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Effect of surface treatment on the electron field emission property of nano-diamond films

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Abstract

Nano-diamond films having grain size around 20 nm were deposited by bias enhanced growth (BEG) method. Different surface treatments were carried out to increase their field emission properties and their effects are clearly noticed. Surface morphology of different surface treated nano-diamond films was examined. There was no significant change in the curve of Raman spectra of different surface treated samples. Raman spectra were typically of similar nature to nano-diamond film. Field emission results were more interesting. Biased in hydrogen plasma treated nano-diamond film has shown best electron emission behavior and low turn-on-field (E_0). The turn-on-field of bias-treated nano-diamond film was 19.5 V/μm. The decrease of turn-on-field (~6 V/μm) of biased treated nano-diamond film from as-grown BEG film was attributed to the formation of thin sp^2 layer and more defects on the surface of film by hydrogen ion bombardment. Moreover, hydrogen-plasma treated nano-diamond film was also found to be good for electron emission but there was no improvement in electron emission as in the case of air plasma treated nano-diamond films.

Keywords: Electron field emission; Nano-diamond; Surface treatment; Boron doping

1. Introduction

Due to its wide viewing angle and low response time, field emission displays (FED) have a potential market for display industry and it can capture the present day's liquid crystal display market [1]. The prime requirement in FEDs has been an efficient and stable cold cathode material. An efficient cold cathode material has low turn-on-voltage with adequate electron emission, which reduces operating voltage thereby power consumption of device to make it more cost effective. Diamond is one of the most preferred electron emitting materials due to its low or negative electron affinity [2], superior mechanical [3] and chemical properties [4]. Diamond films grown in a chemical vapour deposition (CVD) process can easily be fabricated to FED in comparison to fabrication of a cathode having an array of sharp tip from metals or semiconductors. The electron field emission properties from the microcrystalline diamond surface have been studied widely and well understood [5]. High field emission behavior with a turn-on field as low as 3.3 V/μm from nitrogen doped nano-diamond thin film has been reported [6]. Smaller grain size of diamond resulting in improvement of electron field emission property. This phenomenon may due to larger proportion of grain boundary, which contains graphitic carbon and increases conductivity of nano-diamond films [7].

It is well recognized that surface of diamond films plays important role in the emission characteristics. When the surface of diamond film is bonded with different atoms, the resulting band structure below the surface is also altered and changes the emission properties. However, no systematic research has been conducted on the effect of different surface treatment on emission of electron in nano-diamond thin films.

In our current work, field emission behaviors of different surface treatments of nano-diamond films have been studied. Nano-diamond films were subjected to three different surface treatments as follows: (1) negative biasing in hydrogen plasma for forming a thin sp^2 layer on as-grown nano-diamond film by

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hydrogen ion bombardment (2) hydrogen plasma treatment to obtain a H-terminated surface and (3) air plasma treatment to obtain an O-terminated surface. Our previous result has shown a substantial increase of field emission properties by decreasing of grain size of diamond in nano-diamond films [8]. Therefore, surface treatment of nano-diamond film was also carried out and their field emission property is compared with as-grown and surface treated nano-diamond films.

2. Experimental

The nano-diamond films were grown using a 2.45 GHz ASTeX 5400 microwave plasma enhanced chemical vapor deposition (MPECVD) system on p-type mirror polished Si (100) substrates by bias enhanced growth (BEG) in methane–hydrogen plasma (CH_4/H_2: 15%) for 10 min. A microwave power of 1.5 kW, total pressure of 55 Torr and 300 sccm H_2 flow rate, temperature about 850 °C were used during continuous negative bias (−125 V) to produce nano-diamond film on silicon surface. The as-grown nano-diamond film was divided into four parts. One part of as-grown nano-diamond film was kept for comparison and the other three parts were subjected to three different post-treatment processes to study their field emission properties. In the first method, we have applied negative bias again to the as-grown nano-diamond film under hydrogen plasma to create a thin layer of sp^2 layer by hydrogen ion bombardment. This biasing was carried out for 2 min at −100 V, 1.5 kW MW power, 55 Torr pressure and 100 sccm H_2 flow, temperature about 800 °C. In the second method, the as-grown nano-diamond film was placed in hydrogen plasma for 30 min at microwave power of 900 W, 30 Torr pressure and 50 sccm H_2 flow, temperature was about 600 °C to get a H-terminated diamond surface. In similar way, as-grown nano-diamond film was kept in mixture of oxygen (10 sccm) and nitrogen plasma (40 sccm) for 2 min at microwave power of 600 W, 0.6 Torr pressure, temperature about 250 °C to obtain oxygen-terminated nano-diamond surface. Both the oxygen and hydrogen plasma treatment was done in IPLAS CYRANNUS-I system.

Surface morphology of nano-diamond films was examined using a field emission scanning electron microscope (JEOL 6010) operated at 15 kV accelerating voltage. Crystal quality of nano-diamond films was investigated by micro-focused Raman spectroscopy system using 514.5 nm argon laser beam (Renishaw). Field emission characteristics of the prepared nano-diamond films were measured with Keithley 237 electrometer.

3. Results and discussion

Bias enhanced nucleation (BEN) in CH_4-H_2 plasma is one of the most widely used nucleating techniques for the growth of diamond films [9,10]. Several authors have proposed the growth of nano-diamond phase by extending BEN to bias enhanced growth (BEG) process [11]. The formation of nano-diamond phase on silicon acts as nucleation center for the growth of either nano-crystalline diamond or microcrystalline depending on the deposition parameters used. In the present study, we have used the same BEG method to grow nano-diamond films for studying field emission properties with different surface treatments. Fig. 1 shows the SEM image of as-grown nano-diamond film obtained after 10 min BEG in a mixture of CH_4/H_2 plasma (ratio 15%) at −125 V and corresponding three types of surface treated nano-diamond film as mentioned in the Experimental section. BEG forms a continuous nano-diamond film of grain size in the range of 20–30 nm on the silicon surface (Fig. 1a). When the same nano-diamond film is again biased treated in presence of hydrogen plasma, it formed a thin layer of amorphous carbon on the surface. Fig. 1b shows the SEM image of biased treated nano-diamond film. The surface morphology of bias treated nano-diamond film shows poorly visible grain boundaries compared with as-grown nano-diamond film. The poor visibility of grain boundaries and surface is resulted from the formation of a thin amorphous carbon layer due to hydrogen ion bombardment on the surface of diamond film. Fig. 1c shows more distinct and clear grain and grain boundaries after 30 min H_2 plasma treatment due to partial etching of non-diamond carbon from surface of BEG nano-diamond film. After air plasma treatment, the surface morphology (Fig. 1d) is similar to the as grown nano-diamond which may due to homogeneous etching ability of diamond and non-diamond carbon.

To have an insight whether H_2 and air plasma treatment form respective bond with carbon on the surface of nano-diamond film, we have carried out a simple test. It is known that diamond surface is highly inert towards any kind of solvent or acid or water and secondly, diamond is being non-polar and its covalent bonding arrangements have poorer chance to form bond with polar solvents like water in the absence of any highly energetic environment. Both the BEN and biased treated nano-diamond film show almost same angle of contact (~80°). Similarly, H_2 plasma treated nano-diamond surface also shows acute angle of contact but to a great extent (~30°) due to higher number of H-terminated carbon bond in the surface. However, if the diamond surface is terminated with oxygen, it should behave as a highly hydrophilic substrate. A lowest acute angle of contact (~10°) between water droplets and air plasma treated nano-diamond film strongly supports the hydrophilic and oxygen-terminated surface.

Fig. 2 shows the Raman spectra of different surface treated nano-diamond film. There is no significant change in the Raman spectra of different surface treated nano-diamond thin films. Visible Raman spectrum of nano-diamond thin film normally shows four broad peaks at around 1140, 1350, 1480 and 1580 cm^{-1}. The Raman spectra obtained in our cases are very similar to as reported in literature [12]. The peaks at 1140 and 1480 cm^{-1} are sometimes assigned to nano-diamond phase [13]. However, there is certain ambiguity in these two peaks. Ferrari and Robertson have assigned these two peaks to *trans*-polyacetylene segments present at the grain boundaries and surfaces of diamond film [14]. Recent study of Kuzmany et al. believes that these two peaks did not originate from the

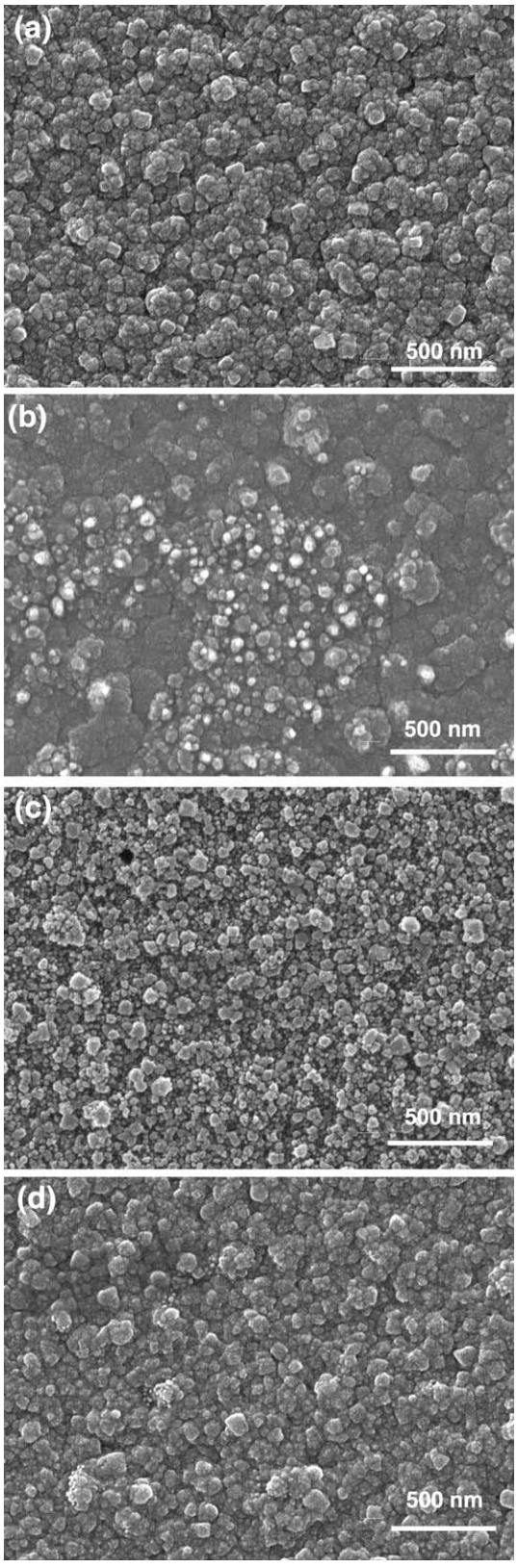

Fig. 1. SEM images of nano-diamond films (a) as grown; (b) bias treatment; (c) H_2 plasma treatment; (d) air plasma treatment.

nano-diamond phase [15]. However, these two peaks are most commonly observed in nano-diamond thin film and can be a convenient probe for nano-diamond films.

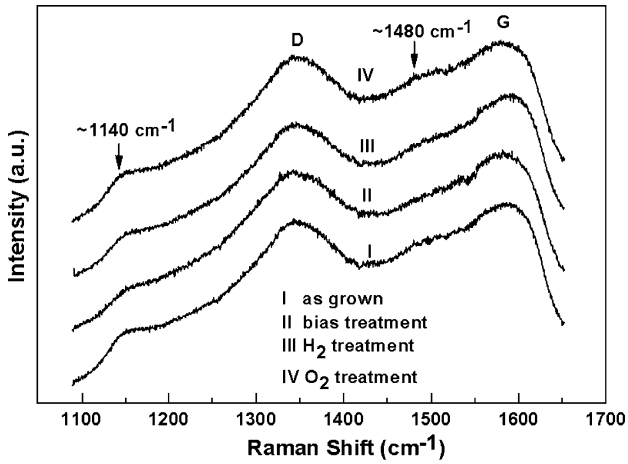

Fig. 2. Raman spectra of nano-diamond films after different surface treatments.

Electron field emission property of a material is normally measured from $J-E$ curves and Fowler–Nordheim (F–N) plots. Fig. 3 shows the dependence of emission current density on the applied field of the different plasma treated nano-diamond films. Table I shows the detailed emission current density (J_e) and turn-on-field (E_0) from different treated nano-diamond films. The field emission properties varied markedly with surface treatments of nano-diamond films. It is a well-accepted fact that the presence of more defects and non-diamond carbon in the grain boundaries increases the electron emission. We have intentionally created a conductivity layer of carbon by hydrogen ion bombardment on the nano-diamond film using a negative bias. This hydrogen ion bombardment could possibly create some more defects on the surface of nano-diamond film too. This effect is clearly seen in the electron emission properties of bias treated nano-diamond film. There is a significant decrease in turn-on-field and sharp increase in emission current density (see Table 1).

The effect of hydrogen plasma treatment on nano-diamond film is found to be more interesting in their field emission behavior. There is a sharp decrease in turn-on-field of nano-diamond film by hydrogen plasma treatment. The reason of this

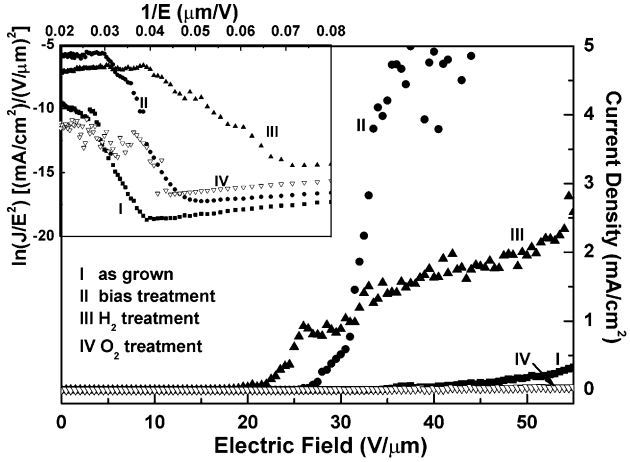

Fig. 3. Electron field emission properties ($J-E$) plot of surface treated nano-diamond films. Inset shows the plot of F–N plot.

Table 1
The electron field emission characteristics different surface treated nano-diamond films[a]

	As grown	Bias treatment	H_2 plasma treatment	Air plasma treatment
E_0 (V/μm)	25.5	19.5	14	24
J_e (mA/cm^2)	0.61	9.6	2.6	0.04
Φ_e (eV)	0.10942	0.11890	0.03652	0.14822

[a] Electron field emission characteristics: E_0=turn-on field, J_e=emission current density at 55 V/μm; and Φ_e=effective work function.

low emission in hydrogen-plasma treated nano-diamond film is not clear yet.

Han et al. reported the enhancement of field emission property with oxygen-terminated diamond surface [16]. They believed that chemisorption of oxygen atoms at the surface of diamond reduces the work function which leads the enhancement of field emission properties of oxygen-terminated diamond surfaces with lower turn-on field. To study this effect, we have treated nano-diamond film under air plasma. However, we did not observe any enhancement of field emission. The air plasma treatment process has greater chance of cleaning some non-diamond carbon and oxidizing surface of diamond film, which leads to a decrease in conductivity at the surface and also with the electron emission. However, turn-on-field of both O_2-plasma treated and H_2-plasma treated nano-diamond surfaces were markedly less than O- and H-terminated microcrystalline diamond surfaces.

4. Conclusions

The effects of surface treatment on the properties of nano-diamond films were investigated. In this study, nano-diamond films were prepared from methane–hydrogen mixture by MPECVD system (ASTeX 5400). The nano-diamond films were grown on mirror-polished p-type (100) Si substrate by BEG technique without any substrate pre-treatment process.

In order to study the effects of surface varieties on the electron field emission property, three different surface treatment methods were used. The first method uses bias bombardment in hydrogen plasma to create a thin sp^2 layer on the surface; the second method uses hydrogen plasma treatment to obtain a H-terminated diamond surface; the third method uses air plasma treatment to obtain an O-terminated diamond surface. Different treatments will alter the surface condition, and change the interface between nano-diamond films and vacuum. The possible mechanism is discussed.

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