The field emission properties of high aspect ratio diamond nanocone arrays fabricated by focused ion beam milling

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Abstract

High aspect ratio diamond nanocone arrays are formed on freestanding diamond film by means of focused ion beam (FIB) milling technology and hot-filament chemical vapor deposition (HFCVD) method. The structure and phase purity of an individual diamond nanocone are characterized by scanning electron microscopy (SEM) and micro-Raman spectroscopy. The result indicates that the diamond cones with high aspect ratio and small tip apex radius can be obtained by optimizing the parameters of FIB milling and diamond growth. The diamond nanocone arrays were also used to study the electron field emission properties and electric field shielding effect, finding high emission current density, low threshold and weak shielding effect, all attributable to the high field enhancement factor and suitable cone density of the diamond nanocone emitter.

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1. Introduction

The outstanding physical and chemical properties of diamond, such as highest hardness, outstanding chemical inertness and highest thermal conductivity, etc. make it an excellent candidate for both mechanical and electronic applications [1]. Furthermore, diamond as a material with negative electron affinity is suitable for electron field emission and display device applications. Electron field emission from diamond has been intensely studied for the last decade and observed to yield high emission current at a low applied electric field [2–4]. However, most reported diamond emitters are comprised of planar, irregular ion-etched diamond film or non-uniformly diamond coated silicon tips with low aspect ratio. This non-uniformity of emitter microstructures leads to inconsistent or poor emission behavior and long-term instability. It is known that a good candidate for field emitter arrays should be a structure of high aspect ratio and appropriate density to gain enhanced field emission. Yet too much emitter density is disadvantageous for improvement of emission because of the shielding effect resulting from the proximity of emitters, so the emitter with controllable density is required [5]. Focused ion beam (FIB) milling technology is convenient for controlling the density of patterns and producing a hole geometry of high aspect ratio, and hence diamond nanocone arrays with high aspect ratio and controllable density can be achieved by filling chemical vapor deposition (CVD) diamond grains in the FIB-milled patterns, which can be expected to exhibit enhanced field emission properties.

In this work, we report a novel method to obtain enhanced field emission from high aspect ratio diamond nanocone arrays with controlled density on a freestanding diamond film. The diamond nanocone arrays are fabricated via FIB milling and hot-filament chemical vapor deposition (HFCVD) technologies on silicon substrate. The controllable aspect ratio and density of nanocone arrays can be achieved by changing the pitches of milled hole patterns and the parameters of ion beam. The electron field emission from diamond nanocone arrays was studied and compared with that from the back surface of diamond film, and the electric field shielding effect induced by the proximity of emitters is also discussed.
2. Experimental

For fabricating diamond nanocone arrays, first, a silicon mold with high aspect ratio, inverted conical-shape hole patterns was formed by FIB milling method. The commercial FEI DB235 FIB system can produce a focused Ga\(^{+}\)-ion beam with a maximum energy of 30 keV and a beam current of 1 pA-5 nA. The diameter, depth and pitch of the hole pattern can be preset by a special software in this system. Before FIB milling, a poly-methylmethacrylate (PMMA) of 0.5 \(\mu\)m thickness was spin-coated on the silicon wafer serving as a protective layer to prevent sputtered silicon debris from re-deposition at the edge of etched holes during FIB milling, and avoid any influence of the silicon debris on the subsequent growth of diamond nanocones. Second, the protective layer was dissolved in acetone and the Si was thoroughly cleaned in ethanol, and the patterned silicon substrate was then ultrasonically pretreated in an ethanol solution containing nanodiamond powder in order to enhance diamond nucleation and improve diamond film growth on the patterned Si substrate. Third, diamond film was deposited on the patterned silicon substrate by HFCVD, the reaction gas is a mixture of CH\(_4\) and H\(_2\), and the CH\(_4\) concentration is 1.5\%, the total pressure is 16 Torr. A tantalum filament with diameter of 0.5 mm is heated to 2200 °C. The distance between the filaments and substrate is 10 mm. The substrate temperature of 850 °C is measured by a thermocouple mounted on the substrate. The rate of deposition for diamond film is 1 \(\mu\)m/h under the above parameters. After deposition for 6 h, the FIB milled holes were fully filled with diamond grains and formed a diamond film of about 6 \(\mu\)m-thickness on the silicon surface. A further step was to turn the diamond deposited wafer upside down and glue it to another silicon wafer using conductive epoxy. Finally, the diamond nanocones arrays, with precise replications of the hole geometry, are formed on the back surface of a freestanding diamond film after removing the silicon substrate and bears the cones. Fig. 1(a) shows an SEM micrograph of diamond nanocone arrays with a pitch of 20 \(\mu\)m. The total number of cones is about 6400 in the area of 1.6 mm \(\times\) 1.6 mm. For each diamond cone, as shown in the Fig. 1(b), the apex radius is about 100 nm, the base radius is about 1 \(\mu\)m and the height is measured to be about 9 \(\mu\)m. In order to obtain information about a diamond nanocone’s phase purity, micro-Raman spectroscopy was employed to characterize an individual cone. The detected Raman spectrum is shown in Fig. 2, where the first order diamond line at 1332 cm\(^{-1}\) and a broad peak at about 1500 cm\(^{-1}\) for sp\(^2\) bonded carbon [7] were also detected.

3. Results and discusses

By optimizing the FIB milling conditions such as beam current, initial diameter and depth of the hole, sputtering dose and scan scheme, high aspect ratio inverted conical shape hole patterns with controllable pitch can be achieved, and hence high aspect ratio diamond nanocone arrays with controllable pitch can be precisely replicated by filling HFCVD diamond grains in the holes and forming an diamond film that is freestanding after removing the silicon substrate and bears the cones. Fig. 1(a) shows an SEM micrograph of diamond nanocone arrays with a pitch of 20 \(\mu\)m. The total number of cones is about 6400 in the area of 1.6 mm \(\times\) 1.6 mm. For each diamond cone, as shown in the Fig. 1(b), the apex radius is about 100 nm, the base radius is about 1 \(\mu\)m and the height is measured to be about 9 \(\mu\)m. In order to obtain information about a diamond nanocone’s phase purity, micro-Raman spectroscopy was employed to characterize an individual cone. The detected Raman spectrum is shown in Fig. 2, where the first order diamond line at 1332 cm\(^{-1}\) and a broad peak at about 1500 cm\(^{-1}\) for sp\(^2\) bonded carbon [7] were also detected.
The moderate sp² contents of the diamond nanocone may originate mainly from the high density of grain boundaries and impurity at the interface between the diamond film and the silicon substrate during the early stage of film growth.

In order to evaluate the field emission properties from diamond nanocone arrays, the field electron emissions from diamond nanocone arrays on a freestanding diamond film and the back surface of diamond film were measured and compared. The as-deposited diamond nanocone arrays shown in Fig. 1(a) were used for the study of field emission. At the same time, a sample of diamond film deposited on silicon substrate without patterned holes was also prepared for studying the field emission from the back surface of diamond film. As a result, an enhanced field emission from diamond nanocone arrays was observed. The current versus electric field (I–E) curves and Flower–Nordheim (F–N) plots of field emissions from the diamond nanocone arrays and the back surface of diamond film are shown in Fig. 3(a) and (b), respectively. For the diamond nanocone arrays, the emission current increased rapidly at an applied voltage of about 2 V/µm and reached 88 nA at 5 V/µm. For the back surface of diamond film, the emission characteristic shifted to the high voltage region, the emission current began to increase gradually at about 9 V/µm and only reached 10 nA at 15 V/µm. So the resulting emission current from as-formed cones is about 78 nA (88–10 nA) at 15 V/µm, and hence the average emission current from an individual diamond cone is estimated to be about 13 nA. As shown in the characterization from SEM, the apex radius of the cone is about 60 nm. Therefore, the average emission current density per cone was about $5.8 \times 10^4$ mA/cm² if the majority of the electrons is considered to be emitted from the hemispherical apex of the cone [8]. It is obvious higher than the emission current density of $\sim 5 \times 10^2$ mA/cm² at 16.5 V/µm from carbon nanotube (CNT) emitters, which suggests that the diamond nanocone can be an electron source with high brightness [9–11]. The results indicated that diamond nanocone arrays on a freestanding diamond film have a greatly enhanced field emission property compared with that of the back surface of diamond film. This can be attributed to the enhancement of electron emission due to the increase of sp² bonded carbon on the surface of diamond nanocone [12], and besides, the cone structure of diamond nanocone arrays, such as the high aspect ratio that can be calculated from the ratio of height (9 µm) and apex radius (100 nm) of a cone and the appropriate density of diamond nanocone arrays, which improves the field enhancement factor of diamond nanocone emitters. In the following we will discuss the enhanced electron field emission due to the high aspect ratio of as-deposited cone arrays, and the shielding effect is also discussed therein.

It is known that the field enhancement factor $\beta$ is a key parameter, which reflects the enhanced electron emission due to the localized electronic states by the geometrical configuration of the emitters. In theoretical case, $\beta$ can be expressed as $h/r$, where $h$ is the height of emitter and $r$ is the tip radius of it. Yet in fact, the value of $\beta$ can be modified by other effects such as shielding effect due to the proximity of emitters. So we have to introduce an effective field enhancement factor $\beta_{\text{eff}}$ to describe the actual field enhancement, which can be obtained from the measured...
slope of F–N plots as shown in Fig. 3(b). Using original F–N equation [13]:

\[ J = \frac{AE^2}{\phi F(y)} \exp \left( -\frac{B \phi^{3/2} V(y)}{E} \right) \text{ cm}^2 \text{ V}^{-3/2} \text{ A}, \]  

(1)

the slope of F–N plots \( S(E \ln (J/E^2)) \) can be expressed as:

\[ S = -\frac{BE^{3/2} \phi_{eff}}{\beta_{eff}}, \]  

(2)

where \( B \) is a constant with the value \( 6.831 \times 10^3 \text{ eV}^{-3/2} \text{ V} \mu\text{m}^{-1} \), and the effective work function \( \phi_{eff} \) of diamond is 0.08 eV, as introduced in Ref. [14]. The calculated \( \beta_{eff} \) is about 45. For the back surface of the freestanding diamond film, \( \beta_{eff} \) is about 2, which shows that the back surface of diamond film also has a certain field enhancement capability due to the surface is not very flat.

It is well known that shielding effect is disadvantageous for field emission, especially for densely distributed emitter arrays. In the following we analyze the shielding effect on the field emission of as-formed diamond cone arrays. The local field without shielding effect can be expressed as:

\[ E_{local} = \frac{\beta V}{d}, \]  

(3)

where \( d \) is the distance between the cathode and anode, \( \beta \) is the aspect ratio (\( h/r \)) of the as-formed emitter, and \( V \) is the applied voltage. While for the case that the field enhancement is fully shielded, the local field can be expressed as:

\[ E_{local} = \frac{V}{d}. \]  

(4)

when considering the actual case, which has to be a compromise between those limited cases, the following phenomenological formula can be employed, as used in Ref. [15]:

\[ E_{local} = \frac{s \beta V}{d} + \frac{(1-s) V}{d}, \]  

(5)

where \( s \) is a parameter describing the degree of the screening effect, which ranges from 0 for very densely arranged emitters to 1 for very sparsely arranged emitters. And it is a function of the height and inter-distance of the emitter in the arrays. From Eq. (5) we can have:

\[ \beta_{eff} = s \beta + 1 - s \approx s \beta. \]  

(6)

using \( \beta_{eff} \) (45) calculated from F–N plots and \( \beta \) (90) estimated from SEM observation, the \( s \) for cone arrays can be calculated to be about 0.5, which shows the shielding effect is rather weak. For comparison, severe shielding effect (\( s \) is about 0.06) of the field emission properties for densely aligned carbon nanotubes has been studied in Ref. [15]. Therefore, it can be concluded the diamond cone density used in our experiment is quite advantageous for decreasing shielding effect.

4. Conclusions

High aspect ratio diamond nanocone arrays with controllable density and aspect ratio were successfully fabricated by FIB milling and CVD diamond. With optimized FIB milling conditions, diamond nanocones with high aspect ratio and small tip apex radius can be obtained. The Raman spectrum shows the dominant diamond line at 1332 cm\(^{-1}\) and a weak peak at about 1500 cm\(^{-1}\) for moderate sp\(^2\) bonded carbon. The electron emission property from the diamond nanocone arrays on a freestanding diamond film was studied and compared with that from the back surface of diamond films. The results show that the diamond nanocone arrays have obviously enhanced emission compared with that from the back surface of the diamond films at the same applied electric fields. This can be attributed to the enhancement of electron emission due to the high aspect ratio and the increase of sp\(^2\) bonded carbon on the surface of diamond nanocone. Weak shielding effect resulted from the appropriate patterning density also improves the field enhancement factor of diamond nanocone emitters. The fact that the applied voltage of 15 V/\( \mu \text{m} \) can produce the emission current density of about \( 5.8 \times 10^4 \text{ mA/cm}^2 \) for such sparse diamond nanocone arrays suggests that it can be a candidate electron source with super-high brightness.

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References

[1] C.E. Nebel, F. Ertl, C. Sauerer, M. Stutzmann, C.F.O. Graeff, P. Bergonzo, O.A. Williams, R.B. Jackman, Low temperature properties of the p-type surface conductivity of diamond, Diamond Relat. Mater. 11 (2002) 351–354.
[2] N.A. Fox, W.N. Wang, T.J. Davis, J.W. Steeds, P.W. May, Field emission properties of diamond films of different qualities, Appl. Phys. Lett. 71 (1997) 2337–2339.
[3] M. Nagao, T. Kondo, Y. Gotoh, H. Tsuji, J. Ishikawa, K. Miyata, K. Kobashi, Influence of surface treatment and dopant concentration on field emission characteristics of boron-doped diamond thin films, Appl. Phys. Lett. 71 (1997) 2806–2808.
[4] I. Lee, K. Liu, I. Lin, Effect of substrate materials on the electron field emission characteristics of chemical vapor deposited diamond films, J. Appl. Phys. 82 (1997) 3310–3312.
[5] J.S. Suh, K.S. Jeong, J.S. Lee, I. Han, Study of the field-screening effect of highly ordered carbon nanotube arrays, Appl. Phys. Lett. 80 (2002) 2392–2394.
[6] Z.L. Wang, C.Z. Gu, J.J. Li, Z. Cui, A novel method for making high aspect ratio solid diamond tips, Microelectron. Eng. 78–79 (2005) 353–358.
[7] E. Oesterschulze, W. Scholz, C. Mihalcea, D. Albert, B. Sobisch, W. Kulisch, Fabrication of small diamond tips for scanning probe microscopy application, Appl. Phys. Lett. 70 (1997) 435–437.

[8] H.J. Li, J.J. Li, C.Z. Gu, Local field emission from individual vertical carbon nanofiber grown on tungsten filament, Carbon 43 (2005) 849–853.

[9] H. Dai, E.W. Wong, C.M. Lieber, Probing electrical transport in nanomaterials: conductivity of individual carbon nanotubes, Science 272 (1996) 523–526.

[10] S. Frank, P. Poncharal, Z.L. Wang, W.A. De Heer, Carbon nanotube quantum resistors, Science 280 (1998) 1744–1746.

[11] J.C. She, N.S. Xu, S.Z. Deng, J. Chen, H. Bishop, S.E. Huq, L. Wang, D.Y. Zhong, E.G. Wang, Vacuum breakdown of carbon-nanotube field emitters on a silicon tip, Appl. Phys. Lett. 83 (2003) 2671–2673.

[12] A. Wisitsoraat, W.P. Kang, J.L. Davidson, D.V. Kerns, A study of diamond field emission using micro-patterned monolithic diamond tips with different sp² contents, Appl. Phys. Lett. 71 (1997) 3394–3396.

[13] C.A. Spindt, I. Brodie, L. Humphrey, E.R. Westerberg, Physical properties of thin film field emission cathodes with molybdenum cones, J. Appl. Phys. 47 (1976) 5248–5263.

[14] J.Y. Luo, K.S. Liu, J.S. Lee, Z.N. Lin, H.F. Cheng, The influence of film-to-substrate characteristics on the electron field emission behavior of the diamond films, Diamond Relat. Mater. 7 (1998) 704–710.

[15] V. Fillip, D. Nicolaescu, M. Tanemura, F. Okuyama, Modeling the electron field emission from carbon nanotube films, Ultramicroscopy 89 (2001) 39–49.