Structure and Electrochemical Properties of Nitrogen Doped Diamond-like Carbon Film Synthesized by Low Temperature Neutral Beam Enhanced Chemical Vapor Deposition

Qiuhe Wang[1], Xijiang Chang[1, 2], Yoshiyuki Kikuchi[2, 3], Kumi. Y. Inoue[4, 5], Tomohiro Kubota[2], Tomokazu Matsue[4, 5, 6], Toshihisa Nozawa[3] and Seiji Samukawa[2, 6]*

[1] College of Electronic & Electric Engineering, Shanghai University of Engineering Science, Shanghai, 201620, China
[2] Institute of Fluid Science, Tohoku University, Sendai, 980-8577, Japan
[3] TEL Technology Center Sendai, Tokyo electron limited, Sendai, 981-3137, Japan
[4] Micro System Integration Center (μ-SIC), Tohoku University, Sendai, 980-0845, Japan
[5] Graduate School of Environmental Studies, Tohoku University, Sendai, 980-8579, Japan
[6] World Premier International Center Initiative, Advanced Institute for Materials Research, Tohoku University, Sendai, 980-8577, Japan
*E-mail: 091031001@fudan.edu.cn

We report nitrogen doping diamond-like carbon film synthesis by a new technique called neutral beam enhanced chemical vapor deposition. The deposition is processed in UV/electron damage-free environment, and the substrate temperature is controlled at room temperature. The film structure was investigated by X-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy. The N/C ratio is 0.26, and doped nitrogen atoms exist in forms of amine and inside the aromatic ring, which helps increase film electrical conductivity. Cyclic voltammograms were carried out and the results indicate the DLC: N film qualified as electroanalysis sensor material.

1. INTRODUCTION

Diamond-like carbon (DLC) has recently been focused on due to its unique characteristics such as high hardness, wear resistance, chemical inertness, high electrical resistivity, and optical properties [1-4]. Because of these characteristics, DLC film has been widely applied in fields such as magnetic storage disks, biomedical coatings, solar cells, automotive engineering and tribological applications [5-

11]. As reported, nitrogen (N) doped DLC film (DLC: N) can obtain significantly lower electrical resistivity [12-16], which has led to a new direction of electrode materials for electrochemical application. Carbon materials have been widely used in electroanalysis, especially for biological sensing, due to a number of advantageous properties such as a wide potential window and superior biocompatibility [17-19]. DLC based film can be synthesized using many methods, including plasma chemical vapor deposition (PECVD), sputtering, electron beam evaporation, pyrolysis of polymeric thin films and ion beam deposition [20-27]. Results from these studies show that the carbon films more or less require the electrochemical properties for sensor electrode material, but during the synthesis processing, sometimes high temperatures over 600°C are applied, which is destructive to many substrates of new advanced biosensors such as Bio-LSI [28]. New technique is required to deposit high quality DLC film with low temperature and furthermore, the film structure is expected to be controlled via different experimental conditions. In this work, we present a new technique which can satisfy these requirements and N doped conductive DLC film is deposited on a room temperature, which is significant for applying such material on bio-sensor related applications.

2. EXPERIMENTAL

In our laboratory, we have employed a natural beam technique for series work on highly selective and energy-controllable etching, oxidization, and low-k material film deposition [29-36]. The advantages of the neutral beam technique for plasma processing are the UV/electron damage-free and energy controllability of the neutral beam, which is found in CVD processing. Thanks to these advantages, the precursor dissociation can be tightly controlled, so then the film structure can be designed [32-34]. Hence, the new CVD technique based on neutral beam, which we call neutral beam enhanced chemical vapor deposition (NBECVD), is a promising technique for the film deposition on substrates that are thermal sensitive or easily damaged by exposure to plasma.

The DLC: N film deposition has been done with the same equipment used by Kikuchi *et al* [33]. Figure 1 shows the experimental setup and schematic illustration of deposition process.
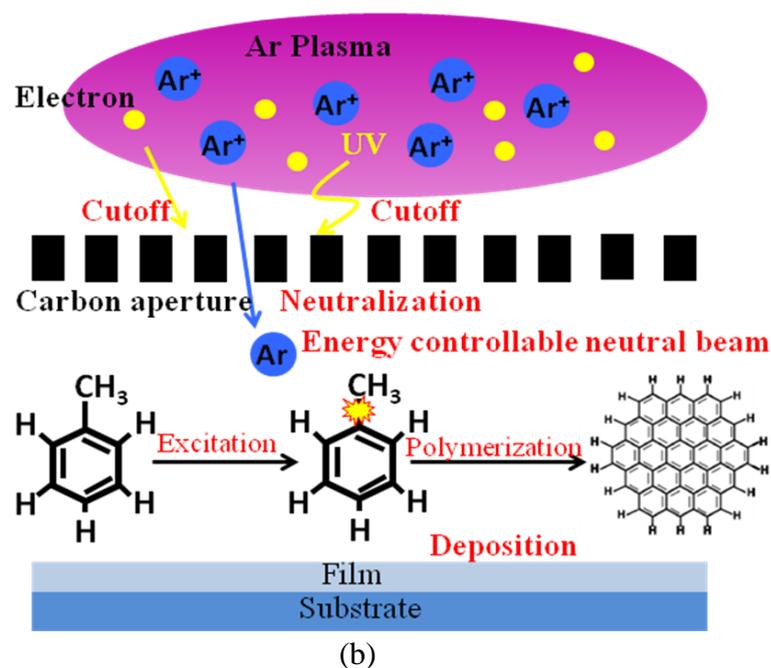

(a)

(b)
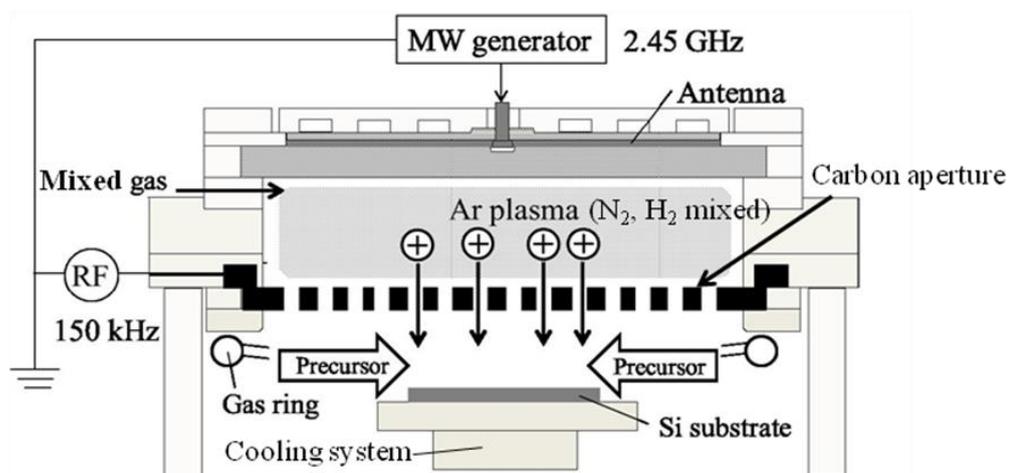
Figure 1. Schematic of NBECVD system and illustration of deposition process: (a) experimental setup; (b) illustration of DLC deposition processing with toluene as precursor.

The substrate is an 8-inch silicon wafer with a 100 nm platinum interlayer (sputter-deposited, L-332S-FH; Avelva Corp., Japan), which is treated as a real sensor substrate to investigate the adhesion between DLC: N film and metal surface. The platinum surface is cleaned by the hydrogen neutral beam bombardment to remove attached gas molecules before the deposition. Toluene is selected as a precursor for the formation of a polycyclic aromatic hydrocarbon structure, which can provide a conjugated system with delocalized π electrons for high electrical conductivity [33-34]. Argon, hydrogen, and nitrogen mixture gas with a ratio of 100:10:30 (sccm) is used for plasma generation with a 3.25 kW microwave, and then a corresponding mixture neutral beam is obtained in the deposition chamber by neutralization by a carbon aperture. Next, 150 W RF bias is added on the aperture to increase the neutral beam energy to break the benzene ring of toluene. Nitrogen doping is done during film growth. After deposition of thirty minutes, the deposited DLC: N film thickness is found to be in the range of 80-120 nm by measuring with scanning electron microscope (SEM, Hitachi High-Technologies Corporation, S-5500) and ellipsometer (Gaertner, LSE-2A2W). During the processing, the cooling system under the substrate is set at -50°C. As a result, the temperature on the wafer upper surface is below 50°C, which can be realized as room temperature. A four-probe resistivity system (Kokusai Semiconductor Equipment Corporation, VR-120s) is used to check the film, and the average volume resistivity is 3.4×10^{-2} $\Omega \cdot$cm. To investigate the film structure properties, photoelectron spectroscopy (XPS, KRATOS, AXIS Ultra DLD) and Fourier transform infrared (FTIR, Thermo Scientific, Nicolet 6700) are employed.

To investigate the electrochemical properties of the DLC: N film, cyclic voltammetry measurements were done by potentiostat (CompactStat, Ivium Technologies, Netherlands). The DLC: N sample was prepared in the same conditions mentioned above and cut into 1 cm×2 cm pieces. We used Elegrip Tape (GD-60-23A, Denka, Japan) pasting on the samples to form a circular electrode area

with a diameter of 2.0 mm. The voltammograms of DLC: N electrode in H_2SO_4 (H_2SO_4, Wako Pure Chemical Industries, Ltd., Japan) was done to check the potential window with a scan rate of 100 mV/s. Also the cyclic voltammograms obtained at working electrodes of the DLC: N and glassy carbon (GC) electrode with 2 mM ferrocenemethanol (FMA, 97%, Sigma-Aldrich Co., USA) in 0.1 M KCl (Wako Pure Chemical Industries, Ltd., Japan) solution, separately. The scan rate dependence of the cyclic voltammograms with DLC: N electrode in FMA/KCl solution was studied with different scan rates from 0.1 to 5.0 V/m.

3. RESULTS AND DISCUSSION

Figure 2 shows the FTIR spectrum of the N-DLC film deposited on a Si wafer with Pt interlayer. The absorption bands in the range of 1000-1700 cm^{-1} are widely observed in CN related papers [37-40], with several components at ~1570 cm^{-1} and 1370 cm^{-1}, which correspond to the G and D graphite peaks observed in Raman spectra. The major bonds are assigned as follows: ~1650 cm^{-1} as C=N stretching vibration mode, ~1550 cm^{-1} as NH_2 symmetric stretching mode, ~1440 cm^{-1} as CH_2 bending mode, ~1400 cm^{-1} and ~1210 cm^{-1} as C–N starching mode, ~700 cm^{-1} as CH out of plane bending at the edge of PAH, and C=C and C=N vibration modes. The absorption band around 2200 cm^{-1} is attributed to C≡N stretching mode [41-42]. Furthermore, imine (R–N=C), isonitrile (R–N^+≡C^-), and carboimide (N=C=N) groups can also give the absorption band here [43-45]. The N–H stretching vibration mode and C–H vibration modes appear at 2350 cm^{-1} and 2356 cm^{-1}, respectively.
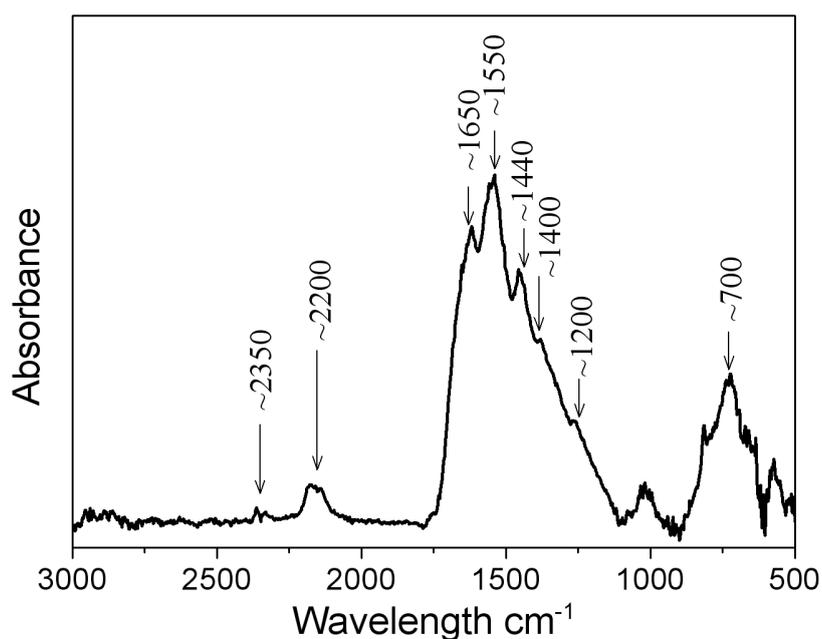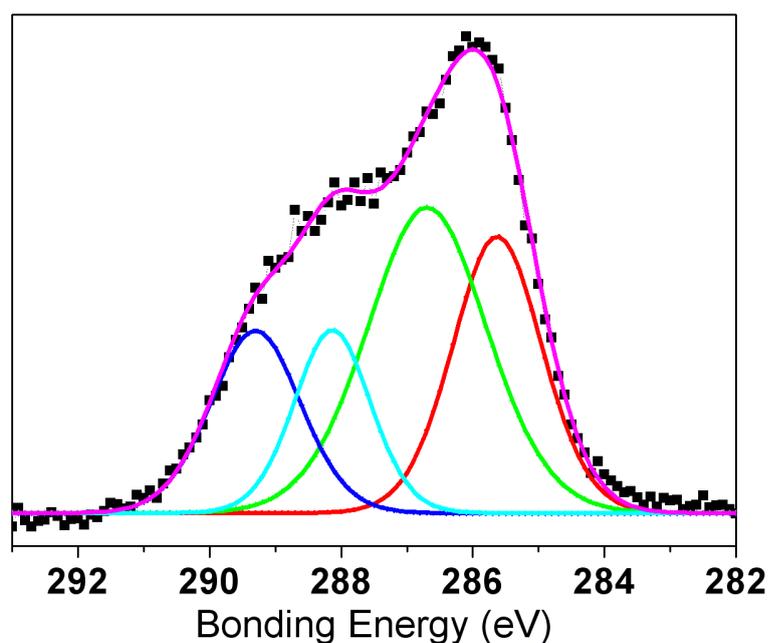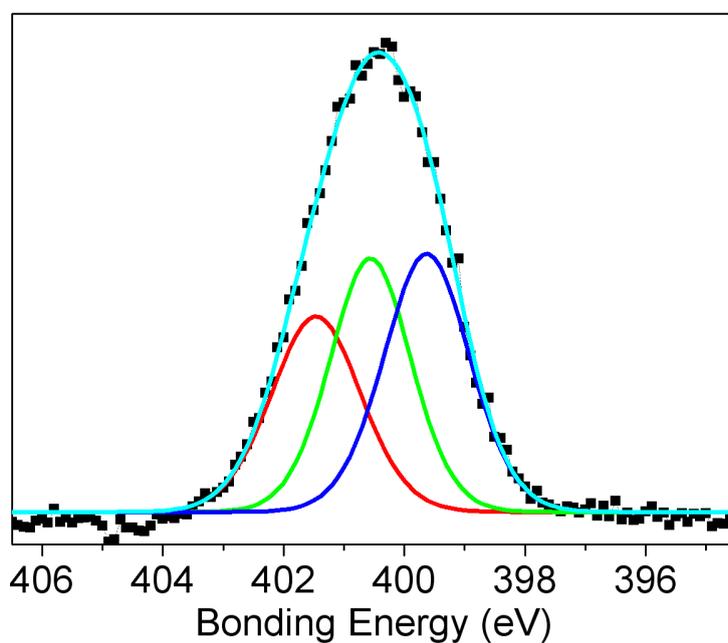

Figure 2. FTIR spectrum of DLC: N film

(a)

(b)

Figure 3. XPS spectra from DLC: N film: (a) C 1s; (b) N 1s.

The C 1s and N 1s photoelectron spectra of the N-DLC film are displayed in Fig. 3 (a) and (b), respectively. From the XPS data, the nitrogen concentration in the film was calculated, and the N/C ratio present in the film was 0.26. Because of the existence of nitrogen and aromatic content, the C 1s center peak shifted to a higher bonding energy than that of DLC. The C 1s region was deconvoluted

into four peaks at 285.6, 286.7, 288.1 and 289.3eV [46-48]. Similarly, the N 1s region was divided into peaks at 399.7, 400.4 and 401.5 eV [48-49]. The peak at 400.4 eV can be assigned to sp^2 NC_3 in the aromatic-ring-like pyrrolic or pyridinic structures. The peak at 399.7 eV corresponds to an amine-like structure, and that at 401.5 eV indicates the protonated nitrogen. For C 1s spectra, the binding energy at 285.6 eV is assigned to sp^2 C bound to a nitrogen atom inside an aromatic structure. The binding energies at 286.7 and 288.1 eV are assigned to sp^3 CN and sp^2 CN binding, respectively. The peak at 289.3 eV can be assigned to the sp^2 hybridized carbon in the aromatic ring attached to the NH_2 group. The XPS analysis is in good agreement with FTIR analysis and indicates that the nitrogen is present in the DLC: N film in both forms of amine and ring structures. The nitrogen acted as a weak donor in common DLC doping processing, but in our case, during the deposition processing, the participation of nitrogen enhanced the formation of a PAH structure, in which the conjugated system with delocalized π electrons can provide electrical conductivity for the film. As a result, the DLC: N film can express higher electrical conductivity than that prepared by other methods [50-51].
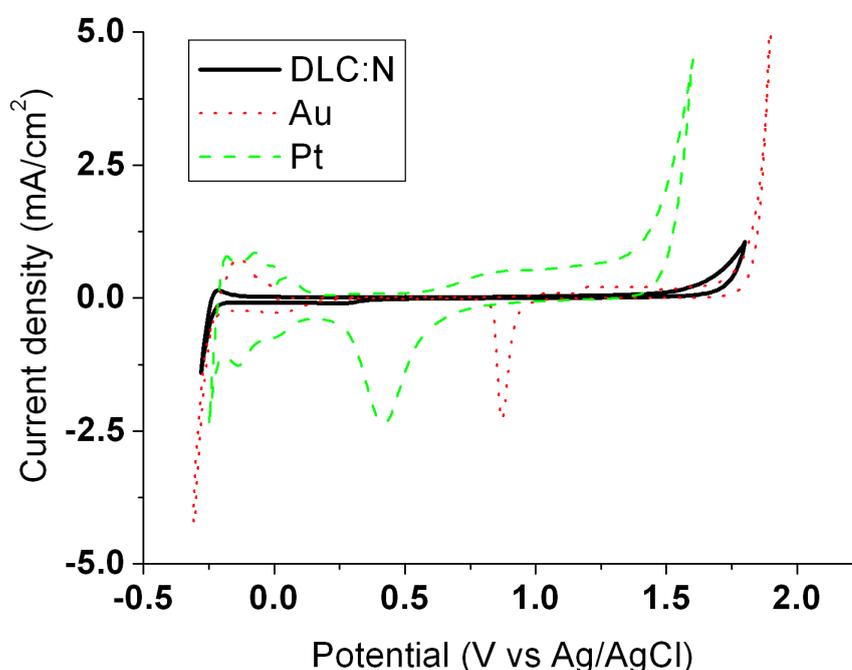

Figure 4. Cyclic voltammograms depicting the working potentials windows obtained with DLC: N, Au and Pt electrodes in 0.5 M H_2SO_4. Scan rates are 100 mV/s.

Figure 4 is the voltammograms of DLC: N in 0.5 M H_2SO_4 with a scan rate is 100 mV/s. Results with Pt and Au electrodes at same solution are also shown as references. No electrochemical processes occur on the DLC: N surface in the range between oxygen and hydrogen evolution, which shows a flat potential window with a width about 1.8 V. This value is close to the results of DLC: N electrode synthesized by the PECVD method [52-53]. Fig. 5 (a) shows the cyclic voltammograms obtained at working electrodes of the DLC: N and GC electrode with 2 mM ferrocenemethanol in 0.1 M KCl solution. The DLC: N and GC electrodes show almost the same CV curves with ΔE_p of 85 mV, which indicates the DLC: N film has good electrocatalytic activity for the redox reaction of ferrocene

[54]. The scan rate dependence of the cyclic voltammograms was studied, as shown in Fig. 5 (b). The peak current increases in a linear relationship with the square root of scan rate in the range of 10-5000 mV/s, which indicates the process is diffusion-controlled [55]. With these preliminary results, such DLC: N film can be competent as electrochemical electrode material, which is especially important for the chips that cannot be processed under plasma environment directly or at high temperature.
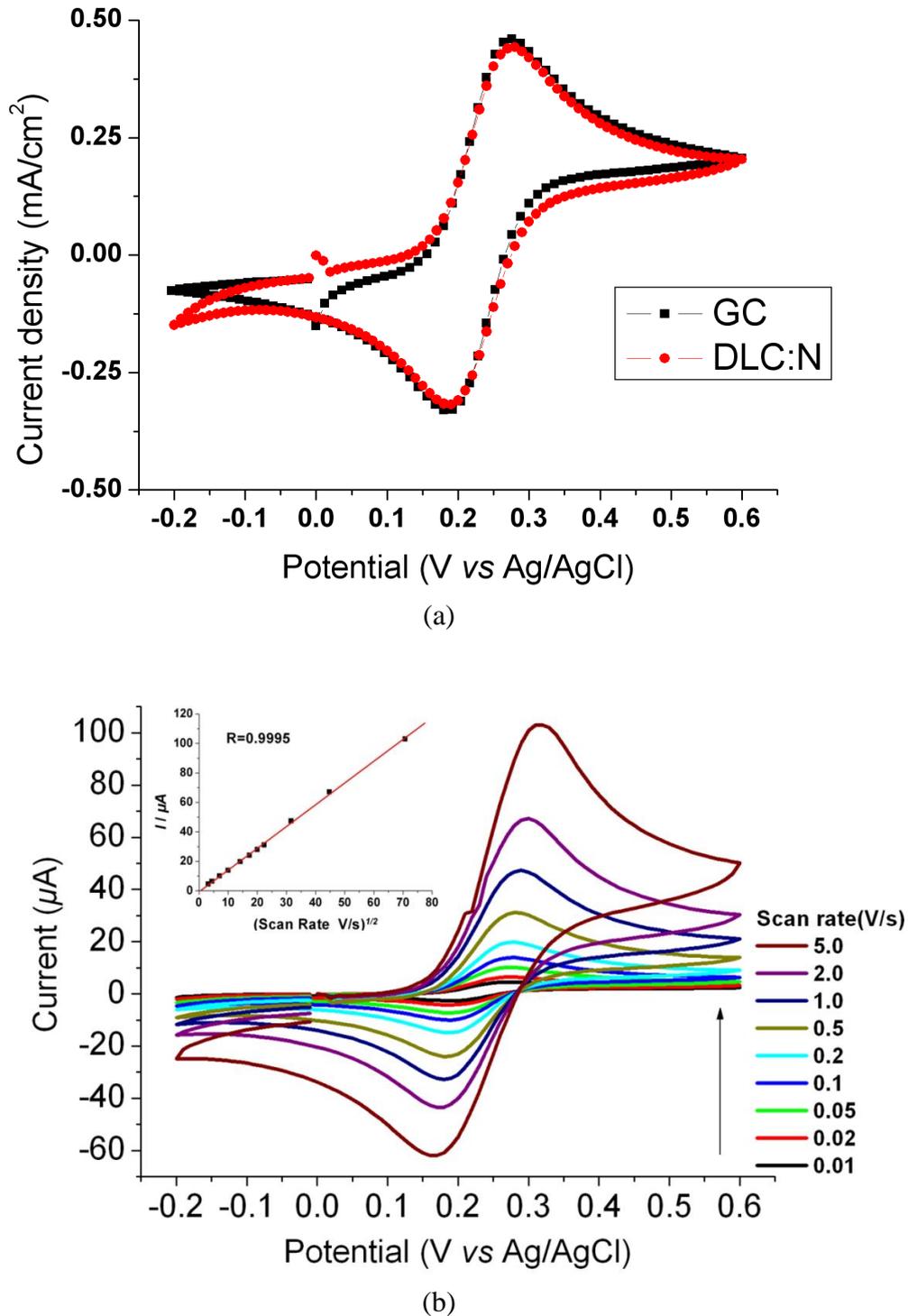

(a)

(b)

Figure 5. Cyclic voltammograms in 2 mM ferrocenemethanol (FMA) in 0.1 M KCl solution: (a) CVs of DLC: N and glassy carbon electrode with scan rate of 100 mV/s. (b) CVs of DLC: N electrode at different scan rates.

4. CONCLUSION

As a conclusion, neutral beam enhanced chemical vapor deposition is used for DLC film synthesis. Toluene is selected as a precursor for the formation of a large polycyclic aromatic hydrocarbon structure, which can provide a conjugated system with delocalized π electrons for high electrical conductivity. Argon/nitrogen/hydrogen mixed plasma is employed for the neural beam generation, and the neutral beam energy can be adapted in advance to control the deposited film structure. XPS and FTIR analyses of the film were done, and the aromatic hydrocarbon structure was confirmed. The doped nitrogen atoms exist in the film in forms inside the aromatic-ring-like and amine-like structures. Cyclic voltammetry measurements were done with the DLC: N film to examine its electrochemical properties. It has a wide potential window in 0.5 M sulfuric acid, which is similar to a graphite electrode, and the cyclic voltammograms in 2 mM FMA solution is the same as that from a standard glassy carbon electrode. Thus, the DLC: N film is a superior electrochemical electrode material and can be a candidate for many sensor electrodes, especially bio-sensors, due to the good biocompatibility of carbon. The remarkable advantages of this technique are that the deposition processing is totally electron/UV damage resistant to sensor substrates and that the temperature is kept at room temperature, so it can be used for deposition on heat-sensitive materials. Furthermore, this technique is expecting to be used in the improved fabrication of advanced electrochemical sensors such as bio-LSIs.

References

1. A. Grill, *Diam. Rel. Mater.*, 8 (1999) 428
2. A. Erdemir, C. Donnet, *J. Phys. D. Appl. Phys.*, 39 (2006) 311
3. J. Wang, J. Pu, G. Zhang, L. Wang, *Tribol. Int.*, 81 (2015) 129
4. J. Solis, H. Zhao, C. Wang, J. A. Verduzco, A. S. Bueno, A. Neville, *Appl. Surf. Sci.*, 383 (2016) 222
5. P. R. Goglia, J. Berkowitz, J. Hoehn, A. Xidis, L. Stover, *Diam. Rel. Mater.*, 10 (2001) 271
6. G. Dearnaley, J. H. Arps, *Surf. Coat. Technol.*, 200 (2005) 2518
7. J. Endrino, R. E. Galindo, H. S. Zhang, M. Allen, R. Gago, A. Espinosa, A. Anders, *Surf. Coat. Technol.*, 202 (2008) 3675
8. X. Li, Z. Lv, H. Zhu, *Adv. Mater.*, 27 (42) (2015) 6767
9. D. Bociaga, P. Komorowski, D. Batory, W.Szymanski, A. Olejnik, K. Jastrzebski, W. Jakubowski, *Appl. Surf. Sci.*, 355 (2015) 388
10. M. R. Price, A. Ovcharenko, B. Raeymaekers, *Tribol. Lett.*, 62 (1) (2016) 1
11. S. Wan, J. Pu, D. Li, G. Zhang, B. Zhang, A. K. Tieu, *J. Alloy. Compd.*, 695 (2016) 433
12. H. Dimigen, H. Hubsch, R. Memming, *Appl. Phys. Lett.*, 50 (1987) 1056

13. V. Anita, T. Butuda, T. Maeda, K. Takizawa, N. Saito, O. Takai, *Diam. Rel. Mater.*, 13 (2004) 1993
14. L. Wang, S. Gong, C. Yang, J. Wen, *Nanotechnol. Rev.*, 5 (5) (2016) 461
15. E. Mohagheghpour, M. Rajabi, R. Gholamipour, M. M. Larijani, S. Sheibani, *Appl. Surf. Sci.*, 360 (2) (2016) 52
16. S. Hussain, H. Erikson, N. Kongi, M. Merisalu, P. Ritslaid, V. Sammelselg, K. Tammeveski, *Int. J. Hydrogen Energ.*, 42 (9) (2017) 5958
17. M. Hupert, A. Muck, J. Wang, J. Stotter, Z. Cvackova, S. Haymond, Y. Show, G. M. Swain, *Diam. Rel. Mater.*, 12 (2003) 1940
18. R. G. Compton, J. S. Foord, F. Marken, *Electroanalysis*, 15 (2003) 1349
19. N. R. Lee, Y. Sle. Jun, K. I. Moon, C. Sunyong. Lee, *Jpn. J. Appl. Phys.,* 56 (3) (2017) 035506
20. D. Lusk, M. Gore ,W. Boardman, T. Casserly, K. Boinapally, M. Oppus, D. Upadhyaya, A. Tudhope, M. Gupta, Y. Caoand, S. Lapp, *Diam. Rel. Mater.*, 17 (2008) 1613
21. A. Zeng, E. Liu, S. N.Tan, S. Zhang, J. Gao, *Electroanalysis*, 14 (2002) 1110
22. S. Hirono, S. Umemura, R. Kaneko, *Appl. Phys. Lett.*, 80 (2002) 425
23. O. Niwa, H. Tabei, *Anal. Chem.*, 66 (1994) 285
24. J. Jia, D. Kato, R. Kurita, Y. Sato, K. Maruyama, K. Suzuki, S. Hirono, T. Ando, O. Niwa, *Anal. Chem.*, 79 (2007) 98
25. Y. V. Pleskov, M. D. Krotova, V. I. Polyakov, A. V. Khomich, A. I. Rukovishnikov, B. L. Druz, I. Zaritskiy, *J. Electro anal. Chem.*, 519 (2002) 60
26. F. Stock, F. Antoni, F. L. Normand, D. Muller, M. Abdesselam, N. Boubiche, I. Komissarov, *Appl. Phys. A*, 123 (9) (2017) 590
27. B. Liao, J. Yu, Y. Wang, B. Bian, Q. Jiang, J. Luo, X. Zhang, X. Wu, M, Ying, *Appl. Phys*. A, 123 (8) (2017) 544
28. K. Y. Inoue, M. Matsudaira, R. Kubo, M. Nakano, S. Yoshida, S. Matsuzaki, A.Suda, R. Kunikata, T .Kimura, R. Tsurumi, T. Shioya, K. Ino, H. Shiku, S. Satoh, M. Esashia, T. Matsue, *Lab Chip*, 12 (2012) 3481
29. S. Samukawa, Jpn. J. Appl. Phys., 45 4A (2006) 2395
30. M. Igarashi, R. Tsukamoto, C. H. Huang, I. Yamashita, S. Samukawa, *Appl. Phys. Exp.*,4 (1) (2011) 481
31. A. Wada, R. Zhang, T. Shinichi, S. Samukawa, Appl. Phys. Lett., 100 (21) (2012) 2224
32. Y. Kikuchi, A. Wada, T. Kurotori, M. Sakamoto, T. Nozawa, S. Samukawa, *J. Phys. D: Appl. Phys.*, 46 (39) (2013) 5203
33. Y. Kikuchi, A. Wada, K. Kurotori, M. Nakano, K. Y.Inoue,T. Matsue, T. Nozawa, S. Samukawa, *Carbon,* 67 (2014) 635
34. Y. Kikuchi, X. Chang, Y. Sakakibara, K. Y. Inoue, T. Matsue, T. Nozawa, S. Samukawa, *Carbon*, 93 (4) (2015) 207
35. N. P. Stepina, A. F. Zinovieva, A. V. Dvurechenskii, S. Noda, M. Z. Molla, S. Samukawa, *Appl. Phys. Lett.*, 110 (20) (2017) 1245
36. D. Ohori, A. Fukuyama, K. Sakai, A. Higo, C. Thomas, S. Samukawa, T. Ikari, *Jpn. J. Appl. Phys.*, 56 (2017) 050308
37. R. Kurt, R. Sanjines, A. Karimi, F. Le´vy, *Diam. Rel. Mater.*, 9 (2000) 566
38. S. Rodil, N. A. Morrison, W. I. Milne, J. Robertson, V. Stolojan, D. N. Jayawardane, *Diam. Rel. Mater.*, 9 (2000) 524
39. W. Yang, Y. Guo, D. Xu, J. Li, P. Wang, P. Ke, A. Wang, *Surf. Coat. Tech.*, 261 (2015) 398
40. T. Kimura, R. Nishimura, *Jpn. J. Appl. Phys.*, 54 (1S) (2014) 01AD06
41. J. C. Sanchez-López, C. Donnet, F. Lefèbvre, C. Fernández-Ramos, A. Fernández, *J. Appl. Phys.*, 902 (2001) 675
42. P. Ye, F. Xu, J. Wu, S. Tian, X. Zhao, X. Tang, D. Zuo, *Surf. Coat. Tech.,* 320 (2017) 183
43. P. Hammer, F. Alvarez, *Thin Solid Films,* 116 (2001) 398

44. M. Aono, T. Harata, N. Kitazawa, Y. Watanabe, *Jpn. J. Appl. Phys.*, 55 (1S) (2016) 01AA03
45. S. Bhattacherjee, H. Niakan, Q. Yang, Y. Hu, J. Dynes, *Surf. Coat. Tech.*, 284 (12) (2015) 153
46. Y. J. Cho, H. S. Kim, S. Y. Baik, Y. Myung, C. S. Jung, C. H. Kim, J. Park, H. S. Kang, *J. Phys. Chem.* C, 115 (2011) 3737
47. J. Senthilnathan, C. C. Weng, J. D. Liao, M. Yoshimura, *Sci. Rep.*, 3 (2013) 2414
48. S. Bhattacharyya, J. Hong, G. Turban, *J. Appl. Phys.*, 83 (7) (1998) 3917
49. A. P. Dementjev, A. de Graaf, M. C. M. van de Sanden, K. I. Maslakov, A. V. Naumkin, A. A. Serov, *Diam. Rel. Mater.*, 9 (11) (2000) 1904
50. S. Kundoo, S. Kar, *Adv. Mater. Phys. Chem.*, 3 (9) (2013) 191
51. S. Nakao, T. Kimura, T. Suyama, K. Azuma, *Diam. Relat. Mater.*, 77 (2017) 122
52. H. Zanin, P. W. May, R. L. Harniman, *Carbon,* 82 (2) (2014) 288
53. Tanaka Y, Furuta M, K. Kuriyama, R. Kuwabara, T. Kondo, A. Fujishima, K. Honda, *Electrochimi. Acta,* 56 (3) (2011) 1172
54. D. V. And, R. L. Mccreery, *Anal. Chem.*, 71 (20) (1999) 4594
55. K. R. Mahanthesha, B. E. K. Swamy, K. V. Pai, U. Chandra, B.S. Sherigara, *Anal. Bioanal. Chem.*, 4 (1) (2010) 1962