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The induction of a graphite-like phase by Fe-coating/post-annealing process to improve the electron field emission properties of ultrananocrystalline diamond films ☆

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ABSTRACT

The electron field emission (EFE) process for ultrananocrystalline diamond (UNCD) films was tremendously enhanced by Fe-coating and post-annealing processes. The extent of enhancement changes with the granular structure of the UNCD films and the post-annealing conditions (temperature and atmosphere). The best EFE properties are obtained by post-annealing the films at 900 °C in an H_2 environment for 5 min. The EFE behavior of the films can be turned on at $E_0 = 1.28$ V/μm, attaining a large EFE current density of 772 μA/cm^2 at an applied field of 8.8 V/μm. Microstructural analysis indicates that the mechanism for the improvement in the EFE process is the formation of graphene-like phase (a-few-layer graphite) with good crystallinity, surrounding the Fe (or Fe_3C) nanoclusters. Presumably, the nanographites were formed via the reaction of Fe-clusters with diamond films, viz. the Fe-clusters dissolved the carbons in the diamond grains and the re-precipitated them on the surface of the other side of clusters, a process similar to the growth of carbon nanotubes via Fe clusters as catalyst.

1. Introduction

Diamond films possess many desirable physical and chemical properties [1–3] and have been the focus of intensive research since the successful synthesis of diamonds in the low pressure and low temperature chemical vapor deposition (CVD) process [4]. Due to the negative electron affinity (NEA) [5,6] characteristics of the reconstructed (100) surface of diamond films, the diamond is considered to have great potential for applications as electron field emitters [7]. Generally, a good electron field emitter requires a sufficient supply of electrons from the back contact of materials, effective transport of electrons through the films and efficient emission from the film surface. The large electronic band gap (5.45 eV) of diamond films hinders their electron field emission (EFE) behavior tremendously due to the lack of conducting electrons required for field emission. Doping the diamond films with boron or nitrogen species provides abundant interband energy levels, which have been observed to markedly enhance both the supply of electrons and facilitate the transport of electrons and hence improve the EFE properties of the materials [8–12]. However, the EFE properties for these diamonds are still not satisfactory due to the fact that most of the emitting surfaces do not possess NEA characteristics because they are not re-constructed (100) or H-terminated surfaces. Modification on the surface characteristics of diamond to enhance the EFE process has thus been the main focus of research [5,13–15]. Among various approaches, a thin metallic coating was observed to influence the EFE properties of diamond films prominently [14]. Post-treatment in an environment containing Fe species was also observed to tremendously improve the EFE properties of microcrystalline diamond [15,16], but the related effect on the ultrananocrystalline diamond (UNCD) films is not clear.

In this paper, the effect of Fe-coating and post-annealing processes on the surface characteristics and the EFE behavior of UNCD films was systematically examined. Transmission electron microscopy (TEM) was used to investigate the microstructure of the films, and the possible mechanism is discussed based on the observations.

2. Experimentals

The diamond films were grown on a p-type silicon substrate by a microwave plasma enhanced CVD (MPE-CVD) process. The substrates were first thoroughly cleaned by rinsing the Si wafer sequentially in water-diluted hydrogen peroxide/ammonium hydroxide and hydrogen peroxide/hydrochloric acid solution. The cleaned Si-substrates were then ultrasonicated in a methanol solution containing nano-sized diamond powders and Ti-powders (<32.5 nm) for 45 min. The substrates were ultrasonicated again in methanol to remove the nano-particles, which were possibly adhered on the Si-substrates. The UNCD films were grown in a $CH_4/H_2/Ar = 4/0/196$ or 4/12/184

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sccm plasma, excited by a 1200 W (2.45 GHz) microwave with a 150 torr total pressure for 1 h. Thus obtained diamond films were designated as $UNCD_I$ and $UNCD_{II}$ films, respectively. The UNCD films were then coated with a thin layer of Fe by a DC sputtering process for 1 min to a thickness around 5 nm. They were then thermally post-annealed in an NH_3 (or H_2) atmosphere (100 sccm) for 5 min with heating and cooling rates of 15 °C/min. These films were designated as $(Fe/UNCD_I)_{an}$ and $(Fe/UNCD_{II})_{an}$ films, respectively.

The morphology and structure of the films were investigated using scanning electron microscopy (SEM, Joel JSM-6500 F) and Raman spectroscopy (Renishaw inVia Raman microscopes), respectively. The detailed microstructure was examined using transmission electron microscopy (TEM, Joel 2100). The EFE properties of the diamond films were measured using a parallel plate setup, in which the cathode-to-anode distance was set by a fixed spacer (125 μm) and the current–voltage (I–V) characteristics were acquired by a Keithley 2410 at 10^{-6} torr. The EFE properties were analyzed by the Fowler–Nordheim (F–N) model [17], and the turn-on field was designated as the interception of the lines extrapolated from the high-field and low-field segments of the F-N plots.

3. Results and discussion

Fig. 1(a) and (b) show the SEM morphology of $UNCD_I$ and $UNCD_{II}$ films, respectively, indicating that the UNCD films are conformally deposited on the Si-substrate. There is no pinholes or voids on the UNCD films. Both of the UNCD films contain ultra-small grains with equi-axised geometry. However, detail examination using TEM reveals a subtle difference in granular structure of the two films. Fig. 1(c) shows that the $UNCD_I$ films grown using $CH_4/0\%H_2/Ar$ plasma contain equi-axised diamond grains about 5 nm in size, whereas Fig. 1(d) indicates that the $UNCD_{II}$ films grown using hydrogen containing plasma ($CH_4/6\%H_2/Ar$) contain diamond rods about 100 nm in size.

Fig. 2(a) shows the EFE properties of the $UNCD_I$ and $UNCD_{II}$ films with the inset showing the F–N plots, from which the turn-on field was deduced. This figure indicates that the $UNCD_I$ films can be turned on at 2.2 V/μm, attaining EFE current density of $Je = 9.0\ \mu A/cm^2$ at an applied field of 8.8 V/μm, whereas the $UNCD_{II}$ films can be turned on at 3.9 V/μm, achieving $Je = 5\ \mu A/cm^2$ at the same applied field (8.8 V/μm). The addition of H_2 (6%) into the films results in slight degradation on the EFE properties. The coating a thin layer of Fe (~5 nm) almost completely suppressed the EFE properties of the films (not shown). Raman spectra shows in Fig. 2(b) reveals that both films contain typical Raman resonance peaks of the UNCD films. The Raman resonance peaks are very broad due to the smallness in the diamond grains [18]. Generally, the Raman spectra contain υ_1-band ($1140\ cm^{-1}$) and υ_2-band ($1480\ cm^{-1}$), which represents transpolyacetylene along the grain boundaries [19], and the D*-band ($1350\ cm^{-1}$) and G-band ($1580\ cm^{-1}$), which represents disordered carbon and graphitic phase contained in the UNCD films [20]. The Raman characteristics were not changed due to Fe-coating (not shown).

Post-annealing processes after Fe-coating markedly improved the EFE properties for the UNCD films. Fig. 3 indicates that the extent of enhancement varies with the granular structure of the UNCD films and the parameters (temperature and atmosphere) used for post-annealing the samples. To more clearly illustrate the Fe-coating/post-annealing effect on improving the EFE properties of these films, the important EFE parameters, the turn-on field (E_0) and EFE current density (J_e, at an applied field of 8.8 V/μm) were extracted from these J-E curves and were plotted in Fig. 4 against the post-annealing temperature (T_a). Fig. 4(a) and (b) show, respectively, the variation of E_0- and J_e- values with respect to T_a, where the E_0 and J_e of the starting materials ($UNCD_I$ and $UNCD_{II}$ films) were plotted as dotted lines to facilitate the comparison. Generally, in the range of post-annealing temperature of interest, the turn-on field (E_0) decreases, whereas the EFE current density (J_e) increases,

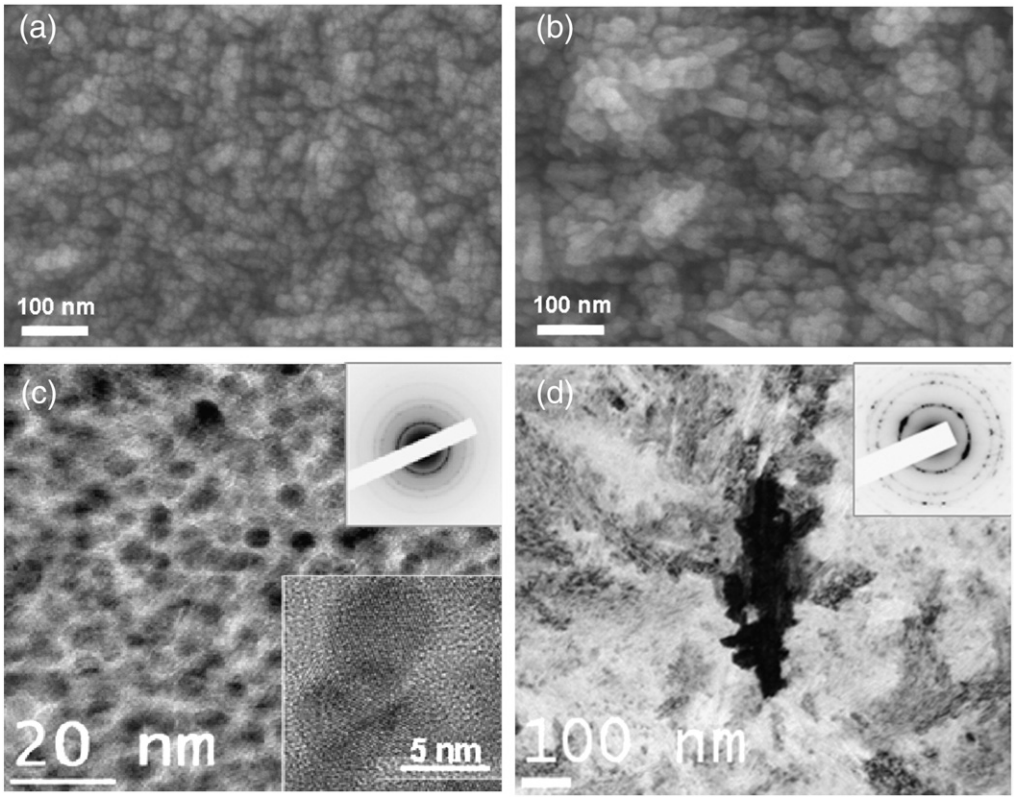

Fig. 1. (a, b) The SEM micrograph and (c, d) the TEM micrograph of the as-grown UNCD films, which were grown in $CH_4/H_2/Ar$ plasma with $H_2 = 0\%$, $UNCD_I$ (a, c) or $H_2 = 6\%$, $UNCD_{II}$ (b, d).