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Low temperature growth of ultrananocrystalline diamond film and its field emission properties

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Abstract

Ultrananocrystalline diamond (UNCD) film is deposited at a substrate temperature lower than 500 °C. This film possesses diamond crystal of nanometer size embedded in a graphitic (or non-diamond carbon) phase. The presence of non-diamond carbon in the grain boundaries of diamond crystal plays a crucial role to the film properties and its corresponding application such as electron field emission. The present work reports the growth of UNCD films at different methane concentrations to alter the film properties that could make it suitable for higher electron field emission. The surface morphology of an as-grown film was examined with a field emission scanning electron microscope. Nucleation density in the range of 10^{11}–10^{12}/cm^2 is obtained in the as-grown films. The grain size of diamond increases from 5 nm to 25 nm with an increase in CH_4 concentration from 1% to 7.5% in the argon plasma. The presence of different carbon phases in the diamond films was investigated qualitatively by Raman studies. Near edge X-ray fine structure study ascertains that the as-grown films mainly possess diamond phase. A direct correlation of field emission properties with the CH_4 concentration during UNCD growth is obtained.

Keywords: Diamond properties and applications; Nanocrystalline diamond; Field emission

1. Introduction

The properties of materials with nanometric dimensions are significantly different from those of atoms or bulk materials. Appropriate control of the properties of nanometer-scale structures can lead to new science as well as new products, devices and technologies. There are substantial researches carried out on the growth, properties and applications of single-crystalline and micro-crystalline diamond (MCD) in the last few decades. Recently main focus has been directed towards the synthesis and properties of nanocrystalline (NCD) and ultra-nanocrystalline diamond (UNCD) films. Unlike MCD, hydrogen free plasma is usually used to synthesize UNCD films [1]. The UNCD film possesses many excellent properties and several of them actually exceed those of diamond [2]. As the diamond grain size in UNCD film is less than 10 nm, surface smoothness increases markedly making it a promising material for tribological applications [3]. Additionally, the decrease in diamond grain size increases the grain boundaries containing non-diamond carbon in the film, therefore resulting to significant improvement in electrical properties. The non-diamond contents and the crystal size of diamond grains in the films play a crucial role to applications like electron field emission. A very high electron field emission characteristic has been reported from nanodiamond film [4]. In the present study, we have varied the methane concentration during UNCD growth to increase the non-diamond content in the film and measured the electron field emission. It is believed that an optimum quantity of non-diamond carbon in the diamond film will enhance the electron emission by free conduction of electron inside the film. Secondly, the nucleation and growth of diamond is not an easy task at a lower substrate temperature (<500 °C). However, for wider uses of substrate, low temperature diamond deposition is highly demanding. Therefore we

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Table 1
Conditions under which diamond deposition was performed

Process parameters	Deposition conditions
Microwave power	1200 W
CH_4/Ar	1 to 7.5%
Flow rate	200 sccm
Pressure	150 torr
Substrate temperature	~475 °C
Deposition time	Varied (30 min to 3 h)
Sample position	Immersed in plasma

made a solemn effort to nucleate and grow UNCD at a lower substrate temperature (< 500 °C).

2. Experimental

All deposition was carried out using IPLAS microwave plasma CVD of 2.45 GHz capacity. N-type mirror polished Si (100) substrates were used to grow diamond film. The substrates were first ultrasonically cleaned by acetone to remove any surface contamination and then dipped in HF for 1 min to remove native oxides. Surface pretreatment was carried by ultrasonic abrasion of substrate using 30 nm diamond powder slurry of methanol. Then substrate was again ultrasonically cleaned twice in deionized water to remove diamond particles sticking to the surface and at the end Si substrate was dried in nitrogen gas blow before inserting into MPCVD reactor. Table 1 shows the experimental growth parameters for UNCD growth. The temperature was measured to be 475 °C by placing a K-type thermocouple at the bottom surface of molybdenum substrate holder on which Si substrate was kept for deposition. No external heater was used to heat the substrate and the substrate temperature was in the range of 460–475 °C due to plasma heating.

The surface morphologies of as-grown films were examined by FE-SEM and the crystalline quality of the deposited continuous films was monitored by Raman measurements. Raman measurements were carried out using a Renishaw spectrometer. The measurements were performed using the Ar line at 514.5 nm in a backscattering geometry. The laser beam spot size was about 1 μm and the incident power was 120 mW. The C K-edge X-ray absorption spectra were obtained using a high energy spherical grating monochromater-20A beamline by the sample current mode at the National Synchrotron Radiation Research Center in Hsinchu, Taiwan. Electron field emission measurements were done using a Keithley power supply. The cathode voltage was applied by an analog programmable 1 kV power supply under computer control, and the measured emission current was logged at each voltage. The measurements were carried out under a low 10^{-6} torr ambient pressure. The movement of the anode tip (1 mm diameter) was measured digitally and the gap between emitter and collector was confirmed by optical microscope.

3. Results and discussion

The surface morphologies of UNCD film grown at different methane concentrations are displayed in Fig. 1. A minimum

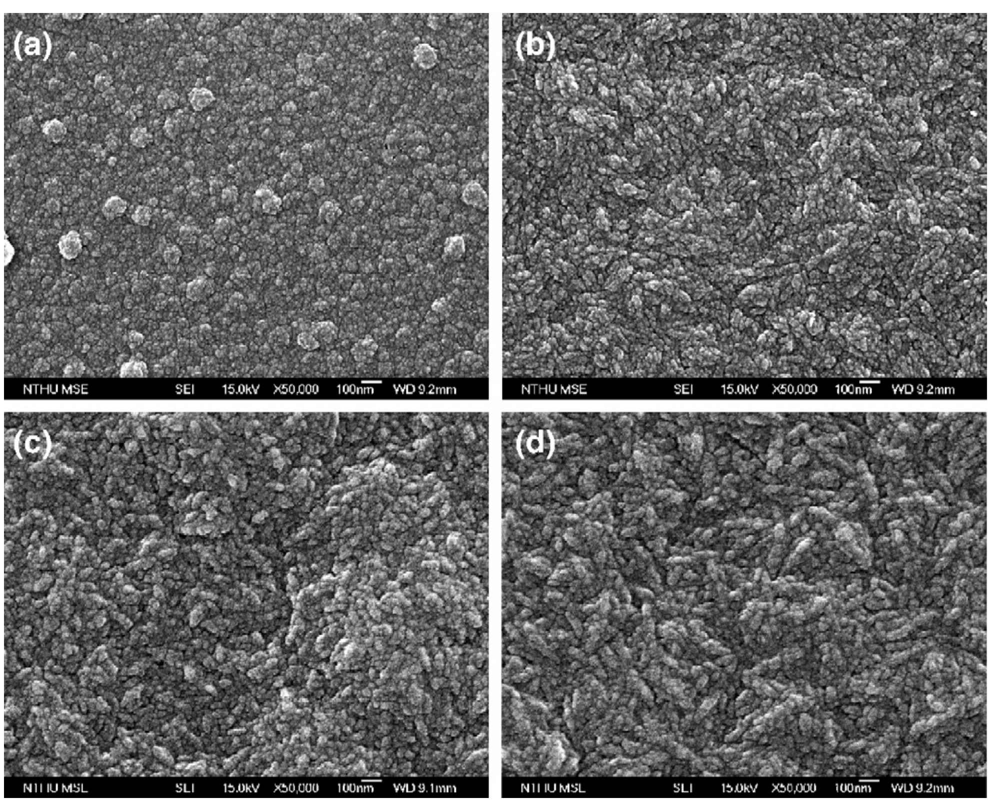

Fig. 1. High resolution FE-SEM image of UNCD films grown at different methane concentrations (a) 1% (b) 2% (c) 5% (d) 7.5%. The scale bar in all images corresponds to 100 nm.

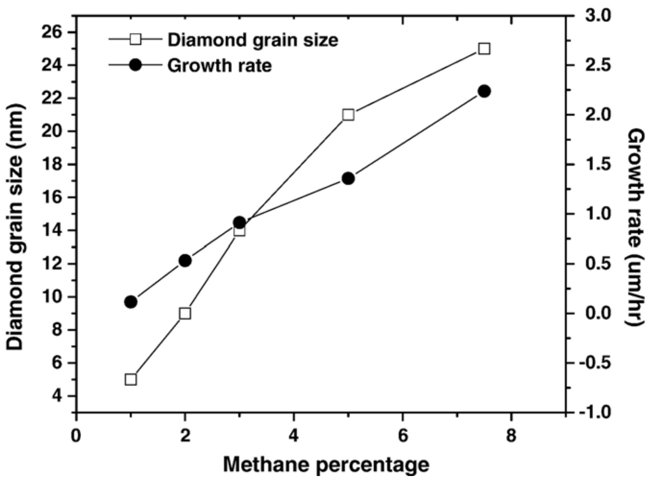

Fig. 2. The variation of growth rate and grain size versus methane percentage during UNCD growth.

90 min of growth time was needed to obtain a continuous film with 1% CH_4. The nucleation density was estimated to be around 10^{11}–10^{12}/cm^2 in 90 min of growth time. However, continuous film was obtained at a shorter deposition time with higher methane concentration. Interestingly, at a higher methane concentration, diamond grains were found to form elongated clusters compared to rounded clusters at a lower methane concentration. Furthermore the average grain size measured from a high resolution FE-SEM image was found to linearly increase with methane concentrations. The variation of grain size and growth rate with different methane concentrations is represented in Fig. 2. For the growth rate measurement, UNCD was deposited for 3 h at a methane concentration of 1 to 3%. However, growth was carried out for 1 h when methane concentration increases to 5 and 7.5%. The increase in grain size with methane percentage is opposite to nanocrystalline diamond (NCD) growth in CH_4-H_2 plasma. Wu et al. reported formation of a smaller diamond crystal with the increase in methane concentration [5-6]. The increase of grain size in the present case is most probably due to coating of non-diamond carbon on the diamond grains because graphitic carbon content increases with higher methane percentage [5].

Fig. 3 shows the Raman spectra of UNCD films. Each spectrum shows four broad peaks at around 1140–1180, 1350, 1470 and 1580 cm^{-1}. Peaks located at 1350 and 1580 cm^{-1} are designated as D-band and G-band respectively, and are due to the disorderliness of carbon phase present in the grain boundaries of UNCD films. The absence of a sharp peak at 1332 cm^{-1} is due to very small sized diamond grains in the film and the use of visible Raman spectrometer. However, when the same type of film is characterized by UV-Raman, a sharp peak is normally observed at 1332 cm^{-1} [7]. Other two peaks observed in UNCD films were at ~1180 cm^{-1} and 1470 cm^{-1} [8-9]. These two peaks are sometimes assigned to nanocrystalline diamond phase or *sp*^{3} rich carbon phase [10-11]. However, there is certain ambiguity in these two peaks. Ferrari et al. have assigned these two peaks at ~1140 cm^{-1} and ~1480 cm^{-1} to C═C bond stretching vibration (ν_1) and C–C bond stretching vibration (ν_3) respectively, of transpolyacetylene segments present at the grain boundaries and surfaces of diamond film

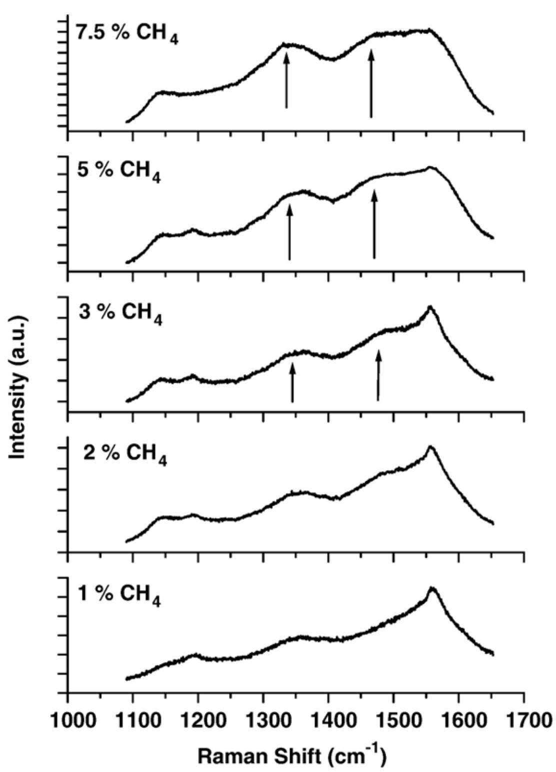

Fig. 3. Raman spectra of UNCD films grown at different methane concentrations.

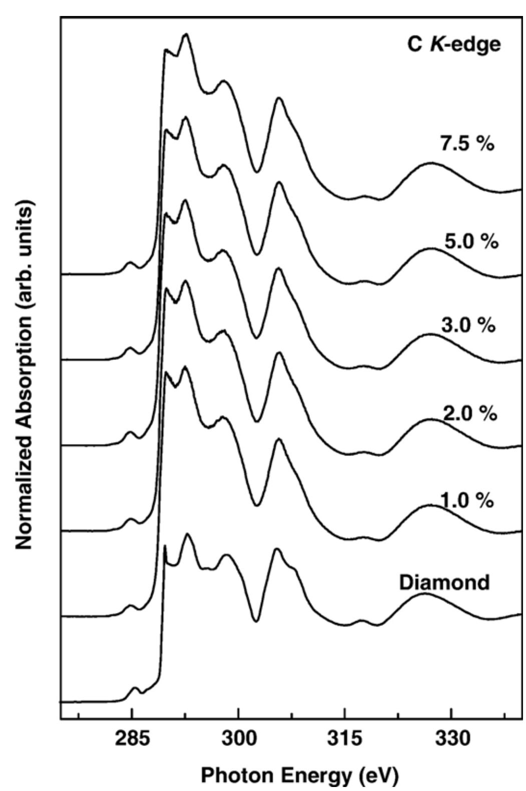

Fig. 4. NEXAFS spectra of UNCD films grown at different methane concentrations (polycrystalline diamond was used for references).

[12]. Recently, Kuzmany et al. has given much stronger evidence that the peaks at ~1180 cm^{-1} and ~1470 cm^{-1} do not originate from the diamond or sp^3 phase of carbon [13]. These two peaks are more distinct in the UNCD films due to large grain boundary areas containing transpolyacetylene. In the present case, the relative Raman peak intensities change considerably with the methane concentrations. The peak intensity at 1350 and 1470 cm^{-1} is higher in the UNCD films deposited at a higher methane concentration (Fig. 3). This clearly suggests the increase of disorder carbon and transpolyacetylene segment of carbon with increase in methane percentage during growth process.

Raman spectroscopy is very much sensitive to sp^2 bonding. However, the relative sensitiveness of near edge X-ray fine structure (NEXAFS) to sp^2 and sp^3 bonding is roughly the same. Therefore NEXAFS studies of all UNCD films were carried out to ascertain the presence of sp^3 phase. The NEXAFS spectra were very much similar to those in earlier studies reported by Xiao et al. [14]. Xiao et al. studied it on UNCD film deposited at various substrate temperatures and the spike of C_{1s} peak intensity decreases with substrate temperature. In the present study, we observe the decrease in the spike C_{1s} core exciton peak intensity at 289.5 eV with increase in methane concentration. Fig. 4 shows the NEXAFS spectra of UNCD films grown at different methane percentages. The decrease of C_{1s} core exciton spike with higher methane concentration indicates global increase of sp^2 bonded carbon in the film. Although, the concentration of the diamond crystallites is strongly methane concentration dependent, the lack of a prominent ~π-π^* plasmon indicates the absence of large and numerous graphitic clusters.

Fig. 5 shows J-V measurement from the UNCD films' growth at different methane concentrations and the corresponding F-N plot in the inset. The onset electric field obtained from UNCD films grown at different methane concentrations is depicted in Fig. 6. The current at the onset field was ~10 μA/cm^2. However, the onset electric field was measured by extrapolating two straight lines in both lower and higher

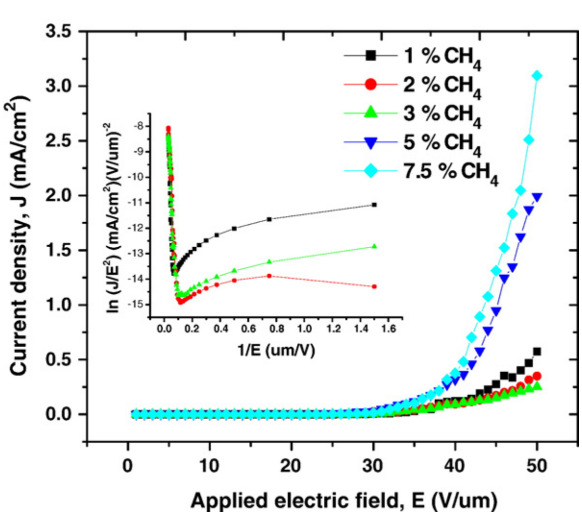

Fig. 5. Current density versus applied voltage from different UNCD films. Inset shows the representative F-N plot for three UNCD films.

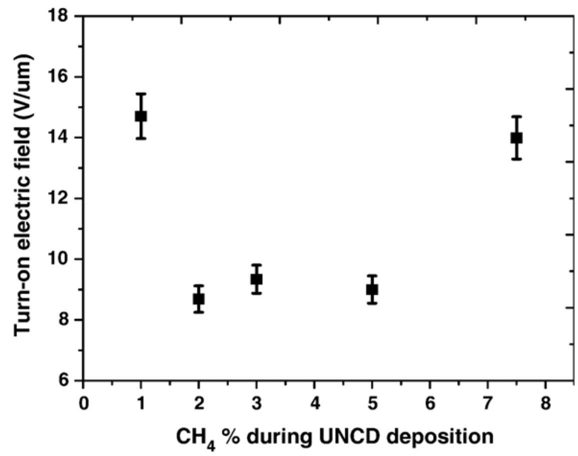

Fig. 6. Onset voltage (E_{to}) from UNCD films versus methane percentage during deposition.

electric fields of F-N plots [15]. The onset field was measured to be less than 10 V/μm from the UNCD films grown at 2–5% methane concentration. However, it is higher than that of films grown at 1% and 7.5% CH_4 concentration. We propose that at lowest methane concentration (1%), electrons do not find enough conduction path and therefore a relatively higher onset electric field. However, at a higher methane concentration (7.5%), grain boundaries contain the graphitic carbon above the optimum value and that leads to a higher onset electric field due to higher work function of graphite (5.0 eV). Cui et al. have described in detail the effect of electron emission on the higher work function of graphic carbon present in the grain boundaries of diamond films [16]. An optimum graphitic content was obtained at 2–5% methane concentration during UNCD deposition for emission at lower onset electric field (<10 V/μm). Wu et al. have also reported that nanodiamond film obtained at 2% CH_4 shows best electron field emission compared to higher methane concentration during growth [5]. However, higher electric current (in mA range) at the onset field in their study is due to growth in N_2 medium. Nonetheless, electric current at the onset field obtained in the present study is higher for polycrystalline diamond films [17] and in the same range for UNCD films. Additionally, we observe the higher emission current (3.1 mA/cm^2) at higher electric field (50 V/μm) from the UNCD film grown at a higher CH_4 (7.5%) concentration. This suggests that, graphitization of films enhances the electron emission behavior [18].

4. Conclusions

Ultrananocrystalline diamond film is deposited at a low substrate temperature (<500 °C). The growth rate and grain size of diamond are found to increase with methane concentration. Raman studies of UNCD film support the increase of disorderliness and transpolyacetylene carbon in the UNCD films grown at higher methane concentrations. This is reconfirmed by NEXAFS measurement with the overall increase of non-diamond carbon. The electron field emission studies demonstrate that the optimum non-diamond contents in the UNCD film is obtained at 2–5% of CH_4 for onset electric field less than 10 V/μm in electron field emission.

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