

The characterization of nitrogen content, diamond-like carbon field emission arrays using a magnetic filtered arc method

C.-F. Chen*, C.-H. Shen, C.-L. Lin

Institute of Materials Science and Engineering, National Chiao Tung University, Hsinchu 30050, Taiwan

Abstract

Uniform and large area pyramid-shape diamond-like carbon (DLC) field emission arrays are successfully deposited using the filtered arc deposition (FAD) system. Nitrogen gas serves as the dopant source to deposit the diamond-like carbon films on the inverted pyramid-shape SiO₂ substrates. Experimental results indicate that the current-voltage (I–V) value of field emission arrays is closely related to the diamond-like carbon film quality. The amount of N₂ content in the film influences the composition of the diamond-like carbon, sp² bonding carbon and graphite. It was found that the sp² bonding carbon content of the diamond-like carbon increases with increasing N₂ doping. With nitrogen doping, the emission anode current of the diamond-like carbon film significantly increases, eventually reaching 142 μA at a voltage of 30 V, at heavily N-doped concentrations (10 sccm), when the films reach a high defect density. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Diamond-like carbon; Field emission arrays; Filtered arc deposition

1. Introduction

Field emission arrays (FEAs), the source of electrons are in the form of arrays with microfabricated sharp tips, typically with an integrated extraction electrode, namely a gate. When the gate is biased to a sufficiently large positive potential with respect to the tips, electron emission occurs from the tip into the vacuum, via electron tunneling through the solid-vacuum potential barrier, a phenomenon termed as field emission. Although the field emission effect itself has been investigated since the beginning of this century, it is only with the emergence of modern microfabrication techniques that it is possible to realize microdevices based on this phenomenon.

Field emission displays (FEDs) have received increasing attention, as the flat panel displays of the next

generation. The FEDs are emissive displays in vacuum packages using field emission arrays as the electron source, fabrication based on the most advanced fine technology and phosphors that emit light when hit by electrons. The FEDs are extremely thin (6–10 mm) and lightweight devices. Other features include the fact that no backlight is required, excellent legibility, a wide viewing angle, low power consumption and a high reliability.

Diamond has recently emerged as an attractive material for FEDs due to its high conductivity, negative electron affinity (NEA) [1], high chemical stability and high immunity to particle bombardment. Diamond-like carbon contains a mixture of sp³ and sp² and sp¹ hybridized carbon. It can be considered to be an intermediate between diamond and graphite. The original interest in investigating the emission properties of diamond or diamond-like carbon films stemmed from the fact that certain crystallographic orientations of diamond exhibit negative electron affinity. This means that the bottom of the conduction band of the diamond

*Corresponding author. Tel.: +886-3-5731898; fax: +886-3-5723811.

E-mail address: cfchen@cc.nctu.edu.tw (C.-F. Chen).

structure lies above the vacuum level, and therefore, there is no potential barrier for electron emission from the conduction band.

The utilization of advanced fine semiconductor technology made it possible to develop FEDs that were derivable at commercial voltages. This work attempted to fabricate miniature pyramid-shaped diamond-like carbon field emission arrays using a transfer mold technique, by filtered arc deposition [2–4].

2. Experimental

Fig. 1 presents the procedure for fabricating the diamond-like carbon field emission arrays. The 4-inch n-type and double-polished silicon substrates were (100) oriented wafers with a resistivity of 1–10 Ωcm and a thickness of 500–550 μm . The wafer was cleaned using an RCA cleaning process, and then spin-dried with nitrogen gas. The cleaned silicon wafer was thermally oxidized at 1180°C for 2 h to produce a SiO_2 layer with a thickness of 1 μm . An array of $4 \times 4 \mu\text{m}$ squares was then patterned onto the SiO_2 layer using the standard lithographic technique. The SiO_2 layer was then etched with buffered oxide etching (BOE), followed by

Table 1
Experimental conditions of FAD

Condition	A	B	C
N_2 flow rate (sccm)	0	3	10
Pressure (mtorr)	0.05	0.2	1.0
Ar flow rate (sccm)		0.8	
Negative bias (V)		–25	
Deposition time (min)		90	

immersing it in a water solution of 25 wt.% KOH for several minutes at 90°C to obtain (111) faceted structures in the Si wafer. The total 50×50 square-patterned area was $0.4 \times 0.4 \text{ mm}$. Following, the above-mentioned anisotropic etching, the sample was dipped in a buffered HF solution, again to remove all the SiO_2 . Finally, the sample was thermally oxidized again at 1180°C for 1 h to obtain a SiO_2 layer with a thickness of 0.5 μm .

The wafer was again cleaned using an RCA cleaning process, placed in the chamber to process the filtered arc deposition and to obtain the diamond-like carbon films. Table 1 lists the deposition conditions, with all the substrates placed in the deposition chamber being biased to a negative voltage of 25 V. The first set of undoped carbon (condition A) was deposited directly by the C^+ beam. Whereas, the second and third sets of samples (conditions B and C, respectively) were deposited by the C^+ beam together with the N_2^+ ion beam, produced under the N_2 flow rate of 3 sccm and 10 sccm, respectively. All substrates were cleaned using an Ar^+ ion beam to remove the oxide layer before deposition.

The diamond-like carbon deposited on the Si substrate was cut to $10 \times 10 \text{ mm}^2$. The cut substrates were then bonded with ITO (indium tin oxide) glass onto the surface of the diamond-like carbon to achieve a strong support and prevent the deposited layers from cracking when the silicon was removed. Next, the Si was removed completely via a water solution of 25-wt.% KOH at 90°C for hours. Following complete removal of the Si, a gate metal was deposited by the dual E -gun system for 200 nm. To produce gated emitter arrays, the metal layer was coated with a resistance layer. The thin resistance layer was etched to reveal only the tips of the emitters. Finally, wet etching of both the gate metal and the oxide was performed to open the gate centered on the emitters.

The deposited diamond-like carbon containing nitrogen was characterized by scanning electron microscopy (SEM), an Auger electron spectrometer, Raman spectroscopy and the I – V measurement system to examine surface morphology, quality, bonding type and to analyze field emission characteristics, respectively.

The I – V characteristics were measured using a triode technique. The same testing instrument has been

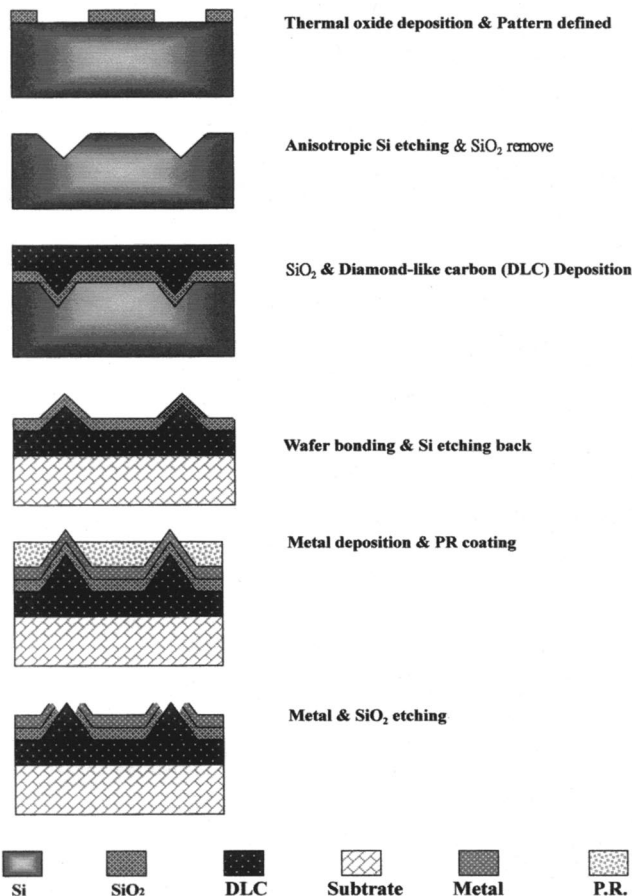


Fig. 1. Process procedures of fabrication of the field emission arrays (FEAs).

illustrated in our previous study [5]. An anode plate, which is an ITO glass, was placed 1 cm above the gate and was biased to +1000 V. The anode current (I_a) was then measured as a function of the gate-to-cathode bias voltage in a vacuum of 1×10^{-6} torr. Next, the gate-to-cathode voltage (V_c) was biased from 0 to 30 V. During testing, the device was in a common emitter configuration with the grounded emitter. The anode and gate were maintained at positive potentials to allow the device to be turned on.

3. Results and discussion

Fig. 2 shows the surface morphology of the diamond-like carbon film. In fact, the various samples do not differ markedly. Fig. 3 displays the morphology of the FEAs with a gate metal and SiO_2 etched to expose the FEA's tips. Meanwhile, Fig. 4 illustrates the

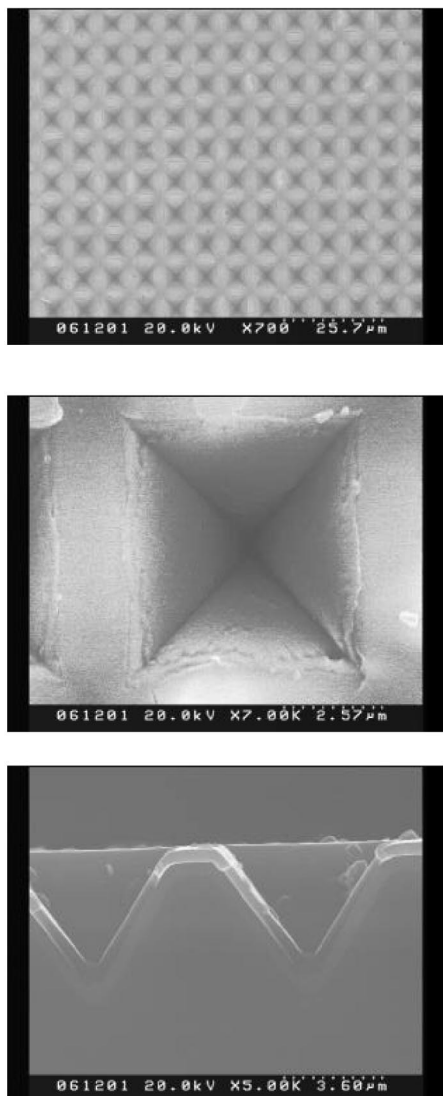


Fig. 2. The surface morphology and a cross section of a diamond-like carbon film.

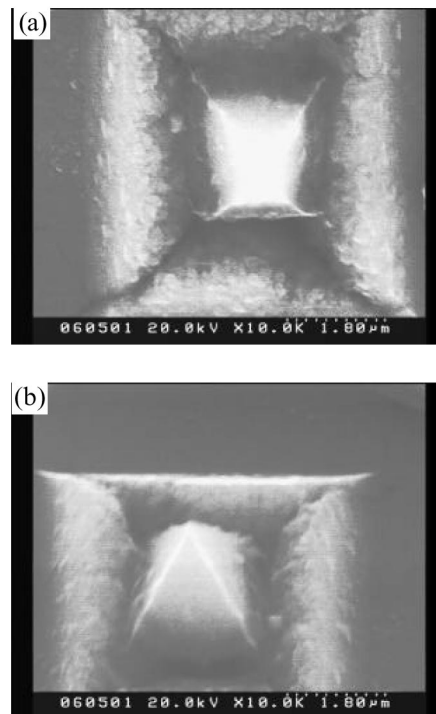


Fig. 3. The morphology of the diamond-like carbon FEAs with gate metal and SiO_2 etched to expose the FEA tip, (a) top view, (b) tilted at 45° .

Auger electron spectra of the samples A, B and C with various nitrogen flow rates. Furthermore, the spectra of the N-doped diamond-like carbon films are compared in Fig. 4, revealing that intensity of the N peak in the low-energy region of sample C is higher than that of sample B. The intensity of the N peak in the low-energy region corresponds to the nitrogen flow rate, indicating that nitrogen was effectively doped into the diamond-like carbon films during deposition.

Fig. 5 illustrates the Raman spectra between 800 and 2100 cm^{-1} and the resulting curve fitting of diamond-like carbon deposited with different nitrogen contents. The curve of the G peak fitting of the Raman spectra in Fig. 5 exhibits a broad distribution in the range of $1400\text{--}1700 \text{ cm}^{-1}$ centered at 1550 cm^{-1} , agreeing with the results reported by other researchers [6,7]. This confirms that the films are amorphous. To analyze the spectra quantitatively, the Raman spectra were fitted to two Gaussian peaks. These two peaks are defined as graphite (G) and disorder (D) peaks. The G peak ($\sim 1550 \text{ cm}^{-1}$) is caused by the in-plane Raman mode of the graphite, while the D peak ($\sim 1420 \text{ cm}^{-1}$) is attributed to the small domain-size graphitic regions. The G line width is determined by several factors, namely cluster size, cluster size distribution and stress in the carbon film, whereas the G line peak position is influenced by such factors as cluster size and nitrogen content. Obviously, a narrowing of the G band indi-

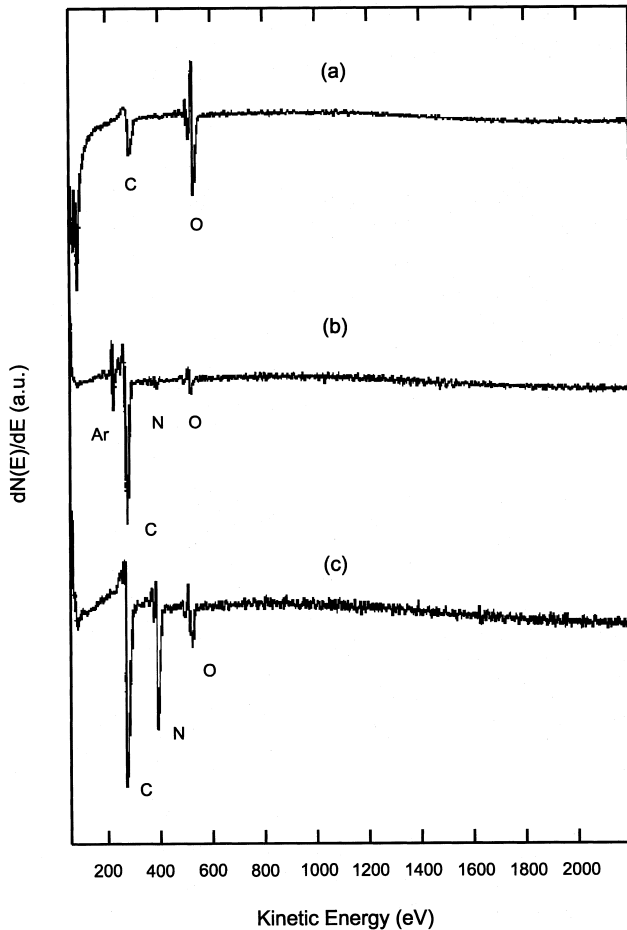


Fig. 4. The Auger electron spectra of samples with various nitrogen gas flow rates (a) condition A, 0 sccm, (b) condition B, 3 sccm and (c) condition C, 10 sccm.

icates a lower compressive stress in the films. The relative intensity ratio I_D/I_G can be used as a parameter for sp^3 content [8,9], a smaller I_D/I_G ratio corresponding to a higher sp^3 content [7]. The undoped diamond-like carbon films have the lowest intensity I_D/I_G ratio, of 0.573, indicating that the films have a high sp^3 content. The heavily N-doped diamond-like carbon films that were produced with 10 sccm N_2 flow rate have the highest intensity I_D/I_G ratio of 1.541, indicating that the films have a low sp^3 content.

Fig. 6 summarizes the I–V characteristics, revealing that the diamond-like carbon film possesses excellent field emission properties. The N-doped diamond-like carbon film has better emission properties than those of the undoped diamond-like carbon film. The emission anode current (I_a) of the samples resulting from related to conditions A, B and C were approximately 23 μA , 82 μA and 142 μA at the gate voltage of 30 V, respectively. The threshold voltage (V_{th}) is defined as the intersection of the F–N plots with the abscissa. The threshold voltages were 10–15 V for the diamond-like

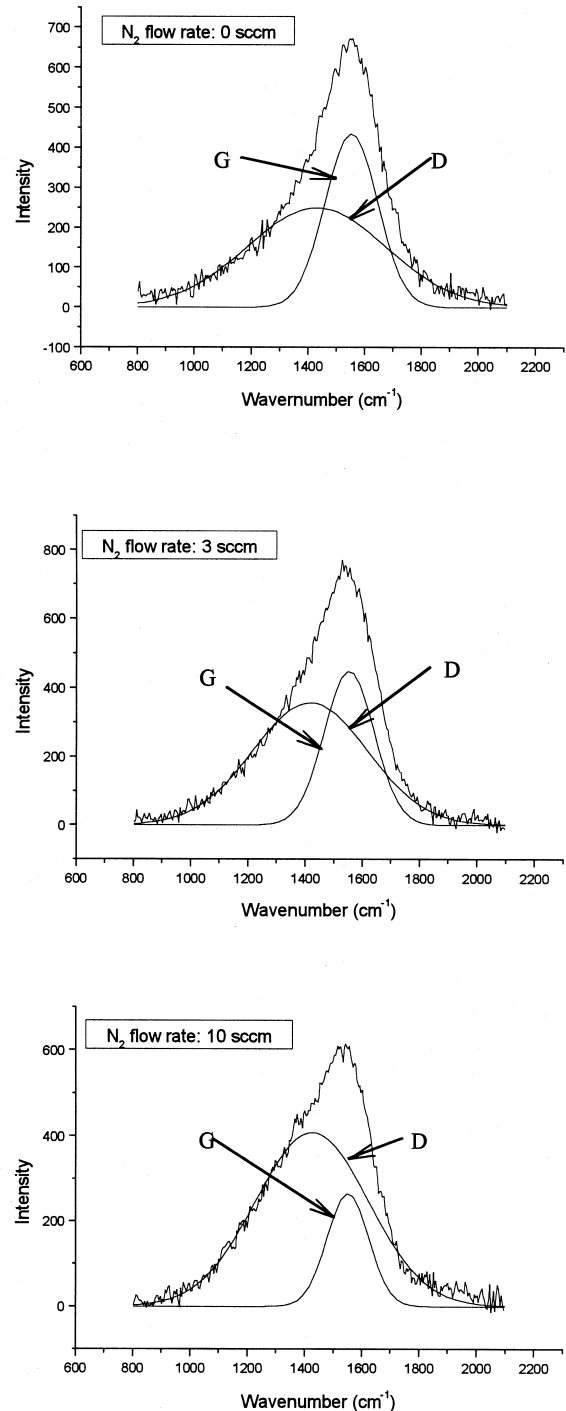


Fig. 5. The Raman spectra and the resulting curve fitting of diamond-like carbon deposited with nitrogen flow rate of (a) 0 sccm, (b) 3 sccm and (c) 10 sccm.

carbon FEAs. Thus, the turn on voltages of these samples, were all clearly lower than that of conventional metals. The sample heavily N-doped (10 sccm) has the lowest turn on voltage due to the Zener tunneling arising from the severe band bonding [10].

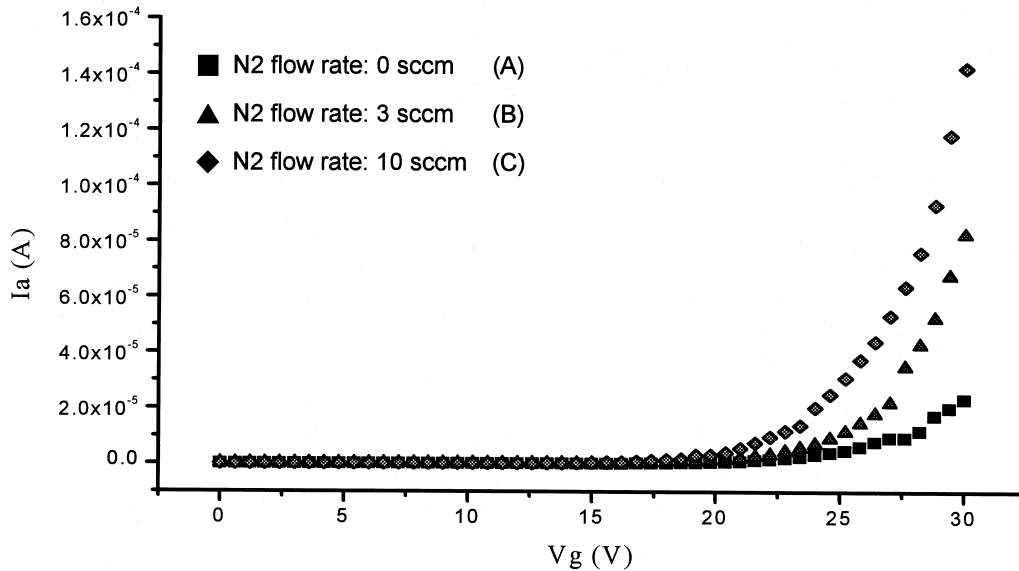


Fig. 6. Illustration of the I–V characteristics of conditions (A), (B) and (C).

4. Conclusions

The filtered arc deposition technique is used to deposit uniform diamond-like carbon successfully on a large area. Nitrogen can be efficiently doped into the diamond-like carbon films owing to the high ion energy feature of the FAD system. The quality of the pyramid-shape diamond-like carbon tips significantly influenced the emission efficiency. Nitrogen doping markedly increases the emission current of the diamond-like carbon films. Finally, the emission current is maximized under heavily N-doped (10 sccm), when the films reach a high defect density. Likewise, the undoped diamond-like carbon films exhibit the lowest emission efficiency.

Acknowledgements

The authors would like to thank the National Science Council of the Republic of China for financially

supporting this research under contract No. NSC89-2216-E-009-007.

References

- [1] E.J. Himpsel, J.A. Knapp, J.A. Van Vechten, D.E. Eastman, *Phys. Rev. B* 20 (1979) 624.
- [2] T. Sakai, T. Ono, M. Nakamoto, N. Sakuma, *J. Vac. Technol. B* 16 (1998) 2.
- [3] W.P. Kang, A. Wisitsora, L.L. Davidson, V. Kerms, *J. Vac. Sci. Technol. B* 16 (1998) 2.
- [4] E.S. Baik, D.R. Jeon, Y.L. Baik, *Diamond Relat. Mater.* 8 (1999) 89.
- [5] C.F. Chen, H.C. Hsieh, *Diamond Relat. Mater.* 9 (2000) 1258.
- [6] V.S. Veerasamy, G.A.J. Amaratunga, W.I. Milin, P. Hewitt, P.J. Fallon, D.R. McKenzie, C.A. Davis, *Diamond Relat. Mater.* 2 (1994) 542.
- [7] B.K. Tay, X. Shi, H.S. Tan, H.S. Yang, Z. Sun, *Surf. Coat. Technol.* 105 (1998) 155.
- [8] M.A. Tamor, W.C. Vassell, *J. Appl. Phys.* 76 (1994) 3823.
- [9] J. Schwan, S. Ulrich, V. Batori, H. Ehrhardt, S.R.P. Silva, *J. Appl. Phys.* 80 (1996) 440.
- [10] L.K. Cheah, X. Shi, B.K. Tay, S.R.P. Silva, Z. Sun, *Diamond Relat. Mater.* 7 (1998) 640.