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Effect of Gas Sources on the Deposition of Nano-Crystalline Diamond Films Prepared by Microwave Plasma Enhanced Chemical Vapor Deposition

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Abstract Nano-crystalline diamond (NCD) films were deposited on silicon substrates by a microwave plasma enhanced chemical vapor deposition (MPCVD) reactor in C_2H_5OH/H_2 and $CH_4/H_2/O_2$ systems, respectively, with a constant ratio of carbon/hydrogen/oxygen. By means of atomic force microscopy (AFM) and X-ray diffraction (XRD), it was shown that the NCD films deposited in the C_2H_5OH/H_2 system possesses more uniform surface than that deposited in the $CH_4/H_2/O_2$ system. Results from micro-Raman spectroscopy revealed that the quality of the NCD films was different even though the plasmas in the two systems contain exactly the same proportion of elements. In order to explain this phenomenon, the bond energy of forming OH groups, energy distraction in plasma and the deposition process of NCD films were studied. The experimental results and discussion indicate that for a same ratio of carbon/hydrogen/oxygen, the C_2H_5OH/H_2 plasma was beneficial to deposit high quality NCD films with smaller average grain size and lower surface roughness.

Keywords: nano-crystalline diamond thin film, chemical vapor deposition, gas source, ethanol

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1 Introduction

Nano-crystalline diamond (NCD) films have attracted much attention due to their outstanding physical and chemical properties [1]. The techniques for the preparation of NCD films are mainly on hot-filament chemical vapor deposition (HFCVD) and microwave plasma enhanced chemical vapor deposition (MPCVD) [2]. Owing to the electrodeless feature of the MPCVD method, much more attention has been paid to depositing high quality diamond film through MPCVD. By using this method many smooth and transparent NCD films deposited were reported [3~8].

In the growth of high quality NCD films by the MPCVD method, different kinds of gas mixtures were applied to study the influence of the gas source on the quality, morphology and growth rate of NCD films [9~11]. BENEDIC et al deposited NCD films that are suitable for surface acoustic wave (SAW) devices using $Ar/N_2/CH_4$ [12]. SALLY et al discussed the effect of oxygen concentration on the growth of NCD films with low surface roughness [13]. TANG et al deposited NCD films with a growth rate of 2.5 μm/h to 3.5 μm/h and a crystal scale of 31 nm to 45 nm using a mixture of $CH_4/H_2/N_2/O_2$ [14]. In addition, the results of CORVIN et al showed that with the addition of N_2, -CN and -HCN groups would be formed during the phase of diamond growth, which would affect the quality of NCD films [15]. FRENKLACH et al reported that oxygen would be decomposed to oxygen atoms which reacted with C1 (C or CH groups), hydrogen atom or non-diamond carbon to enhance the quality of diamond films [16,17]. Some researchers have discussed the deposition process of NCD films with a mixture of $CH_4/H_2/H_2O$ or C_2H_5OH/H_2. Their results showed that it is feasible to deposit diamond films under low deposition temperature with a high growth rate using substitute contained oxygen atoms instead of O_2 or even a mixture of CH_4/O_2 [18,19].

In this work, NCD films were deposited using H_2 plasma with ethanol gas or a gas mixture of CH_4/O_2 addition in a 5 kW MPCVD reactor. The mechanism for the difference in the surface morphology and the quality of the NCD was investigated while keeping the proportion of C/H/O and all other parameters the same, which may provide a theoretical basis to choose an optimum gas source for the deposition of high quality NCD films.

2 Experimental details

The deposition process of NCD films was carried out in a home-made microwave plasma assisted CVD reactor [20] (2.45 GHz, 5 kW, water-cooled stainless steel chamber). A schematic is shown in Fig. 1. NCD films

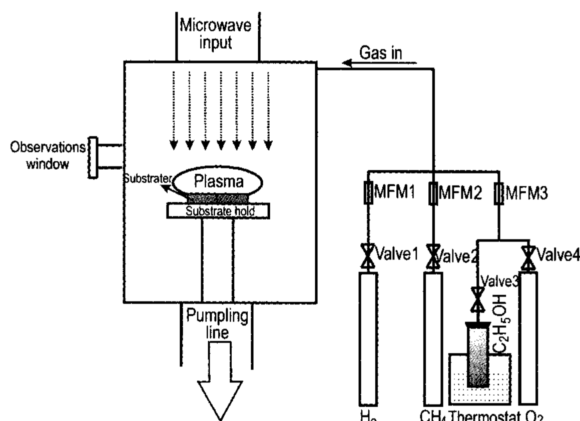


Fig.1 Schematic of the experimental apparatus

were deposited on the surface of polished single-crystalline silicon wafers with a dimensions of 10×10 mm^2, which were pre-scratched before deposition with 15 nm diamond powder on a polishing machine for 10 min. Then the substrates were ultrasonically cleaned using acetone, methanol and deionized water for 2 min. The ethanol (chromatographic grade) was set in the incubator and the temperature was controlled at 40°C. During the growing process, the microwave power, reaction pressure and deposition temperature were maintained at 2100 W, 6.2 kPa and 800°C, respectively. For the growth of NCD film in the C_2H_5OH/H_2 system (sample 1), the concentration ratio of H_2/C_2H_5OH was 65/11.0. In the $CH_4/H_2/O_2$ system, the concentration ratio of $H_2/CH_4/O_2$ was 21.5/22/5.5 in order to keep the same C/H/O proportion as in the C_2H_5OH/H_2 system. The deposition time of both samples was 7 hours. The growth temperature was measured by a two-color infrared radiation thermometer through the quartz viewing ports. The surface morphology and the quality of the deposited diamond films were evaluated by atomic force microscope (AFM), X-ray diffraction (XRD) and micro-Raman spectroscopy.

3 Results and discussion

Fig. 2 shows the surface morphology of NCD films for different reactive gas mixtures. The average surface roughness for sample 1 is 21.7 nm, as shown in Fig. 2(a), and 23.5 nm for sample 2, as shown in Fig. 2(b).

XRD analysis of the deposited NCD films was carried out to characterize the average grain size of the overall diamond films. Fig. 3 shows the XRD patterns of diamond films with 2θ angles ranging from 40° to 80°. Two peaks corresponding to diamond (111) at 44.3°(2θ) and (220) at 75.7°(2θ) were detected for all of the samples. The FWHM of the diffraction peak for sample 1 is larger than that for sample 2, confirming that the average grain size for sample 1 is smaller. The average grain size for two samples was also calculated from the diamond (111) peak width by using the

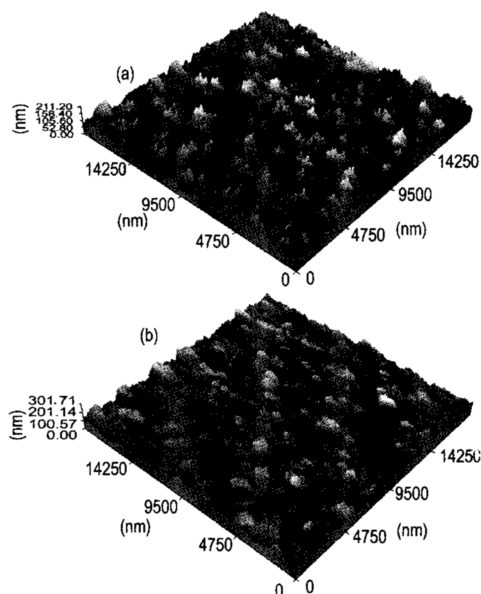


Fig.2 AFM micrographs of (a) sample 1 and (b) sample 2

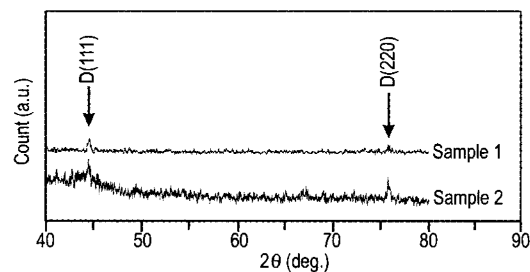


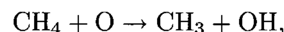
Fig.3 XRD spectra of the NCD films deposited in the C_2H_5OH/H_2 system (sample 1) and in the $CH_4/H_2/O_2$ system (sample 2)

Sherrer formula,

$$D_{\mathrm{hkl}}=\frac{K\lambda}{\beta_{(2\theta)}\cos\theta},$$

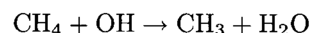
with $K=0.94$, $\lambda=1.54184$ Å while $\beta_{(2\theta)}=0.2$ for sample 1 and $\beta_{(2\theta)}=0.1$ for sample 2. The average grain sizes for sample 1 and 2 were 24.9 nm and 49.8 nm, respectively.

It is known that when O_2 is added to the reaction gas, the content of hydrogen will decrease and, at the same time, oxidation will occur between the O atom and hydrocarbons,



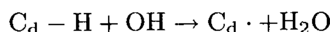
$$CH_4+O\rightarrow CH_3+OH,$$

which indicates that oxygen atoms can inhibit the formation of hydrogen compounds and increase the growth rate of diamond films [21,22]. The OH groups formed by the reaction play different roles in the gas mixture. Firstly, they will dissociate carbon containing groups (such as CH_4),



$$CH_4+OH\rightarrow CH_3+H_2O$$

Secondly, they will remove the H groups from the deposited surface,



$$C_d - H + OH \rightarrow C_d \cdot + H_2O$$

Thirdly, they will etch the non-diamond carbon and thus enhance the quality of the deposited diamond films [23]. In addition, the dehydrogenation of the OH group is much easier than that of H atom [24]. The effect of OH groups in the C_2H_5OH/ H_2 system are shown in Fig. 4. In order to compare the effective capacity of O or OH groups in the growth of diamond films, the main processes containing trace amounts of O and OH groups were presented in Refs. [25, 26].

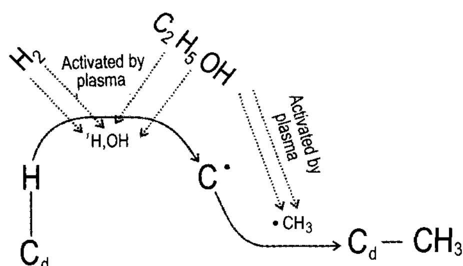


Fig.4 The effect of ethanol in the C_2H_5OH/H_2 system

Consequently, in order to explain the difference in surface roughness between sample 1 and sample 2, attention should be paid to the O and OH groups in this experiment. In a comparison of Fig. 2(a) with Fig. 2(b), it can be seen that both the surface roughness and smallness of the grain size in the C_2H_5OH/ H_2 system were better than those in the $CH_4/H_2/O_2$ system. Since the two samples are deposited under almost the same parameters and nearly the same proportion of elements, the difference may well be attributed to the fact that the energy to break O=O double bond and formatting OH radicals was higher than that to dissociate OH groups from C_2H_5OH directly. In other words, the OH groups, which have the capability of etching the non-diamond carbon and promoting the occurrence of dehydrogenation, are easier to dissociate from C_2H_5OH than forming in the $H_2/CH_4/O_2$ system. Meanwhile, considering the energy distribution in the plasma ball, the trend of energy density decreases from the centre to the edge of the plasma. OH radicals dissociated from ethanol are easier to distribute uniformly in the region covered by plasma, which decrease the surface roughness and thus improve the uniformity and quality of the deposited diamond film. Furthermore, the dissociated energy of the C-C bond (347 kJ/mol) in the ethanol is lower than that of the C-H bond (413 kJ/mol) in the methane, which indicates that a higher concentration of effective carbon-containing groups can be obtained from the C_2H_5OH/H_2 mixture with the same ratio of C/H/O as in the $CH_4/H_2/O_2$ mixture.

Fig. 5 shows the quality of two samples of diamond films. The Raman peak ($1332\ cm^{-1}$) of the NCD film deposited in the C_2H_5OH/H_2 system (sample 1) is sharper than that of sample 2 deposited in the $CH_4/H_2/O_2$ system. Although a G band appears in

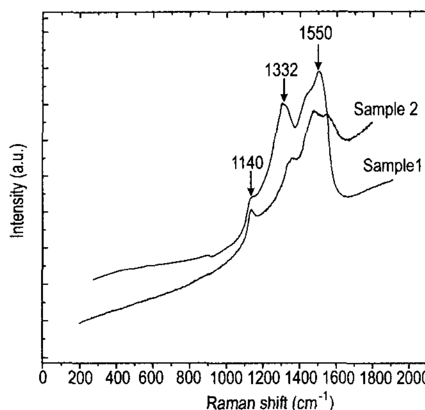


Fig.5 Raman spectra of sample 1 and sample 2

both Raman spectrums, the content of non-diamond carbon in sample 1 is much less than that in sample 2, which indicates the better quality of sample 1. Meanwhile, the obvious Raman peak at $1140\ cm^{-1}$ of sample 1 shows that the proportion of nano-scaled diamond crystals in sample 1 is much higher than that in sample 2. The Raman results may turn out to be a good verification of the above discussion.

4 Conclusion

NCD films were deposited on silicon substrate by MPCVD in C_2H_5OH/H_2 and $CH_4/H_2/O_2$ systems. The results of AFM, XRD and Raman spectroscopy revealed that the NCD films deposited in the C_2H_5OH/H_2 system showed better uniformity of surface morphology and higher quality than those deposited in the $CH_4/H_2/O_2$ system. Based on the investigation of the bond energy of forming OH groups, energy distribution and distribution of OH groups in plasma, the reaction mechanism in the above two systems was analyzed. The results show that for the same ratio of carbon/hydrogen/oxygen in the mixed gas sources, NCD films with high quality and smooth surface are easier to deposit by MPCVD in the C_2H_5OH/H_2 system, than in the $CH_4/H_2/O_2$ system.

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