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The microstructural evolution of ultrananocrystalline diamond films due to P ion implantation and annealing process-dosage effect

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ABSTRACT

The effect of microstructural evolution on the electrical properties of UNCD films, which were P-ion implanted and annealed, was systematically investigated. The electrical resistivity of the UNCD films was markedly lowered when the UNCD films were implanted with P-ions of sufficient dosage ($>1 \times 10^{14}$ ions/cm^2) and followed by annealing at 800 °C for 30 min, but the electronic field emission (EFE) behavior was not enhanced. The incident P-ions mainly alter the granular structure of the region in UNCD films where the P-ions reside, the "interacting zone", which is found at about 300 nm beneath the surface of the films. In this "interacting zone", coalescence of diamond grains occurred and the nano-graphitic clusters were induced, forming interconnected graphitic filaments and resulting in the decrease in surface resistance. However, the UNCD-to-Si interfacial resistance remained at large value that hindered the efficiency for the electron transport crossing the interface of the UNCD films. These microstructural evolution processes account for very well the phenomenon that in spite of enhanced conductivity of the UNCD films along the film's surface due to P-ion implantation and annealing processes, the EFE properties for these UNCD films were not improved.

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1. Introduction

Diamond films have been studied extensively for their application as electron field emitters because of their negative electron affinity and low effective work function [1,2]. While the physical properties of diamond films depend on the crystallinity of the materials, their electrical and optical characteristics are mostly associated to the microstructure of the films [3–7]. Ultrananocrystalline diamond (UNCD) film is a special form of diamond film that has attracted tremendous attention from researchers because of its exclusive granular structure [8,9]. UNCD films have ultra-small diamond grains (5–10 nm) with smooth surface characteristics. The grains of the UNCD films have an sp^3 character and the grain boundaries are composed of a mixture of sp^2, sp^3, hydrocarbon and amorphous carbon (*a-C*) phases, of which the sp^2 phase is predominant [10,11]. Because of the superb electron field emission (EFE) behavior of UNCD films as compared with that of other forms of diamond films (e.g. microcrystalline or nanocrystalline), UNCD films show marvelous potential for applications such as cold cathode field emitters and other vacuum microelectronic devices [11,12].

The enormous guarantee that the diamond or the UNCD films bear as a material for the fabrication of cold cathode emitting devices entails the films to be conductive. Incorporation of N_2 into the growth plasma of UNCD films gives rise to the conversion of *a-C* phase to graphite phase at the grain boundaries, increasing the number of conduction paths in the material and hence efficiently advancing the electrical conductivity and EFE properties of the films. [10–13] However, N_2 incorporation via the addition of N_2 gas to the growth plasma requires high growth temperature (700 °C) [13]. On the other hand, ion implantation has long been utilized to amend the properties of materials through controlled doping, using select dopants [14–17]. Recent reports show that oxygen and phosphorous ion implantation result in the n-type conductivity of the UNCD films [16,17]. But the possible contribution on the electrical properties of the films related to the modification of granular structure has not been well explained yet.

In this paper, the effects of P-ion implantations/annealing processes on the microstructural evolution of UNCD films have been in-depth-investigated using transmission electron microscopy (TEM). Moreover, the mechanism, which modified the conductivity and the EFE characteristics of ion implanted UNCD films, has been explained from a microscopic viewpoint.

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2. Experiments

The UNCD films with ultrasmooth surface characteristics at the nanoscale are prepared for the ion implantation by growing them on *n*-type silicon substrates, using the microwave plasma-enhanced chemical vapor deposition (MPECVD) process (IPLAS-Cyrannus). Prior to the growth of the UNCD films, the substrates are processed by ultrasonication in methanol solution containing a mixture of nanodiamond powders and titanium powders, for 45 min. The deposition of UNCD on substrates is carried out in a CH_4(1%)/Ar plasma with 1200 W and at 150 Torr. The growth process is carried out at low temperatures (465 °C), without heating the substrate, for 120 min to reach a thickness of 600 nm. The thickness of the films is confirmed from the cross-sectional field emission scanning electron microscopy (FESEM, Jeol 6500) image (figure not shown). The UNCD films are then implanted with phosphor at 450 keV kinetic energy to a dosage of 1×10^{13} to 1×10^{15} ions/cm^2 at room temperature and at a pressure of 5×10^{-6} Torr with (HVEE 500 kV Implantor). The TRIM computer code [18] is used to simulate the trajectory of P-ions in the UNCD films. The penetration depth for P-ions of 450 keV kinetic energy in the UNCD films is estimated to be around 300 nm. After implantation, the samples are annealed at 800 °C for 30 min in a H_2 (10%/N_2) medium. The UNCD films are designated as a-UNCD for 1×10^{13}, b-UNCD for 5×10^{13}, c-UNCD for 1×10^{14}, d-UNCD for 5×10^{14}, e-UNCD for 5×10^{15} ions/cm^2 P-ion implanted/annealed samples.

The surface morphology and bonding of the films were analyzed using SEM and Raman spectroscopy (Renishaw, andXPS (PHI, 1600), respectively, whereas the microstructure and local bonding structure of the films are examined using transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS), respectively. The resistivity of the films is ascertained by a four-probe technique, in which the resistance along the films' surface, the "surface resistance", is measured with all the 4 probes placed on the surface of the film and the resistance across the UNCD-to-Si interface, termed as the "interface resistance", is characterized with 2 of the probes placed on the surface of the films while the other 2 probes are placed on the Si surface (the UNCD films in this surface are scratched off). The electron field emission (EFE) properties of the films are measured using a home-made tunable parallel plate setup, where a molybdenum rod of 2 mm diameter is used as the anode. The anode to cathode separation is controlled by a micrometer. A Keithley 2410 electrometer is used to acquire the current densities versus electrical field (J_e–E) characteristics and the data is analyzed by Fowler–Nordheim (F–N) theory [19].

3. Results and discussion

3.1. The materials characteristics and the electrical properties

The SEM images in Fig. 1 show the morphologies of the UNCD films. The pristine UNCD films contain ultra-small grains with a very smooth surface (Fig. 1(a)), whereas implantation of P-ions at a dosage of 1×10^{14} ions/cm^2 smoothened the surface, rendering it featureless (not shown). The granular structure turned out again due to annealing of the P-ion implanted UNCD films (Fig. 1(b)). The increase in dosage for P-ion implantation processes does not markedly alter such characteristics (Fig. 1(c) and (d)). The secondary ion mass spectrometry (SIMS) profile of the as P-ion implanted UNCD films confirms that the P-ions mainly reside at about 300 nm beneath the film's surface (not shown), which is in accord with the TRIM-code simulation. Fig. 2(a) shows the effect of P-ion implantation/annealing on the Raman spectroscopic studies of the UNCD films. Curve "0" in Fig. 2(a) shows that the pristine UNCD films contain mainly a D*-band at ~1350 cm^{-1}, a G-band at ~1580 cm^{-1}, a ν_1-band at ~1140 cm^{-1} and a ν_3-band at ~1480 cm^{-1}. The small size of the diamond grains in the UNCD films gives rise to very broad Raman resonance peaks [20,21]. The D*- and G-Raman resonance peaks represent the sp^2-bonded carbons, i.e., the disordered

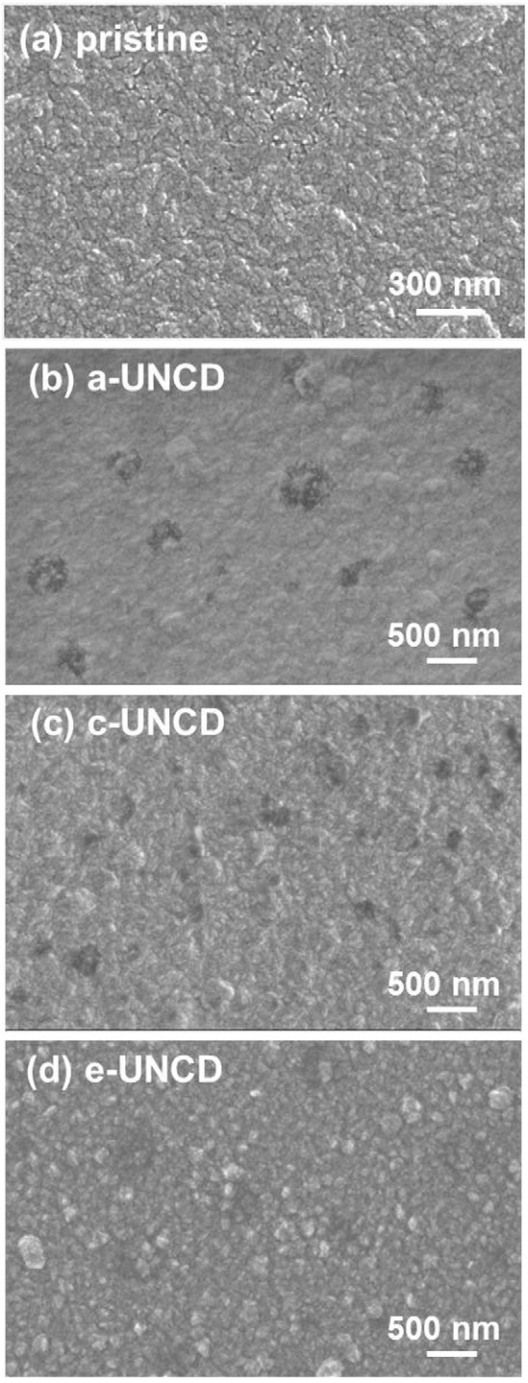

Fig. 1. The SEM micrographs of (a) pristine, (b, c and d) P-ions implanted/800 °C-annealed UNCD films. The dosage of P-ions are (b) 1×10^{13} ions/cm^2, (c) 1×10^{14} ions/cm^2 and (d) 1×10^{15} ions/cm^2.

carbon and graphite, whereas ν_1- and ν_3-bands represent the transpolyacetylene phase [20,21], which is presumably located along the grain boundaries. The typical Γ_{2g} resonance peak near 1332 cm^{-1} (D-band) for the diamond lattices is barely observable. However, the invisibility of the D-band resonance peak does not mean that the materials contain no sp^3-bonded carbon. It is due to the fact that the Raman signal is overwhelmingly more sensitive to the sp^2-bonded carbon than that to the sp^3-bonded ones. Low dosage P-ion implantation ($<1 \times 10^{14}$ ions/cm^2, c-UNCD) does not alter such Raman characteristics (curves I to III, Fig. 2(a)). The Raman peaks were markedly suppressed when the dosage of P-ion implantation was increased larger than 5×10^{14} ions/cm^2 (curves IV to V, Fig. 2(a)), resulting in a large G-band

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