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# Electron emission from nanocrystalline diamond films

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The electron emission properties of nanocrystalline diamond films were described. The nanometer structured diamond films were deposited by the microwave plasma assistance chemical vapor deposition method via continuous H<sup>+</sup> ion bombardment. The grain size of nanocrystalline diamond films can be modified by means of changing the energy of bombarded ions. Scanning electron microscopy and Raman spectroscopy indicated the nanometer structure of the films. The results suggested that low-field electron emission and high emission current can be obtained from the films consisting of nanosized diamond grains. © 2001 American Vacuum Society.

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## I. INTRODUCTION

Diamond can possess a negative electron affinity surface that allows its surface to emit electrons under low electric field. Compared with the complicated and costly process of fabricating metal or semiconductor sharp microtips to provide geometric field enhancement, diamond films can show a planar electron emission property at low electric field and be manufactured inexpensively. Although a considerable research effort on diamond field emission has been made in the past few years,<sup>1,2</sup> the influences of crystalline structure of diamond films on emission properties are not yet completely understood.<sup>3</sup> Further study is necessary using theory and experimental methods for developing a stable and efficient diamond planar display device. In this article we reported that strong electron emission at low applied fields is obtained from nanocrystalline diamond films.

## II. EXPERIMENT

A microwave plasma assistance chemical vapor deposition (MWPACVD) reactor equipped with a 1.5 kW generator and a substrate bias system was employed for diamond nucleation and growth. A three-step process was used. It consists of: (1) *in situ* substrate etching in a hydrogen plasma for 40 min at a temperature of 860 °C to remove the native surface oxide layer; (2) Bias pretreatment for the film nucleation at a temperature of 845 °C in a 5% methane-in-hydrogen plasma at 20 mbar and 840 W power. Where the negative bias voltage was -150 V relative to the vacuum chamber which was electrically grounded. The nucleation density was about 10<sup>10</sup> cm<sup>-2</sup> after a 17 min nucleation dura-

tion; (3) H<sup>+</sup> ion bombardment assisted growth of diamond films at different negative dc-bias voltages (0–140 V), substrate temperatures (780 °C), and total pressures (25 mbar). The substrate temperature was controlled by a separate heater under the substrate holder and measured by an optical pyrometer. The experimental details are given in Table I.

The morphology of the diamond films was evaluated by scanning electron microscopy (SEM). Micro-Raman spectroscopy was used to obtain information about the phase purity of the films with various grain sizes. Field emission experiments were performed at a pressure of 10<sup>-8</sup> Torr. Sputtered indium-tin-oxide glass was used as the anode. The anode-cathode spacing was approximately 120 μm.

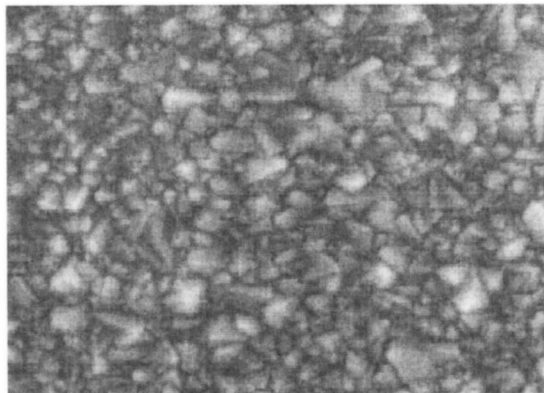
## III. RESULTS AND DISCUSSION

Figure 1 shows the SEM images of the films prepared at the bias voltages of 0, -80, and -140 V at 780 °C and 25 mbar for 1 μm film thickness. From Fig. 1 we can see the clear changes in morphology and grain size when the bias voltage is increased from -80 to -140 V. Figure 1(a) shows an image of a film deposited at 0 V which displays randomly oriented diamond particles with the average grain size of about 0.3 μm and a relatively rough surface. A morphology change occurred first at a negative voltage of -80 V. As the film became more [001] oriented [Fig. 1(b)], the average grain size had a slight increase from 0.3 to 0.4 μm. The details of H<sup>+</sup> ion etching to non-[001]-oriented diamond particles for forming high [001]-oriented films have been described in our previous works.<sup>4,5</sup> At bias voltages of -140 V, secondary nucleation occurs. The number density of small grains increases significantly. The average grain size rapidly decreases to 40 nm at -140 V [Fig. 1(c)]. The change of grain size as a function of negative bias voltage is summa-

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TABLE I. Deposition parameters for nanocrystalline diamond films.

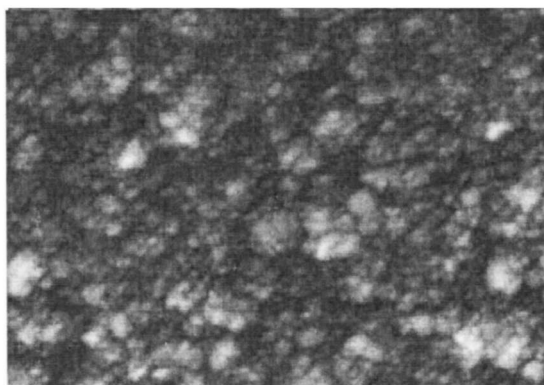
Step	1	2	3
CH <sub>4</sub> flow rate (seem)	0	15	0.5–5
H <sub>2</sub> flow rate (seem)	300	285	250
Microwave power (W)	840	780	900
Substrate temperature (°C)	860	845	780
Total pressure (mbar)	25	20	25
Bias voltage (V)	0	–150	0 to –140
Time (min)	40	17	240–600



(a) 1 μm



(b) 1 μm



(c) 100 nm

FIG. 1. SEM morphology of the films prepared under different substrate bias voltages of: (a) 0 V, (b) –80 V, and (c) –140 V.

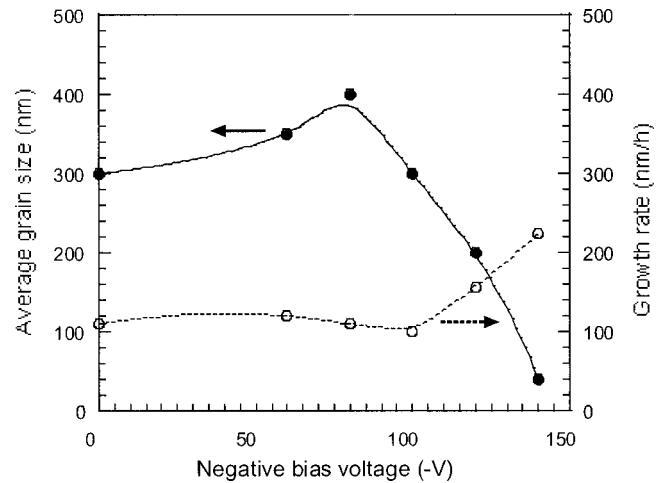


FIG. 2. Grain size and growth rate of diamond films as function of the negative substrate bias voltage.

ized in Fig. 2. In Fig. 2 the growth rate as a function of bias voltage is also shown. From 0 to –100 V, the growth rate keeps a constant at 100 nm/h. The growth rate increases clearly when the bias voltage is more than –100 V and reaches 250 nm/h at –140 V.

Micro-Raman spectroscopy was performed to obtain the phase purity of films with various grain sizes. The Raman spectra shown in Fig. 3 were obtained with a laser spot size on the samples of approximately 2 μm in diameter. For the

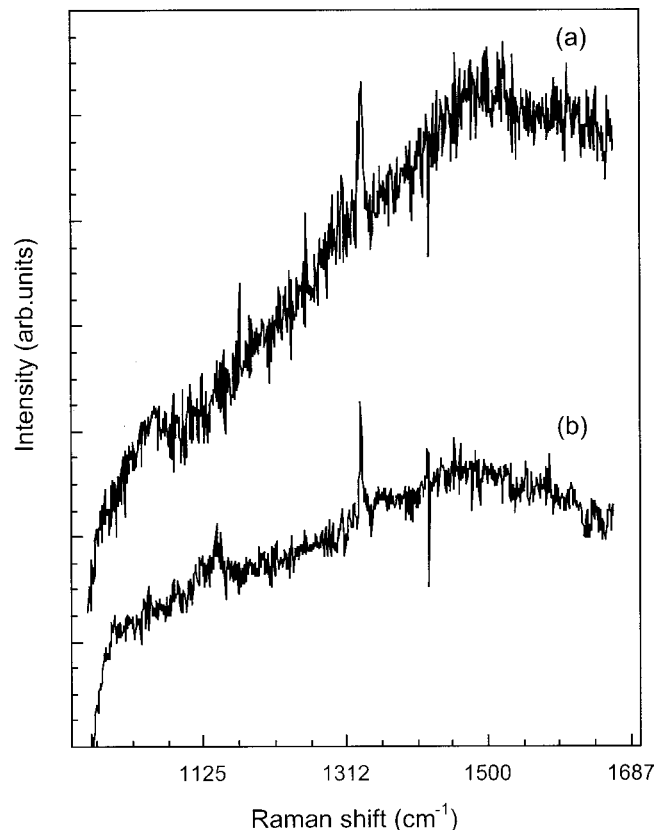


FIG. 3. Raman spectra obtained from diamond films deposited at different bias voltages of: (a) 0 V and (b) –140 V.

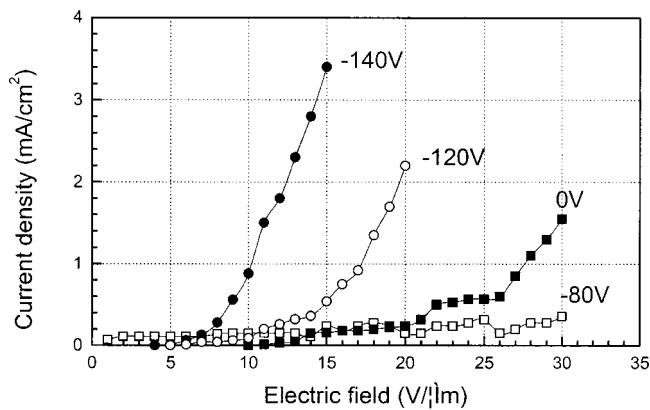


FIG. 4.  $I$ - $V$  curves of diamond films deposited at different bias.

film deposited without biasing the substrate, a sharp peak at  $1331\text{ cm}^{-1}$ , the well-known phonon fingerprint of diamond was observed. A low broad signal from  $1400$  to  $1600\text{ cm}^{-1}$  caused by  $sp^2$  bonded carbon was also detected. With increasing substrate bias, the diamond peak has a lower intensity and is shifted to a higher frequency, and the amorphous carbon signal increases. For a substrate bias of  $-140\text{ V}$ , a broad feature at  $1355\text{ cm}^{-1}$  was found, indicating an extremely high compressive stress formed in film. We also observed a gradually increasing intensity of the broad peak at around  $1140\text{ cm}^{-1}$  with increasing bias voltage. This Raman feature has been suggested to arise from either small grain size or disorder in a tetrahedrally bonded carbon network.<sup>6</sup> It may be used to characterize nanocrystalline diamond film.

Figure 4 shows the typical current-voltage ( $I$ - $V$ ) curve from the emissions of diamond films deposited at various biases. To the film deposited at  $-140\text{ V}$  (grain size:  $40\text{ nm}$ ), the emission current density increased rapidly at an applied voltage of about  $4\text{ V}/\mu\text{m}$  and reached  $3.4\text{ mA}/\text{cm}^2$  at  $15\text{ V}/\mu\text{m}$ . To the samples deposited at  $0\text{ V}$  (grain size:  $0.3\text{ }\mu\text{m}$ ), the emission characteristics shifted in a high voltage region, the current increased clearly at  $15\text{ V}/\mu\text{m}$ , and reached  $2.2\text{ mA}/\text{cm}^2$  at  $20\text{ V}/\mu\text{m}$ . To the (001) textured film deposited at  $-80\text{ V}$ , there is no clear increase in emission current when increasing the applied voltage to  $30\text{ V}/\mu\text{m}$ . The results show that nanocrystalline diamond films are advantageous to obtaining high emission current and low emission threshold.

Negative bias voltage was usually used during the nucleation stage on mirror-polished Si to obtain highly oriented nuclei for epitaxial growth of diamond films.<sup>7</sup> In this study, the bias enhanced nucleation step is continuous at changed parameters after the first nucleation step at a bias voltage of  $-140\text{ V}$ . A high frequency secondary nucleation is realized. The coalescence and growth of the nuclei could not occur clearly. A diamond film with nanocrystalline structure can therefore be formed. At the same time, high frequency secondary nucleation also results in a high growth rate. The nanocrystalline diamond films with high grain boundary density can provide more efficient emission sites and electron sources, which present the properties of high emission current and low field electron emission.

The negative bias voltage was also used to etch as-grown particles or films for obtaining a surface structure modification.<sup>8,9</sup> Under a lower substrate bias and a lower temperature compared to the nucleation step, the energy, and number of ions is not enough to form nucleation sites and stable nuclei, but the grain surface in the as-grown film may be etched and form a new surface morphology and structure. During the biased etching process, positively charged energetic ions were accelerated toward the substrate, forming ion flux along the direction vertical to the substrate. At a suitable bias voltage (from  $-80$  to  $-100\text{ V}$  in our experiment), the etching efficiency of  $\text{H}^+$  ions on non-(001) faces is higher than that of the (001) face because of their higher face atom density. As a result, the non-(001)-oriented nuclei will be etched faster and (001) faces will survive and become larger. To (001)-textured film, it has a low boundary density and a smoother surface than those of (011), (111), and randomly oriented films, but it cannot supply more efficient emitting microprotrusions. At a lower bias voltage compared with the etching process ( $\leq 60\text{ V}$ ), the etching process by atomic H is dominant and no obvious change on the surface morphology of the films occurs. The microstructured film presents conventional emission characteristics of diamond film consisting of micrometer scale and non-(001) textured grains.

#### IV. CONCLUSION

Nanocrystalline diamond films were prepared by the MWPACVD method assisted by a continuous ion bombardment. During this process, ion bombardment of different energies was induced by applying a negative bias voltage from  $0$  to  $-140\text{ V}$  on the substrate relative to the grounded vacuum chamber. The relationships between the film morphology, grain size, growth rate, and substrate bias voltage were studied by SEM and micro-Raman spectrometry. Diamond films with  $40\text{ nm}$  in grain size can be obtained at  $-140\text{ V}$  bias voltage. The micro-Raman spectroscopy confirmed the diamond phase, and the spectra also show that there is a broad peak at around  $1140\text{ cm}^{-1}$  which can be used to characterize nanocrystalline diamond films. The influences of grain size on surface electron emission properties were investigated. The results indicate that nanocrystalline film deposition at  $-140$  bias voltage has characteristics of low-field electron emission and high emission current, which can be attributed to the high grain boundary density of nanocrystalline diamond films.

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