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A new regime for high rate growth of nanocrystalline diamond films using high power and $CH_4/H_2/N_2/O_2$ plasma ☆

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ABSTRACT

In this work, we report high growth rate of nanocrystalline diamond (NCD) films on silicon wafers of 2 inches in diameter using a new growth regime, which employs high power and $CH_4/H_2/N_2/O_2$ plasma using a 5 kW MPCVD system. This is distinct from the commonly used hydrogen-poor Ar/CH_4 chemistries for NCD growth. Upon rising microwave power from 2000 W to 3200 W, the growth rate of the NCD films increases from 0.3 to 3.4 μm/h, namely one order of magnitude enhancement on the growth rate was achieved at high microwave power. The morphology, grain size, microstructure, orientation or texture, and crystalline quality of the NCD samples were characterized by scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray diffraction, and micro-Raman spectroscopy. The combined effect of nitrogen addition, microwave power, and temperature on NCD growth is discussed from the point view of gas phase chemistry and surface reactions.

1. Introduction

Nanocrystalline materials possess several unique physical properties which are different from those of their coarser grained counterparts due to extremely small grain sizes. These unique properties of nanocrystalline materials stimulated the current worldwide interest in nanotechnology based on nanocrystalline materials such as microelectromechanical and nanoelectromechanical systems (MEMS/NEMS) and make nanocrystalline materials the hot subject of many research activities. Among them, nanocrystalline diamond (NCD) is one of the promising materials for MEMS/NEMS applications [1–4], because it possesses a smoother surface or a lower surface roughness and lower friction coefficient, due to nanometer-scale grain size and high density of grain boundaries, when compared to large-grained polycrystalline diamond (PCD) films.

Investigations on synthesis and characterization of NCD films started two decades ago and have been growing rapidly in recent years. Most of the researches focus on using inert gas Ar/CH_4 (with or without hydrogen) chemistries to deposit NCD and ultrananocrystalline diamond (UNCD) [5–9]. In contrast to conventional microcrystalline diamond, thin NCD film was also grown with low methane in hydrogen with very high initial nucleation densities [4], so-called faceted nanocrystalline diamond, whose grain size and surface roughness will increase with deposition time and film thickness if the growth process is allowed to continue. More details can be found in the review on thin NCD growth, electronic properties, and applications [10]. Alternatively, NCD has also been produced by a few groups using high concentrations of CH_4 in H_2 [11] or CH_4/H_2 gas mixtures together with N_2 [12,13] and/or O_2 addition [14].

Experimental works have shown that the influence of nitrogen addition into CH_4/H_2 mixtures on CVD diamond growth strongly depends not only on the concentration of nitrogen but also on other parameters such as microwave power, pressure, temperature, and methane concentration [15–20].

We have developed a new chemical path for synthesis of NCD using simultaneous addition of both N_2 and O_2 into CH_4/H_2 plasma since they are abundant in natural source air [21] and investigated the relative amount of N_2 and O_2 addition on the morphology and texture of diamond films by keeping all the other growth parameters constantly (for example, microwave power 3000 W, pressure 105 Torr) using a 5 kW MPCVD system [22].

It is well-known that the growth parameter windows for growth of diamond including NCD in a high-power (≥3 kW) MPCVD system are different from those in a low-power (≤1.5 kW) MPCVD reactor. For instance, in a low-power MPCVD system, the substrate temperature can be independently controlled, or even heated separately; while in a high-power MPCVD system, the substrate is directly heated by the microwave plasma and a water cooling of the substrate holder is necessary, the substrate surface temperature is thus actually tuned by

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the microwave power and the pressure applied and the thermal conductivity of the substrate holder.

In this work, we further investigate the influence of other growth parameters such as microwave power (thus substrate temperature) on the microstructure and growth rate of NCD films, by fixing the amount of nitrogen and oxygen addition, in order to optimize the growth conditions for high rate synthesis of NCD films using high-power MPCVD system.

2. Experimental

We fabricated the diamond samples using a 5 kW ASTeX PDS-18 MPCVD reactor. Big silicon wafers of 2 inches in diameter, which were directly put on the Mo substrate holder, were used as substrates and pre-scratched with diamond powder of size 0–0.5 μm to facilitate diamond nucleation. The growth parameters are summarized in Table 1. Samples D1 and D3 were grown with 1 SCCM air addition intentionally. Sample D2 was grown with 0.8 SCCM pure N_2 and 0.2 SCCM pure O_2 addition, and their ratio was chosen to be the same as that of air since N_2 and O_2 are the major ingredient in air (nitrogen 78% and oxygen 21%), so that we can check whether two separate gas addition of pure nitrogen and pure oxygen differ significantly from one single gas addition of air on diamond growth, since air is nature source, and if no significant difference, it thus can drastically reduce the economic cost. For further comparison, sample D4 was grown under the same condition as that of D3, except with only 1 SCCM pure N_2 addition. The total concentration of nitrogen with or without oxygen addition into CH_4/H_2 plasma was kept constant at 0.24% for all the samples studied here. The bottom temperature of the Mo holder was measured by a thermocouple.

Top morphology and cross-sectional microstructures of the NCD samples were characterized by scanning electron microscope (SEM) and atomic force microscopy (AFM). The crystalline quality of the films was checked by a Jobin Yvon Raman spectrometer with a 514.5 nm Ar^+ laser and with a 325 nm He–Cd ultraviolet (UV) laser, respectively. The orientation or texture and grain size of the NCD films were studied by X-ray diffraction using a Philips X-pert diffractometer with Cu-Kα radiation. The (220) diamond diffraction peaks were fitted with Gaussian peak using PeakFit program to obtain their full width at half maximum (FWHM) for calculating the average grain size of the NCD films.

3. Results and discussion

Fig. 1 shows the SEM images, which reveal different microstructures, of the four films D1 to D4 taken from the growth surface. A structure consisting of nanocrystalline clusters or typical featureless morphology of NCD films is observed in all the samples. Well-defined square {100} facets or triangular {111} facets, which are usually observed in large-grained polycrystalline diamond films, cannot be observed in the four samples D1 to D4. However, the fine grains, which made up of the large clusters, do not show much difference in size. Using SEM micrographs, we can roughly distinguish a grain size less than 100 nm for all the nanocrystalline films.

Table 1
The growth parameters and some characteristics of the NCD samples studied here.

Sample name	D1	D2	D3	D4
Power (W)	2000	3000	3200	3000
Pressure (Torr)	95	105	105	105
CH_4/H_2 flow (SCCM)	15/400	16/400	16/400	16/400
N_2 and O_2 flow (SCCM)	1.0	0.8 N_2/0.2 O_2	1.0	1.0 (N_2)
Temperature (°C, Mo holder)	199	297	287	295
Deposition time (h)	75.5	26.5	74.7	73.0
Thickness (μm)	25	90	205	210
Growth rate (μm/h)	0.3	3.4	3.0	2.9
Grain size (nm)—(220)	52	37	24	35

The cross-sectional view of the NCD films from the bottom nucleation side to the top growth surface are shown in Fig. 2. The nanocrystalline nature of the diamond grains made up of the samples is clearly demonstrated by these cross-sectional SEM micrographs. From Fig. 2, one can see that the grain size and surface roughness do not obviously increase with film thickness, and no clear columnar growth, which is commonly found in large-grained polycrystalline diamond films, can be seen in these NCD films. From these cross-sectional SEM micrographs, we can measure the thickness and thus calculate the average growth rate of the samples as given in Table 1 for further analysis and comparison of the samples. From Table 1, one can see that the growth rate of film D2 grown at microwave power 3000 W is 3.4 μm/h, one order of magnitude higher than 0.3 μm/h, that of film D1 grown at low-power 2000 W. So far, the growth rates of thin NCD films produced by different groups using different methods or different gas chemistry are generally less than 1 μm/h [12], with the highest growth rate being 1.6 μm/h reported for NCD films grown using common $Ar/CH_4/H_2$ chemistry [8]. Therefore, we conclude that with increasing microwave power from 2000 to 3000 W, the growth rate of NCD films is enhanced by one order of magnitude.

The top morphology of samples D1 and D3 was also characterized by using AFM to measure the surface roughness. Fig. 3 shows 5 μm × 5 μm AFM topographic images of the growth surface of film D1 and D3. From these AFM images, the RMS roughness of film D1 of 25 μm thick is 73 nm and that of film D3 of 195 μm thick is 157 nm over an area of 25 μm^2. This result is consistent with the SEM cross-sectional view of the samples shown in Fig. 2.

Fig. 4 shows the XRD patterns of the samples. The strongest peak at 69.1° comes from the silicon substrates. A common feature is observed in Fig. 4, that the diamond (220) diffraction peak at 75.3° appears much stronger than the other peaks such as (111) and (311) diamond diffraction peaks except the Si (400) peak at 69.1°. The intensity ratio of (220) to (111) diffraction peak for film D1 is 100, almost two orders of magnitude higher than that of 0.25 for randomly oriented diamond powder, strongly evidencing the <110> preferred orientation of the NCD film. The intensity ratio of (220) to (111) diamond diffraction peak is 2.8 for D2, 3.83 for D3, and 1.89 for film D4. This indicates that all the NCD films studied here show a certain degree of <110> preferred texture, which is consistent with the bright elongated large clusters in the AFM images shown in Fig. 3. It has been suggested that the formation of <110> texture (found in thin nanocrystalline diamond films of 3–4 μm thick) is due to the development of ballas-like particles composed of nanometric growing sectors elongated along the <110> axis [23].

According to the full width at half maximum (FWHM) of the (220) diamond diffraction peak and using the Sherrer's formula [24], the average grain size of the fine grains that are made up of the four films is calculated to be less than 60 nm and listed in Table 1 for comparison. In short, XRD analyses of the samples (Fig. 4) not only confirm the formation of crystalline diamond phase in the samples but also evidence the nanocrystalline nature of the samples.

Fig. 5 shows the micro-Raman spectra of the NCD samples excited by both the 514.5 nm green Ar^+ laser and the ultraviolet (UV) 325 nm He–Cd laser for analysis of their crystalline quality. The occurrence of the first order diamond line around 1333 cm^{-1} in all the Raman spectra especially appearing as a sharp peak in the UV Raman spectra clearly proves the diamond nature of these samples, as the XRD patterns do. A broad band centered around 1500 cm^{-1} in the visible Raman spectra is observed in all the samples. The bands around 1360 cm^{-1} and 1580 cm^{-1} (about1500 cm^{-1} in the visible Raman spectra), are more clearly seen in the UV Raman spectra of the samples (Fig. 5(b)), and they are assigned to D and G band of graphite, respectively [25].

In summary, various NCD films of different growth rates have been produced using microwave powers ranging from 2000 to 3200 W through a small amount of nitrogen and oxygen addition into conventional methane/hydrogen plasma, and one order of magnitude