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Effect of N_2 addition in Ar plasma on the development of microstructure of ultra-nanocrystalline diamond films

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ABSTRACT

The effect of the N_2 and H_2 addition in Ar plasma on the characteristics of the UNCD films was systematically investigated. It is found that, while the N_2/Ar plasma results in UNCD films with ultra-small grains (~5 nm), incorporation of H_2 into the N_2/Ar plasma increased monotonously the size of the grains. Moreover, the diamond grains synthesized in H_2 free plasma are of equi-axed geometry and those grown in H_2-containing plasma are of plate-like one. The optical emission spectroscopic investigation indicated that the increase in electron temperature due to the addition of H_2 into Ar plasma is the main cause, altering the microstructure of the UNCD films. As the H_2 content increases, the spherical diamond grains first agglomerated to form elongated grains, which coalesce to form dendrite clusters. The proportion of grain boundaries is thus decreased that increased the turn-on field necessary for inducing the electron field emission process.

1. Introduction

The properties of materials with nanometer dimensions are significantly different from those of bulk materials. Appropriate control of the 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 of nanocrystalline (NCD) and ultra-nanocrystalline diamond (UNCD) films [1]. The UNCD film possesses many excellent properties and several of them actually exceed those of micro-crystalline diamond [2]. As the diamond grains decrease to a size smaller than 10 nm, the surface smoothness of UNCD films increases markedly making it a promising material for tribological applications [3]. Additionally, the decrease in diamond grain size increases the grain boundaries that contain non-diamond carbons, resulting in significant improvement in electron field emission properties. A very high electron field emission characteristic has been reported from nanodiamond film [4]. The non-diamond contents and the crystal size of diamond grains in the films play a crucial role in applications such as electron field emitters. Unlike the synthesis of MCD films that used H_2-plasma, the growth of UNCD films usually used hydrogen-free plasma [1]. How the processing parameters altered the microstructure of the UNCD films has been widely investigated [5,6] but the results are controversial.

In the present study, we have systematically varied the $H_2/N_2/Ar$ ratio in the plasma during UNCD growth so as to investigate the effect of plasma chemistry on the development of microstructure and the associated electron field emission characteristics. The possible mechanism for the formation of microstructure is discussed based on the observations.

2. Experimental

The UNCD films were deposited using IPLAS microwave plasma enhanced CVD apparatus. N-type mirror polished Si (100) substrates were used to grow diamond films. 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, followed by ultrasonication in diamond powder (30 nm) slurry of methanol. The substrates were again ultrasonically cleaned in deionized water to remove diamond particles sticking onto the surface and then dried by blowing nitrogen gas. The plasma was excited by 1200 W microwave (2.45 GHz) in 100 torr chamber pressure. Total flow rate of the gas mixture is 100 sccm, which contains 1 sccm CH_4, 0–10 sccm H_2 and 5–20 sccm N_2 with the rest of Ar gas. The temperature was measured by placing a K-type thermocouple at the bottom surface of molybdenum substrate holder on which Si substrate was placed. No external heater was used and the substrate temperature was in the range of 460–475 °C due to plasma heating. The UNCD films grown in $(1-x)$Ar–xN_2/CH_4 ($x=0$, 5, 10 and 20%) plasma without the addition of H_2 are designated as N0, N5, N10 and N20 films (N-series), respectively, whereas those grown in

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$(0.95Ar–0.05N_2)_{1-y}(H_2)_y/CH_4$ ($y = 0$, 3.5, 5 and 10%) are designated as H0, H3, H5 and H10 (H-series), respectively.

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. Electron field emission properties were measured using a parallel plate setup. The measurements were carried out under a low 10^{-6} torr ambient pressure. The movement of the anode tip (1 mm diameter) was adjusted by a micrometer and the gap between emitter and collector was measured by an optical microscope. The current–voltage characteristics were acquired using a Kethley 237 electrosource unit and analyzed using Fowler–Nordheim model [7,8].

3. Results and discussion

The effect of N_2 addition in the CH_4(1%)/Ar plasma (without H_2) was examined first. SEM micrographs shown in Fig. 1 indicate that the morphology of the UNCD films insignificantly varies with the nitrogen concentration in the plasma. All the films contain ultra-small equi-axed grains with very uniform grain size distribution. However, the incorporation of N_2 into the Ar plasma markedly influences the electron field emission properties of the UNCD films, which will be discussed shortly. Fig. 2(a) reveals that the Raman peaks are very diffuse and no sharp D-band (at 1333 cm^{-1}) was observable, which can be ascribed to the smallness of the grain size in these films [9,10]. The Raman peaks were fitted with Lorentian distribution function. The Raman peaks at around 1144 cm^{-1} (υ_1-band) and 1480 cm^{-1} (υ_2-band) are assigned as vibrations from trans-polyacetylene groups presenting at the grain boundaries [11]. The 1220 cm^{-1} (D'-band) Raman peak is assigned as disordered sp^3 bonds and the 1580 cm^{-1} (G-band) is assigned as graphite peak [12]. There also appears a shoulder (G^*-band) near 1600 cm^{-1}, which is assigned as amorphous graphite [12]. Raman spectroscopy also indicates that the crystallinity of the films is not changing with the N_2-content in the plasma. However, there is subtle increase in G^*/G ratio for N20 samples, as compared with the N5 and N10 samples, indicating that the N20 samples contain more disordered phase. Such a characteristic will be more detailed investigated by transmission electron microscopy shortly.

Fig. 3(a) shows that the EFE properties of N-series UNCD films, where the EFE parameters, including the turn-on field and EFE current density, were extracted from these J–E curves and were listed in Table 1 to facilitate the comparison. This figure reveals that all the UNCD films exhibit good electron field emission properties. The turn-on field for inducing the EFE process is around $(E_0)_{N5} = 9.3$ V/μm for N5 films and increases with the N_2-content, reaching $(E_0)_{N20} = 21.3$ V/μm for N20 films. The EFE current density at 30 V/μm decreases from $(J_e)_{N5} > 6$ mA/cm^2 for N5 films to $(J_e)_{N20} < 0.012$ mA/cm^2 for N20 films. Such a behavior is contrary to the previous observation by Chen et al. [13], in which, the EFE properties of the nitrogen-doped UNCD films increased with the amount of nitrogen incorporated in the plasma. The possible explanation is that Chen's UNCD films were grown at high temperature (~800 °C), whereas the UNCD films shown in Fig. 3(a) were grown without heater and the substrate temperature was only around 400–500 °C.

To understand the way that the incorporation of N_2 into Ar plasma modifies the EFE behavior of the UNCD films, the microstructure of these films was detailed investigated. Fig. 4 shows typical TEM micrographs for N20 samples, indicating that, besides the equi-axed grains (~5 nm) with uniform size distribution (region 1), there exists some region which are amorphous (region 2). The proportion of amorphous phase increases with the N_2 content in the plasma. Such an observation indicates that the N_2 added in the plasma at such a low substrate temperature was not efficiently incorporated into the UNCD materials. On the contrary, the presence of N_2 in the plasma hindered the crystallization of the UNCD grains. Such an observation is in accord with the Raman spectroscopy for N20 samples (cf. Fig. 2(a)). It is believed that the presence of amorphous phase in the diamond grains is the cause degrading the EFE properties for the films.

How the addition of N_2 into the plasma alters the microstructure of the UNCD films was examined using the optical emission spectroscopy [14,15]. Fig. 5(a) shows that the plasma mainly consists of neutral and excited Ar species and C_2 species (469 and 515 nm). There also exists CN band near 389 nm. The spectral lines shown in Fig. 5 are listed in Table 2. The increase in nitrogen content does not markedly alter these characteristics, except that the CN band (~389 nm) increases in intensity with the N_2 content. The increase in CN band

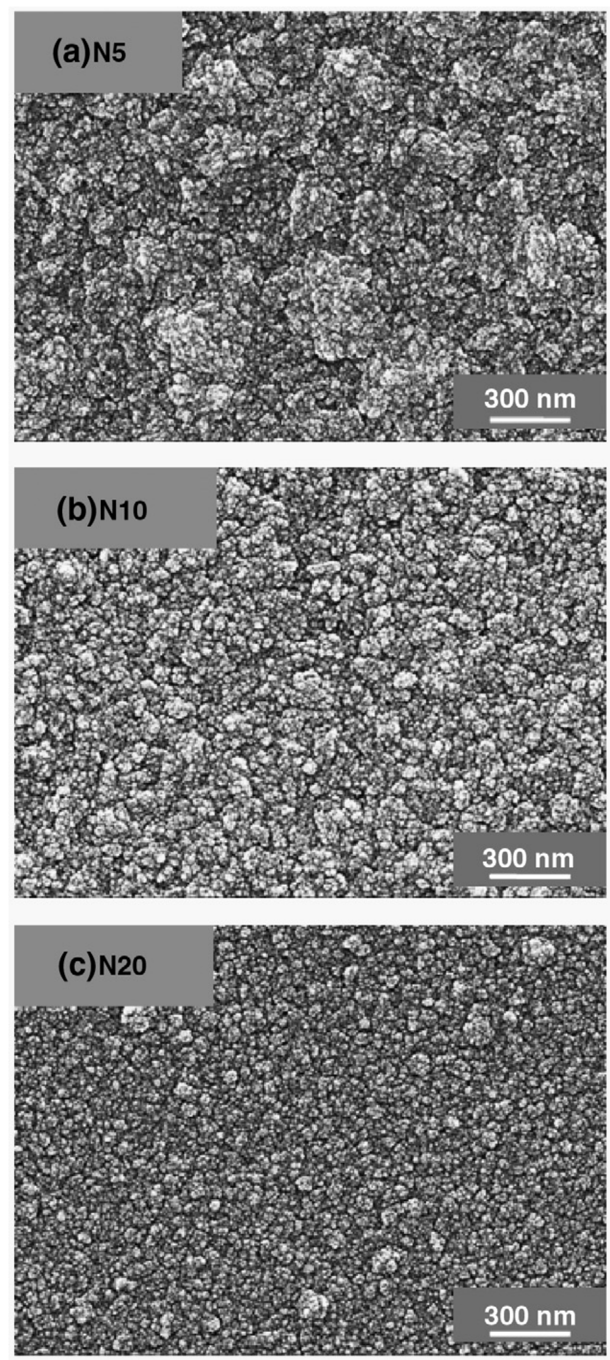

Fig. 1. The SEM micrographs of N-series UNCD samples, which were grown in $(1-x)$ Ar–xN_2/CH_4 plasma with $x =$ (a) 5, (b) 10 and (c) 20%.