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Enhancement of field emission properties in nanocrystalline diamond films upon 100 MeV silver ion irradiation

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ABSTRACT

Enhanced field emission is observed in nanocrystalline diamond (NCD) films upon irradiation with 100 MeV Ag^{9+} ions in the range of fluences from 5×10^{10} to 5×10^{11} ions/cm^2. Field emission characteristics monotonically changes with the ion beam fluence, but does not show any correlation with sp^2 cluster size induced. Enhancement of field emission is presumed to result from the formation of interconnected sp^2 cluster network. The turn-on field (E_0) for inducing the electron field emission (EFE) has been lowered from 28 to 3.2 V/μm, whereas the EFE current density has been increased from 1.4×10^{-6} to 2.086 mA/cm^2. Such EFE properties are comparable with those of carbon nanotubes.

1. Introduction

Diamond films have been extensively investigated for their application as electron field emitters owing to their negative electron affinity and low effective work function [1,2]. While the film properties are found to depend on the microstructure, it is the structure of the grain boundaries which mainly determines the electrical and optical characteristics of the films [3]. When moving from microcrystalline diamond towards nanocrystalline diamond (NCD), decreasing the grain size, the amount of the graphitic inclusions in the grain boundaries decreases [4] and the H content in the grain boundaries increases [3,5]. With respect to electrical properties, sp^2-bonded carbon within the CVD diamond films can be thought of as a conduction promoter, particularly if the sp^2 forms interconnected networks of bonds along which electrons are free to move [6]. Hydrogen is also thought to be located at the grain boundaries since atomic hydrogen can easily react with carbon atoms and form dangling bonds in the grain boundaries during the film growing process, which can then saturate these dangling bonds [6]. Hydrogen remaining within the structure after diamond growth can also play a strong role in conductivity, potentially to increase or decrease conductivity of the resulting structure. There are studies of hydrogen retention and bonding [5,7], conductivity [8], field emission [9,10] of diamond films as a function of grain size.

The sp^2-carbon and hydrogen content are strongly dependent on the growth process. While the hydrogen content in the diamond films can be controlled by post-annealing process, the control on the proportion of sp^2-bonds is not as reliable. Irradiation by energetic heavy ions into the diamond films can break the C–C bonds under controlled manner and, therefore, an efficient and reliable way for controlling the proportion of sp^2-bonds in the materials. There are many reports that discuss the effects of ion beam irradiation effects on type IIa diamond [11], diamond like carbon film [12], taC [13], polycrystalline CVD diamond [14–16], graphite [17] etc. Pandey et al [18] and Koinkar et al.[19] have studied the field emission enhancement by swift heavy ions in CVD diamond. Here we report the effect of 100 MeV silver ion irradiation on changing the morphology and altering the sp^2-bond content, so as to improve the electron field emission properties of the diamond films. The possible mechanism is also discussed.

2. Experimental details

Nanocrystalline diamond (NCD) films of ~1 μm thickness (growth time 90 min) were grown on p-type silicon substrates by the microwave plasma-enhanced chemical vapor deposition process (MPECVD) using an ASTex 5400 reactor [20] at CH_4/H_2 flow rates of 1 sccm/99 sccm and 5 sccm/95 sccm, which were designated as NCD_I and NCD_{II}, respectively. The gas mixture was excited by 1500 W microwaves (2.45 GHz), while the total pressure in the chamber was maintained at 55 Torr. The diamond films were subjected to heavy ion irradiation using 100 MeV Ag^{9+} ions from 15 MV Pelletron accelerator at Inter-University Accelerator Centre, New Delhi, India [16,18,19]. 100 MeV silver ions have a projected range of 7.68 μm and longitudinal straggling of 230.3 nm as simulated with SRIM-2008 [21]. At this energy the ions pass through the diamond films in all the samples and get buried deep into the substrate. The ions have an electronic energy loss of 2.194×10^4 eV/nm and nuclear

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energy loss of 93.18 eV/nm [21]. Electronic energy loss is predominant at this energy and the ions will loose energy by electronic exitations in diamond and the lattice damage effects of nuclear energy loss will be minimum. The current was ~1 particle-nanoampere (pnA) which is equivalent to 6.2×10^{9} ions/s. The samples were mounted inside the scattering chamber which was evacuated to base pressure of 1×10^{-6} Torr. The samples were irradiated with fluences of 5×10^{10} and 5×10^{11} ions/cm^2. The films were characterized using scanning electron microscopy (SEM: JEOL JSM-6500F at 15 kV and Raman spectroscopy (Renishaw, 514.5 nm). Electron Field Emission (EFE) properties of the diamond films were measured with a tunable parallel plate set-up, in which the sample-to-anode distance was varied using a micrometer. The current–voltage (*I–V*) characteristics were measured using an electrometer (Keithley 237) under pressures below 10^{-6} Torr. The EFE parameters were extracted from the obtained *I–V* curves by using the Fowler–Nordheim model [22]. The maximum available voltage of the set-up is 1100 V, and the current was restricted to 10 mA. The turn-on field was designated as the intersection of the lines extrapolated from the low field and high field segments of the Fowler–Nordheim plot.

3. Results and discussion

Fig. 1(a) and (b) shows, respectively, scanning electron microscopic images for NCD_I (99% H_2) and NCD_{II} (95% H_2) samples. The NCD_I sample contains grains of sizes less than 250 nm and roundish in morphology, whereas the NCD_{II} sample consists of grains about twice as large (i.e. ~500 nm) and faceted in geometry. These results imply that the NCD_I grains contain larger proportion of amorphous or are more defective, as compared with the NCD_{II} grains. Fig. 2 shows Raman spectra for as-deposited NCD_I and NCD_{II} films. The Raman peaks are fitted with Lorentzian peaks around 1144 (υ_1), 1220 (D′), 1333 (D), 1343 (D*), 1480 (υ_2) and 1580 (G) cm^{-1}. Both of the films show sharp 1333 cm^{-1} Raman peak (D-band) corresponding to *F2g* zone center optical phonon of diamond, indicating that both films are basically sp^3-bonded. The

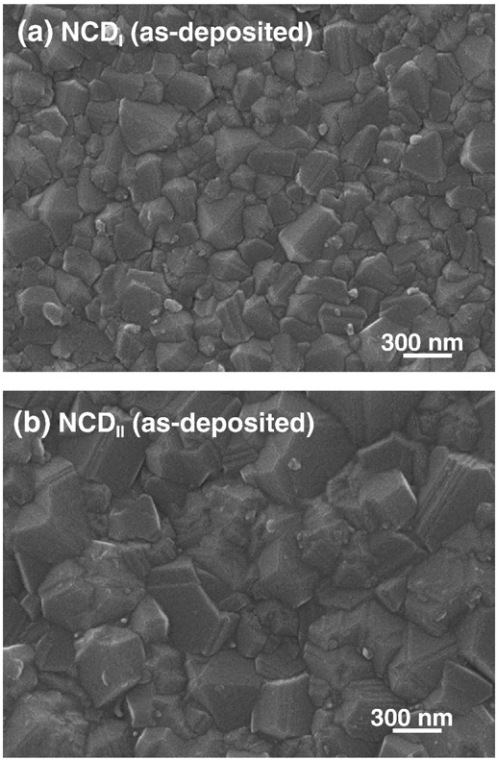

Fig. 1. SEM micrographs of as-deposited (a) NCD_I films, which were grown under 99% H_2 (1% CH_4) and (b) NCD_{II} films, which were grown under 95% H_2 (5% CH_4).

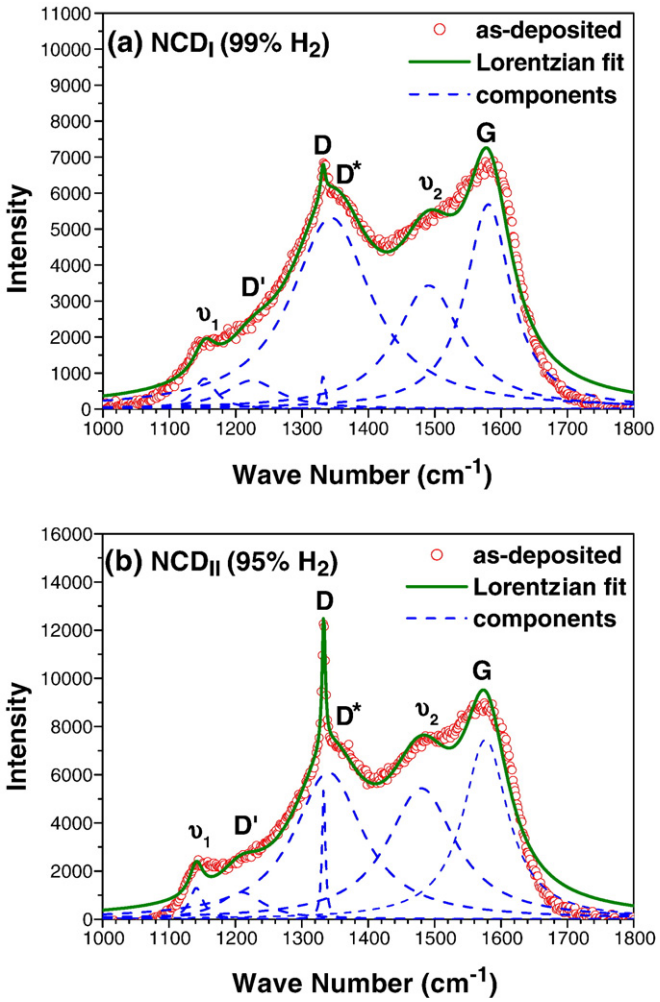

Fig. 2. Raman spectra from as-deposited (a) NCD_I and (b) NCD_{II} samples. Lorentzian peak fitting along with the components are shown with corresponding peaks labeled.

1144 cm^{-1} (υ_1-band) and 1480 cm^{-1} (υ_2-band) Raman peaks are assigned to vibrations from trans-ployacetelene groups present at the grain boundaries [23]. The 1220 cm^{-1} (D*-band) Raman peak is assigned to disordered sp^3 bonds and the 1580 cm^{-1} (G-band) corresponds to graphite peak [24]. This figure reveals that the diamond peak (D-band) is much smaller in intensity and the non-diamond Raman peaks (D′, D* and G-bands) are much more pronounced for NCD_I sample, implying that the grains are more imperfect for NCD_I samples. This is in accord with the SEM image (cf. Fig. 1).

Fig. 3 shows the electron field emission (EFE) characteristics of the as-deposited NCD films (closed circles). The data are analysed by applying Fowler–Nordheim (FN) equation and the F–N plots are shown as insets in this figure. The high field segment of the F–N plot fits with a straight line, indicating that the F–N model can explain these EFE characteristics very well. The details of the field emission parameters, such as turn on field (E_0) and EFE current density (J_e) are given in Table 1. For the as-deposited NCD_I films, the turn-on field is 16 V/μm which is lower than that of as-deposited NCD_{II} samples (28 V/μm). Probably the smaller and more defective grains in NCD_I films will have higher proportion of grain boundaries and more abundant intermediate energy levels, giving raise to better field emission behavior. However, both of the as-deposited NCD samples possess very small EFE current density of 1.6×10^{-6} mA/cm^2 at the applied field of 9 V/μm.

The 100 MeV Ag^{9+} ion irradiation has markedly improved the EFE characteristics of these NCD samples. The turn-on field is found to