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SOME OBSERVATIONS ON THE CHEMICAL VAPOUR DEPOSITION OF DIAMOND FROM WATER-METHANOL MIXTURE

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ABSTRACT: The present paper presents some preliminary results concerning the chemical vapor deposition of diamond layers from methanol-water mixtures in an inductively coupled radio frequency discharge. The paper demonstrates that only appropriate methanol/water flow rate ratios can be used for deposition of polycrystalline diamond layers. Higher methanol concentration in the feed gas increases the amount of non-diamond phase in the layer. Scanning electron microscopy and Raman spectroscopy have been used to characterize the deposited layers. The paper also presents some brief observations on the behavior of the discharge.

KEY WORDS: diamond coatings, chemical vapor deposition (CVD)

1. INTRODUCTION

Potential applications of diamond films are numerous and the foreseen benefits of their applications are considerable. For these reasons, the research and development efforts in this field have been impressive. Since 1981, when first diamond particles were successfully produced by chemical vapor deposition (CVD) with an acceptable growth rate [1], the techniques used for deposition of diamond layers have diversified continuously. While the hot-filament assisted CVD [2,3] was the first and most extensively investigated process, oxy-acetylene torch [4] and plasma [5-8] based processes have also been used for studies and industrial applications of diamond coatings. In the majority of these cases, the precursor gases used for diamond deposition consisted in a mixture of a hydrocarbon (usually 1-2% methane) and hydrogen.

According to classical theory of diamond low pressure deposition [1,9,10], the precursor gases are activated either thermally or by plasma discharges to produce certain carbon containing radicals/molecules - from which diamond and other carbonaceous phases (e.g. graphite) are deposited simultaneously on a substrate heated to a temperature of 600 – 1000 °C – and atomic hydrogen. It is generally believed that methyl radical (CH_3) with sp^3 hybridized orbits, acetylene (C_2H_2) and atomic hydrogen are the most important species for the synthesis of diamond layers under metastable conditions [11]. The key role in this process is played by the atomic hydrogen which dissolves/gasifies the non-diamond phases, such as graphite, from the depositing layer and, thus, promotes the growth of diamond phase [12]. It has been also found that oxygen, introduced in the feed gas either separately or contained in a gas molecule, can dissolve non-diamond phases and favor the growth of diamond [13,14] by playing a role similar to that of hydrogen. In addition, it has been demonstrated that not only hydrocarbons, but other carbon carrier gases such as carbon monoxide, alcohols, ketones etc. can be used in the feed gas for deposition of diamond layers [8,9].

Based on experimental data from literature, Bachmann *et.al.* [12] have shown that a wide variety of

gas mixtures can be used for diamond deposition as long as they contain the right combination of carbon (C), hydrogen (H) and oxygen (O). On their C-H-O ternary phase diagram [12], a region of possible diamond growth is clearly defined. The phase diagram built by Bachmann *et.al.* has been validated later by Wang *et. al.* [13] through theoretical calculations. According to this C-H-O phase diagram, certain organic compounds or their combinations, including methanol, fall into the diamond growth region. Therefore, it is not surprising that attempts to grow diamond from various organic compounds have been successful [11,15]. However, in these studies, hydrogen was used for dilution of the organic compounds.

The present paper presents some results and observations on the deposition of diamond layers from methanol-water mixture by radio frequency (r.f.) plasma-assisted CVD. This deposition technique uses low-cost, non-explosive precursors and can be very attractive for industrial applications. The methanol-water mixture has been previously used by Rudder *et. al.* [16,17] in their plasma based reactor for deposition of diamond. The results reported in the present work bring additional information concerning the influence the feed gas composition on the structure and morphology of the deposited layers and discusses on the role of the graphite plate used as a sample holder.

2. EXPERIMENTAL EQUIPMENT AND PROCEDURE

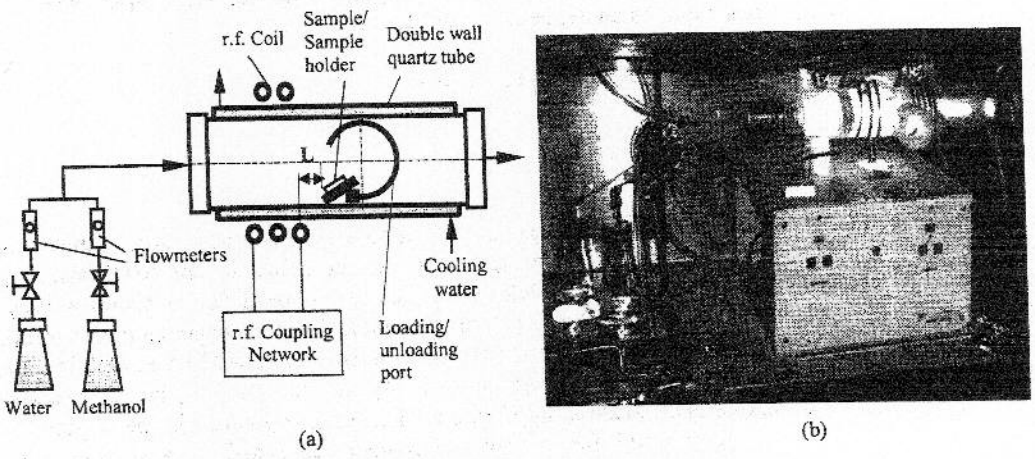

Figure 1. *Schematic diagram (a) and picture (b) of the apparatus used for diamond deposition.*

Figure 1 shows a schematic diagram and a picture of the synthesis apparatus used for diamond deposition. The synthesis reactor consists of a double wall, water cooled, quartz tube with an inner diameter of 50 mm and a length of 500 mm. Before deposition, the reaction chamber was evacuated by a mechanical vacuum pump to a pressure of about 10^{-3} Torr. Water and methanol were stored in separate, closed, glass flasks. Their vapor pressure above the liquid surface was sufficient to provide the required flow rates without additional heating. For diamond deposition, water and methanol were admitted into the reactor with flow rates controlled by variable area flowmeters and regulated by needle valves. A total gas flow rate (methanol + water) of 14 cm^3/min was used for all the experiments. The pressure inside the reactor was adjusted by using a throttle valve placed between the reactor and the vacuum pump. All experiments were carried out at a pressure of 1 Torr. A three-turn coil, made of 6 mm copper tube surrounds the reactor and is coupled to the r.f. power supply (13.56 MHz) through a matching network. The discharge was initiated by coupling the r.f. coil to the r.f. power supply. The r.f. power was measured at the output of the r.f. generator when the matching conditions assured a reflected power lower than 20 W (zero reflected power would

represent optimal matching conditions). All the depositions were carried out using an r.f power of 1200 W which assured a stable discharge.

Samples were made from 0.5 mm thick silicon wafer and had dimensions of 10 x 10 mm. They were introduced into the reactor through a lateral port and positioned at a distance L ≈ 15 mm from the coil. The samples were placed either on steel ((15x15x1 mm) or on graphite (25x20x3 mm) holders leant on a ceramic piece with an appropriate height to give to the sample a tilt angle of about 30° relative to the tube axis (figure 1). The sample temperature was estimated by using sensitive color paints. For all the experiments reported here, the sample temperature was situated between 500 and 550 °C. Placement of the sample closer to the coil or inside the coil led to much higher temperatures.

After deposition, the samples were analyzed by scanning electron microscopy (SEM). The quality of the diamond coatings was mainly assessed by investigation of their surface morphology. Several samples were also analyzed by Raman spectroscopy for confirmation of diamond phase and for a better evaluation of diamond purity.

3. EXPERIMENTAL OBSERVATIONS, RESULTS AND DISCUSSIONS

Regardless of the feed gas composition used, from pure water to pure methanol, the plasma discharge showed some similar characteristics. For example, when the r.f. power was gradually increased from zero, a low luminosity discharge, extending along the whole tube, was formed when the r.f. power level exceeded the gas breakdown. By continuing to increase the power to about 900 W (the exact value varied on the methanol/water ratio), a sudden transition to a very luminous plasma, with well defined boundaries, localized only inside the coil has been observed (figure 1 b). This transition from low to high density plasma in r.f. inductively coupled plasmas has been investigated by Amorim *et. al.* [19] in argon at lower pressure (20-200 mTorr) and has been attributed to a change in the plasma coupling mechanism.

It has also been noticed during experiments that the color of the low density plasma changes from blue tones to red tones as the methanol concentration in the feed gas increases from zero to 100%. This change of the plasma color, also visible in the high density plasma discharge mode, is caused by the concentration variation of different radicals in the plasma, as reported by Rudder *et. al.* [16].

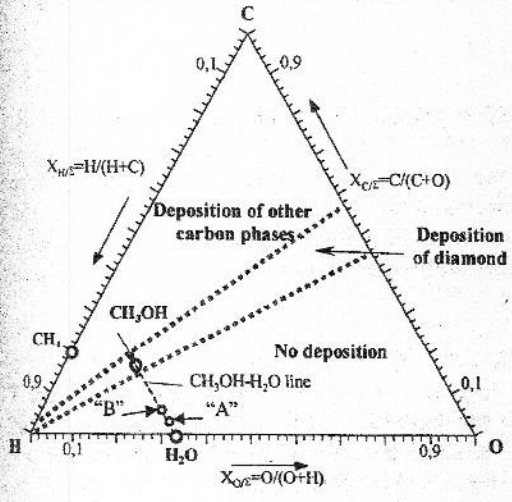

Figure 2. Ternary C-H-O phase diagram according to [12,13] and localization of methanol-water mixtures on this diagram.

Our attempts to grow diamond, in conditions described above, from pure methanol, pure water or their combinations were unsuccessful when the sample was placed on a steel holder. According to C-H-O phase diagram [12,13,18], an atmosphere consisting of pure methanol (CH_3OH) is placed in the "deposition of diamond" region while an atmosphere consisting of pure water (H_2O) vapor is located in the "no deposition" region (figure 2). Any methanol-water combination will be placed on the "CH_3OH-H_2O line". Since no spectroscopic analysis of the plasma were available for this study, it is difficult to

formulate a plausible explanation of the causes that prevented diamond growth even when the feed gas was composed of pure methanol and combinations of methanol and small amounts of water which would fall into the diamond growth region.

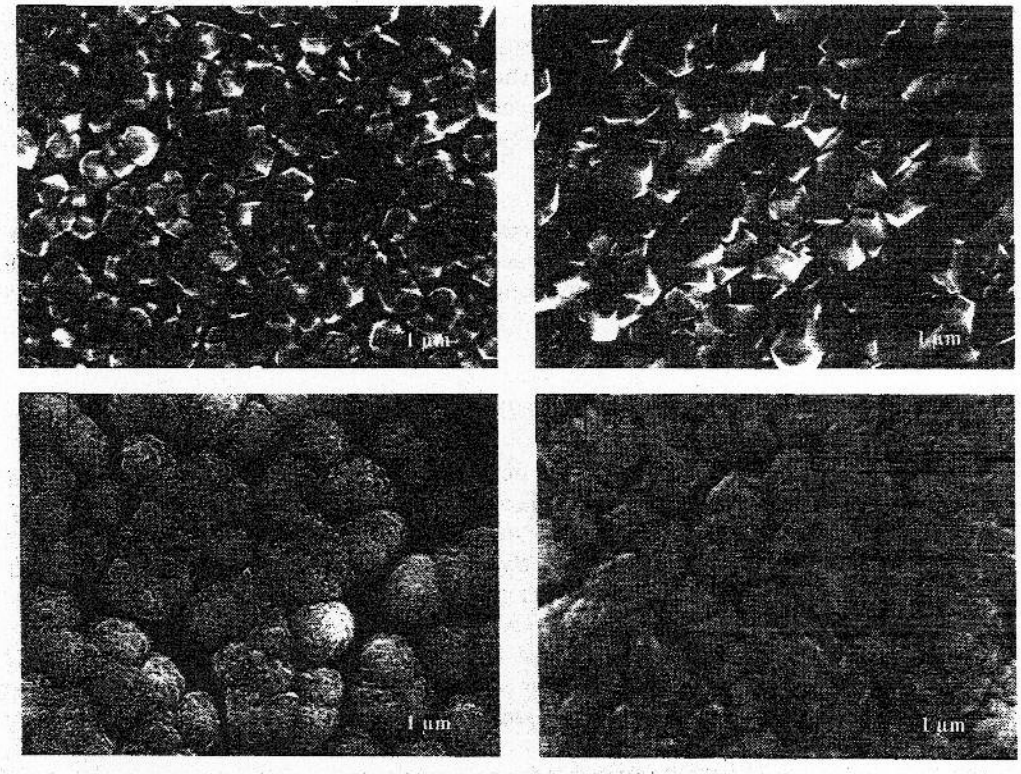

Figure 3. *SEM Micrographs of diamond layers deposited at different methanol/water flow rate ratios: (a) – 1/13 cm^3/min, (b) – 2/12 cm^3/min (point "A" in figure 2), (c) – 4/10 cm^3/min (point "B" in figure 2), (d) – 7/7 cm^3/min.*

The experiments carried out with the sample placed on graphite holder produced different results. The following methanol/water flow rates were used: 1/13, 2/12, 4/10 and 7/7 [cm^3/min]. Deposition time was set to 4 hours. Figure 3 shows the SEM micrographs of the layers produced under these conditions. It can be seen that at low methanol concentration (1-2 cm^3/min) in the feed gas, the layers display well-faceted diamond crystals. By increasing the methanol flow rate to 4-7 cm^3/min, the morphology of the deposited layer changes significantly; the layer consists of microcrystallized "ball-like" grains.

Figure 4 shows the Raman spectra of the layers deposited by using a feed gas with compositions corresponding to points "A" and "B" in the C-H-O diagram from figure 2 (layers shown in figure 3 b and c). Even though, the point "A" is placed in the "no deposition" region, the Raman spectrum of this layer (figure 4 a) shows only a diamond peak situated around 1332 cm^{-1}. By increasing the methanol/water ratio the quality of the diamond layer deteriorates rapidly as shown by SEM analysis (figure 3 c and d) and confirmed by Raman spectroscopy (figure 4 b). The broad peak situated around 1510 cm^{-1} in the Raman spectra of the layer deposited with a methanol/water flow rate ratio of 4/10 cm^3/min indicates large amounts of amorphous carbon incorporated in the layer. The intensity of the diamond peak also becomes smaller.

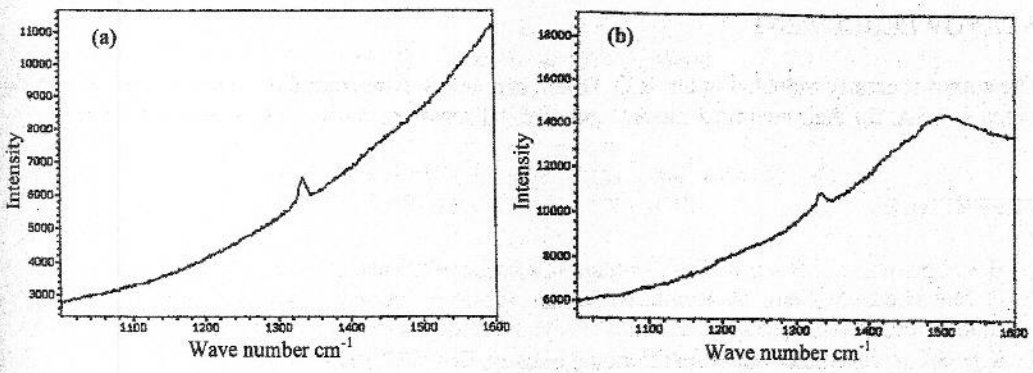

Figure 4. *Raman spectra of diamond films deposited at methanol/water flow rates of 2/14 cm³/min (a) and 4/10 cm²/min (b).*

The graphite plate appears to play an active role in the deposition process. Atomic hydrogen and OH radical produced by dissociation of water can react, at deposition temperature, with graphite to produce gaseous carbon carrier species. In fact, the occurrence of such reaction was confirmed by the thinning of the graphite plate during deposition. Therefore, the deposition of diamond in this case appears to include some chemical transport reactions. The gasification of graphite by H, OH and possibly by other radicals, shifts, near the deposition surface, the C/H/O atomic ratio of the atmosphere from that calculated by taking into account only the composition of the feed gas. Thus, the growth of well-faceted diamond crystals by using a methanol/water ratio which would place this mixture into "no deposition" region is a consequence of the chemical transport reactions, involving the graphite, which sifts the actual atomic ratio near the substrate into "deposition of diamond" region (figure 2). If the concentration of methanol in the feed gas is too high, the actual atomic ratio around the growth area shifts further into the "deposition of other carbon phases" region and, therefore, the amount of amorphous carbon in the deposited layer increases.

4. CONCLUSIONS

A r.f. inductively coupled discharge has been used for deposition of diamond layers from methanol-water mixture. This process uses low-cost, non-explosive precursors and can represent an alternative to the techniques used in the present for diamond deposition. The experiments have demonstrated that diamond layers consisting of well-faceted crystals can be deposited at temperatures as low as 500-550 °C. However, with our experimental settings deposition of diamond layers was possible only by using a graphite plate as a sample holder. Chemical transport reactions between radicals resulted from dissociation of water and methanol (H, OH and possibly others) and graphite lead to gasification of graphite and change the actual C/H/O atomic ratio of the atmosphere near the growth surface from that resulting only from the composition of the feed gas. These chemical transport reactions allow deposition of diamond from a feed gas with a composition which otherwise would result in no deposition of any kind, diamond or non-diamond.

Investigations of the deposited layers by scanning electron microscopy and Raman spectroscopy showed that at low methanol concentration in the feed gas, the layers are made only of polycrystalline diamond with clearly defined facets. Raman spectra of these layers present only a diamond peak at 1332 cm^{-1} wave number. Increasing the methanol concentration in the feed gas modifies the morphology and the phase composition of the deposited layers. These layers are formed of microcrystallized "ball-like" grains, incorporating significant amounts of amorphous carbon as indicated by the broad peak at about 1510 cm^{-1} wave number in the Raman spectra.

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