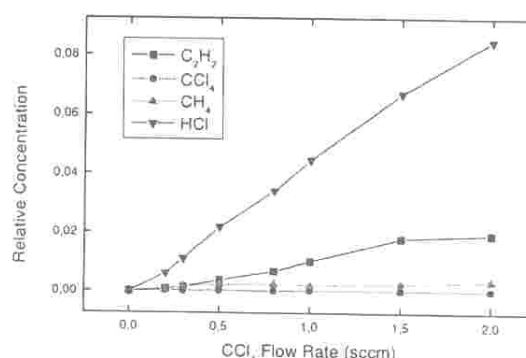


Fig. 2a. Exhaust gas content as a function of CCl_4 concentration.

For halogenated mixtures the presence of chlorine may promote large radical concentration in the gas phase. In the exhaust gas we observe that the halocarbons are

completely converted into hydrocarbons and HCl. The increase of the atomic hydrogen concentration is probably correlated with the relatively easy HCl dissociation by electron impact in the plasma reactor [15-17]. Considering that with 3% of the halocarbons we obtain a mixture with around 12% of acid, its dissociation becomes important in the process as a whole. For this reason, we consider that the high acid concentration and the lower threshold dissociation energies are responsible for the observed increase of atomic hydrogen concentration with the halocarbon mixtures.

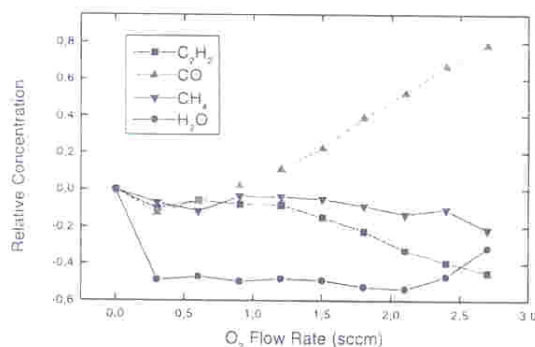


Fig. 2b. Exhaust gas content as a function of O₂ concentration.

The additional increase of atomic hydrogen with O₂ addition is also considerable, around 100% for CCl₄ mixture. This is an indication of the high reactivity in such plasmas, with the formation of more radical species in the medium. This behaviour is completely different from the observed with oxygen addition in CH₄/H₂ mixtures. The increase of atomic hydrogen concentration with O₂ addition observed by Mucha et al. [14] in CH₄/H₂ mixtures is only limited to relatively low oxygen concentrations.

The carbon solubility in the gas phase is normally considered a problem in halogen based reactors in which the formation of solid carbon is thermodynamically favoured [18]. With CCl₄/H₂ mixtures, for example, good quality diamond grows only for carbon contents under 1%. This is attributed to the low carbon solubility in this gas phase. The mass spectrometry in our experiments of oxygen addition to halocarbon/hydrogen mixtures shows that the CO formation actuates as a trap for carbon atoms, increasing the carbon solubility in the gas phase.

3.2. CVD diamond films from H₂-CCl₄-O₂ mixtures

CVD diamond films were grown at a pressure of 60 Torr and at deposition temperature between 700-800°C by microwave plasma system. The concentrations of CCl₄ and O₂ were chosen in order to obtain the appropriated results for the plasma reactor used. The films were analysed by Raman spectroscopy and scanning electron microscopy. Fig. 3 shows the Raman spectra for various films grown from different concentrations of CCl₄ and O₂ in the feed gas. The spectra (a) to (e) represent the following concentrations: 0.5 % CCl₄, 1.0 %

CCl₄, 1.0 % CCl₄ + 0.25 % O₂, 1.5 % CCl₄, and 1.5 % CCl₄ + 0.5 % O₂, respectively.

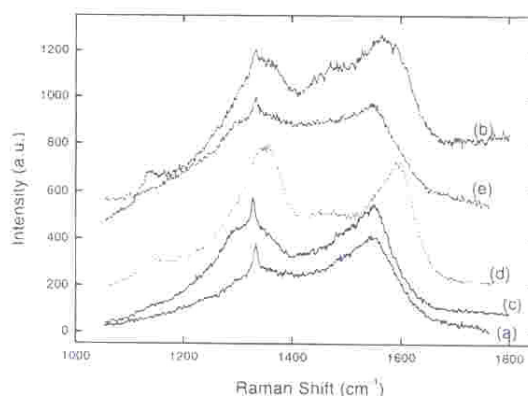


Fig. 3. Raman spectra obtained from diamond films deposited from H₂/CCl₄/O₂ gas mixtures with different concentrations of CCl₄ and O₂. (a) 0.5 % CCl₄, (b) 1.0 % CCl₄, (c) 1.0 % CCl₄ + 0.25 % O₂, (d) 1.5 % CCl₄, and (e) 1.5 % CCl₄ + 0.5 % O₂.

It was observed for all the films a broad structure located around 1480 cm⁻¹ that can be attributed to graphite (graphite G-peak at 1560 cm⁻¹) or to amorphous carbon. The sharp peak at 1332 cm⁻¹ indicates the presence of the diamond phase. This peak overlaps with a broader structure at the same energy attributed to microcrystalline graphite (graphite D-peak at 1360 cm⁻¹). For samples where the diamond peak were not well defined, such as the spectra (c) and (b), it was also detected a broader band around 1150 cm⁻¹. According to others authors [19,20] this peak is assigned to nanocrystalline diamond. This feature is present in films with small amounts of diamond crystalline domains indicating that it could be a precursor structure. The microcrystalline diamond could be traditional or a polytype in the wurtzite structure.

The Raman spectra show clearly that the presence of O₂ in the feed is fundamental to obtain diamond films for CCl₄ concentrations higher than 0.5 %. As can be observed in the spectrum (d) there was no diamond growth with 1.5 % CCl₄. This result agree with the discussion presented by Backmann [10] and Cassidy [18]. Consequently, the CO formation in the gas phase really actuates as a trap for carbon atoms, increasing the carbon solubility in the gas phase. The spectra (c) and (e) confirm the presence of diamond phase for films grown with concentrations of CCl₄ higher than 0.5 % when O₂ is present in the feed gas.

The morphology of the films identified by SEM micrographs are shown in Fig. 4. Fig. 4a represents the film grown with 1.5 % CCl₄ (curve (d) in the Raman spectra). It was observed low nucleation of ball-like particles and a very dark surface. Fig. 4b represents the film grown with 1 % CCl₄ + 0.25 % O₂ (curve (c) in the Raman spectra). This micrograph shows the deposits consisted of diamond crystal exhibiting crystalline planes associated with a higher nucleation than observed in micrograph of the Fig. 4a.

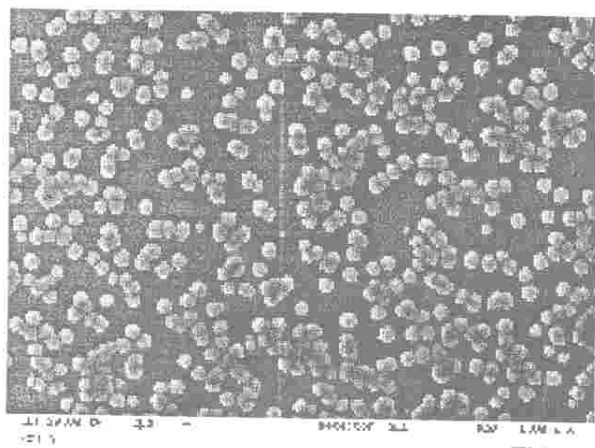


Fig. 4a. Scanning electron micrographs of the deposits on silicon substrate with 1.5 % CCl_4 .

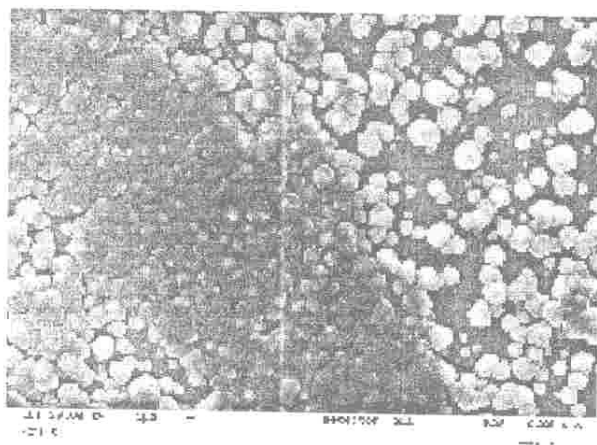


Fig. 4b. Scanning electron micrographs of the deposits on silicon substrate with 1 % CCl_4 + 0.25 % O_2 .

4. CONCLUSION

We have presented the effects of CCl_4 and O_2 addition in the gas mixtures for diamond growth in a microwave plasma-assisted chemical vapour deposition reactor. The atomic hydrogen generation was monitored by optical emission spectroscopy. Mass spectrometry was also used to analyse the stable species in the reactor.

It was evident that the gas chemistry in microwave plasma CVD are significantly influenced by O_2 addition. Due to the high thermodynamic stability of CO at high temperatures, the O_2 addition in such mixtures may inhibit the formation of solid carbon for higher concentrations of chlorine in the gas phase, with large radicals formation and HCl. OES have also shown an additional increase of 100% for the relative intensity of H_α line when O_2 is added in the range of 0 to 2% for mixture of 1% CCl_4 .

A gas mixture containing halocarbons, hydrogen and oxygen looks very promising for CVD diamond growth. The

large increase of atomic hydrogen concentration with the increase of halocarbon content in the feed gas may enable the growth at higher rates even for low power reactors. Besides, the oxygen addition increases the carbon solubility in the gas phase enabling the growth at high carbon content in the feed gas. Both aspects may contribute favourably for better conditions of growth. The first results analysed by scanning electron microscopy and Raman spectroscopy have shown the possibility to grow CVD diamond films from $\text{H}_2/\text{CCl}_4/\text{O}_2$ mixtures with high concentration of atomic hydrogen.

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