

Structural and electrical properties of nanocrystalline diamond (NCD) heavily doped by nitrogen

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Abstract

Gas mixtures containing up to 40% nitrogen by volume and 1% CH₄ with the balance being argon have been used for the deposition of nitrogen doped nanocrystalline diamond (NCD) films by means of microwave plasma enhanced chemical vapour deposition (MPECVD). The CVD plasma was monitored by optical emission spectroscopy to reveal the plasma species, e.g., CN molecules, as a function of the nitrogen additive. Structural properties of the deposited NCD films were studied by FESEM and Raman spectroscopy. Effects of nitrogen doping on the electrical resistivity and electron field emission characteristics of the NCD films were measured. In this work, correlation between the structural and electrical properties of NCD films and the nitrogen additive to the CVD plasma will be presented and discussed.

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1. Introduction

Nanocrystalline diamond (NCD)/ultrananocrystalline diamond (UNCD) with diamond grains in the nanometer scale, possesses meritorious nature in both its mechanical and electrical properties, such as electron field emission characteristics and electrical conductivity. The massive network of grain boundaries composed of sp² bonded carbon are considered to be responsible for these unique properties. Doping of NCD films further promotes their performance and makes them more suitable for practical applications. Nitrogen is among a few suitable dopants for NCD. It is ubiquitously present in almost all single crystal diamond and forms deep donors as a *n*-type dopant at high temperatures [1]. Unlike nitrogen doped single crystal diamond, nitrogen doped NCD/UNCD films exhibit significant electrical conductivity at room temperature, and low turn-on electric fields for electron field emission. These

have been achieved by the addition of N₂ to gas plasmas generated in CH₄/Ar mixtures [2–6]. The structure and the mechanism for electron field emission of NCD films have also been proposed and discussed [7–9].

It has been reported that by increasing the nitrogen content in UNCD films, the electrical conductivity of the nitrogen-doped UNCD films increased to as high as 143 Ohm⁻¹ cm⁻¹ with a much lower thermal activation energy than that of nitrogen dopant in single crystal diamond [2,4,5]. Nitrogen incorporation (up to 20%) increased both the grain sizes and the width of the grain boundaries. The disordered carbon at the grain boundaries is responsible for the substantial changes in electric properties [3,5,9]. Besides, nitrogen preferentially enters the grain boundaries and promotes sp² bonding for neighboring carbon atoms, which in turn improve the electron field emission properties of UNCD films [6–8]. To investigate the nitrogen effects on NCD films, up to 40% nitrogen was mixed with CH₄/Ar. The changes in plasma composition and the morphology, structure and electrical properties of NCD films are correlated and presented in this work.

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2. Experimental

A 5 kW ASTeX 2.45 GHz microwave CVD reactor was used for this work. Before deposition, *n*-type silicon substrates were seeded by a bias enhanced nucleation (BEN) process under an optimized condition, i.e., CH₄/H₂: 45/300 sccm, 1.5 kW, 55 torr, -125V, for 10 min. Different concentrations of nitrogen, up to 40%, were mixed with 1% methane and balanced with argon. The microwave power was fixed at 700 W, the total gas flow rate was 100 sccm, and the molybdenum substrate holder was kept at the same height with respect to the microwave cavity. No extra heater except the plasma itself was used. Gas pressure was adjusted to keep the desired substrate temperature during deposition at about the same value for all experiment. The substrate temperature was monitored by a thermal couple attached to the bottom of the substrate holder.

The optical emission spectra taken for microwave plasmas [10] in gas mixtures with different nitrogen contents are shown in Fig. 1 in comparison with that taken from a microwave plasma in the gas mixture of 1% CH₄/99% H₂. The major species detected in the plasma are C₂ radicals (Swan band, 619.1, 563.6, 473.7, and 438.3 nm) while the optical emission from CN atoms (421.6 and 460.6 nm) and excited N₂ molecules (678.7 nm) [11,12] become more pronounced than that from C₂ radicals as the percentage of nitrogen increases.

The structural characterization of diamond films was examined by UV Raman spectroscopy at 325 nm in wavelength. Raman spectra were featured with four main bands and peaks located at around 1172, 1333, 1380, and 1580 cm⁻¹. Due to the dispersion that resulted from UV laser [13], the band centered at 1172 cm⁻¹ is reasonably assigned to nanocrystalline diamond. Raman features at 1333, 1380, and 1580 cm⁻¹ are indications of sp³ diamond, D-band, and G-band, respectively. Electron field emission was measured using a diode structure. Two 60 μm thick ceramic disks were used as spacers between the anode made of a tungsten rod enclosed in a ceramic block, and the cathode, which was a NCD film coated on Si. The applied voltage, and resulting electron field emission current were controlled and recorded by a computer for further analysis. The surface morphologies and the thickness of NCD films grown with different percentages of nitrogen additive were observed by FESEM for comparison.

3. Results and discussion

Fig. 1 is the optical emission spectrum (OES) of 1% CH₄/Ar/N₂ plasma compared with 1% CH₄/99% H₂ plasma as shown in the inset. It has been well known that hydrogen is critical for the deposition of microcrystalline diamond (MCD). When hydrogen is replaced by noble gases, such as Ar, the C₂ dimers become the dominant species in the

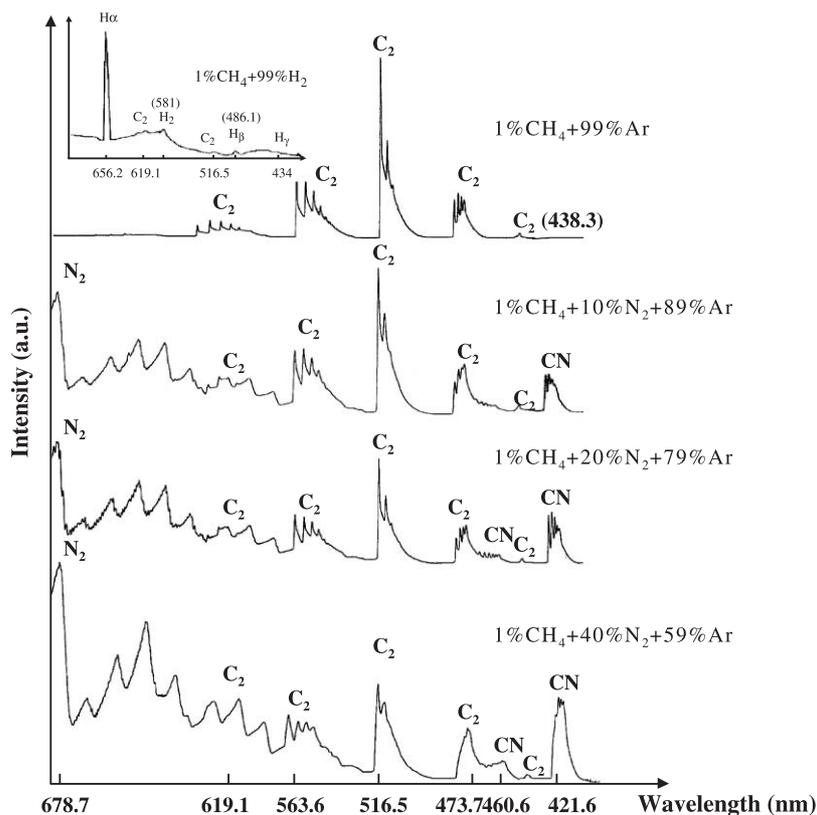


Fig. 1. Optical emission spectra (OES) of microwave plasmas for NCD deposition with or without the addition of N₂.

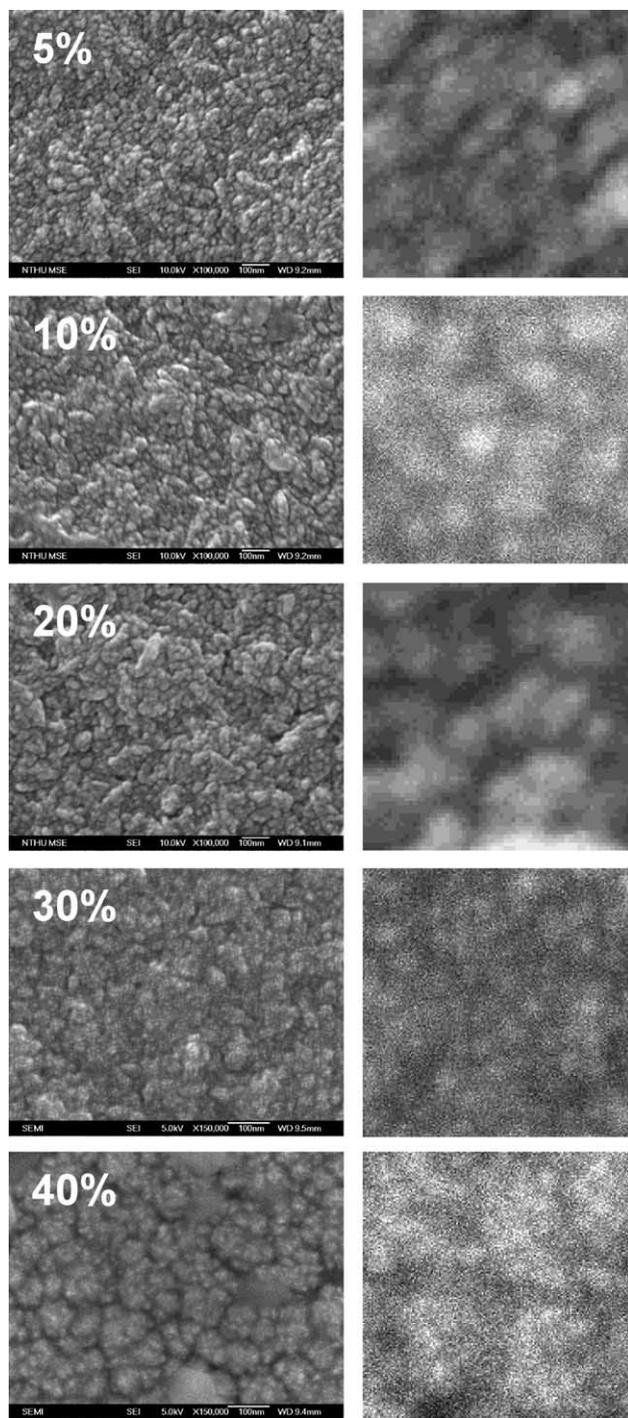


Fig. 2. FESEM images of nitrogen-incorporated NCD films with nitrogen additive in the gas mixture ranging from 5% to 40%. Images on the right hand side are of the size of 100 nm by 100 nm.

plasma resulting in enhancement of secondary nucleation of diamond and leading to the growth of nanocrystalline diamond (NCD) [14]. With the addition of N_2 , the excited N_2 molecules and CN radicals appear in the plasma and their optical emission intensities are comparable to that of C_2 dimers even with only 10% N_2 added in the feedstock. When 40% N_2 was added, the excited N_2 molecules become the dominant species in the plasma. Fig. 2 shows the SEM

images of NCD films with different amount of N_2 additive. The grain size of NCD seems to increase with increasing addition of N_2 at the beginning, i.e., up to 20% of nitrogen. This has previously been revealed by another group by means of TEM [2,3]. However, with further addition of N_2 , the grain size of NCD decreases instead of increasing further. Estimated by the SEM images, the average grain sizes of NCD incorporated with 5%, 10%, 20%, 30%, and 40% of nitrogen are 12–15 nm, 16–19 nm, 20–24 nm, 8–10 nm, and 6–8 nm, respectively. Besides, the alteration of surface morphology can be found while 30% or more N_2 was added. Fig. 3 shows the transition of Raman spectra of NCD films with 5% to 40% N_2 addition to 1% CH_4/Ar mixtures along with what was grown with 5% H_2 addition. Due to much higher sensitivity of sp^3 over sp^2 by UV Raman [15], 1333 cm^{-1} is clear with or without 5% H_2 in 1% CH_4/Ar mixtures. While more and more nitrogen was added to the gas mixtures, sp^3 peak disappeared and the band centered at 1172 cm^{-1} , which is an indication of NCD, still could be seen until 20% N_2 was added. When 40% N_2 was added, not only the NCD peak, but the sp^2 graphite phase at 1380 cm^{-1} , became too broad to be seen clearly.

Previous studies have demonstrated that there is a limitation for nitrogen atoms to be incorporated into diamond lattices [2,3,7]. CN does not by itself participate in the deposition of NCD but rather reduces the secondary nucleation rate for diamond [3,16]. This can probably explain the larger diamond grains for NCD with up to 20% N_2 addition as shown in Fig. 2. Above this level of nitrogen doping, a deteriorating/etching effect has been observed in this work when additional N_2 is added into the 1% CH_4/Ar gas mixture. With 40% N_2 addition, if the gas pressure is not

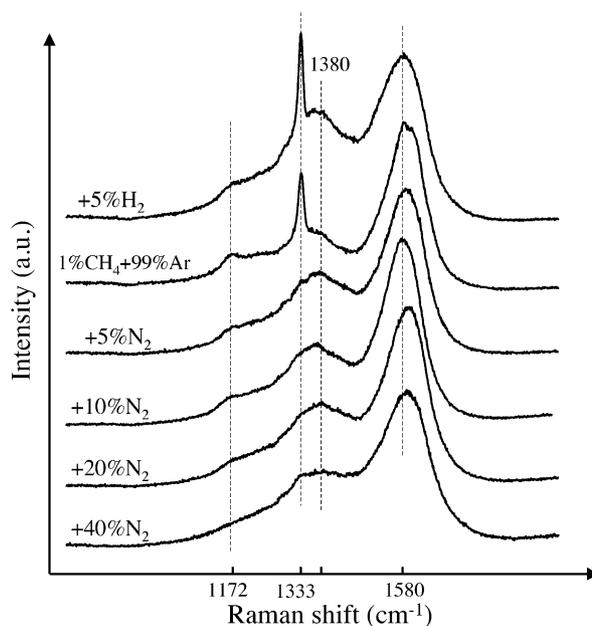


Fig. 3. E325 nm UV Raman spectra of NCD films grown with 0% to 40% N_2 addition in 1% CH_4/Ar mixtures as compared with what is grown by a microwave plasma in the gas mixture of 1% $CH_4/5\% H_2/94\% Ar$.

low enough, e.g. 80 torr in our case, the diamond nucleation layer prepared by the BEN process is etched away, not to mention the growth of NCD films. According to Fig. 2, when the content of N_2 is more than 30% by volume, the grain size of NCD shrinks and the continuously whisker-like surface morphology, which can be seen in the NCD grown with 10% or 20% N_2 addition, gradually changes to isolated islands. Combined with the absence of responses from sp^3 and some sp^2 bonded carbon in Raman spectra, it can be concluded that not only the crystals but the quality of NCD deteriorated by massive inclusion of N_2 . This is similar to the case of MCD deposition [17,18].

Fig. 4 shows the onset electrical field, determined by the transition points in F–N plot, of various NCD films for electron field emission. In general, the turn-on electric field decreases at the beginning when N_2 additive is increased. But, it starts to increase when more than 20% N_2 was added to the gas mixture. According to previous reports [6,7,10], the presence of sp^2 or the increased ratio of sp^2/sp^3 is responsible for the lowered electron field emission threshold electric field which is favored by the addition of N_2 . This trend can be seen in the figure when 20% or lower of N_2 was added. Karabutov et al. [8] used scanning tunnelling-field emission microscope (STFEM) to study the microscopic properties of the emission centers, and found that the emission was associated with diamond/ sp^2 bonded carbon interfaces so that a certain mass ratio of sp^2/sp^3 was needed for well-emitting diamond structure. As evidenced by Raman spectra, NCD films grown with 40% N_2 in gas mixtures possess

little sp^3 bonded structure and exhibits the worst electron field emission characteristic. For the conductivity measurement, nitrogen doped NCD films were deposited on high resistivity Si substrate for 3 hr. Al was sputtered as metal contacts for resistivity measurements by means of a van der pauw structure. Ohmic contacts were reported to be formed on every nitrogen doped NCD films [4]. However, our measured conductivity was not as high as what was reported by Gruen et al. [2,4]. In our case, the conductivity of NCD films was promoted just a little from 3.75 to 6.68 ($\text{Ohm}^{-1} \text{cm}^{-1}$) corresponding to 5% and 30% N_2 addition, respectively.

4. Conclusions

Structural and electrical properties of nitrogen doped NCD films have been studied in this work by means of OES, SEM, Raman, electron field emission, and electrical conductivity. Up to 40% N_2 was added to the plasma and investigated. A deterioration/etching effect on NCD films is found when massive N_2 , over 30% in our case, was added into 1% CH_4/Ar mixtures. With proper deposition conditions, NCD films can be grown with addition of 40% N_2 , exhibiting grains of the size of 6–8 nm, almost no detected sp^3 structure, and poor electron field emission properties. The addition of N_2 in CH_4/Ar plasma lowered the onset electron field for electron field emission from NCD films due to increased sp^2/sp^3 ratios, and/or probably the formation of whisker-like surface morphology.

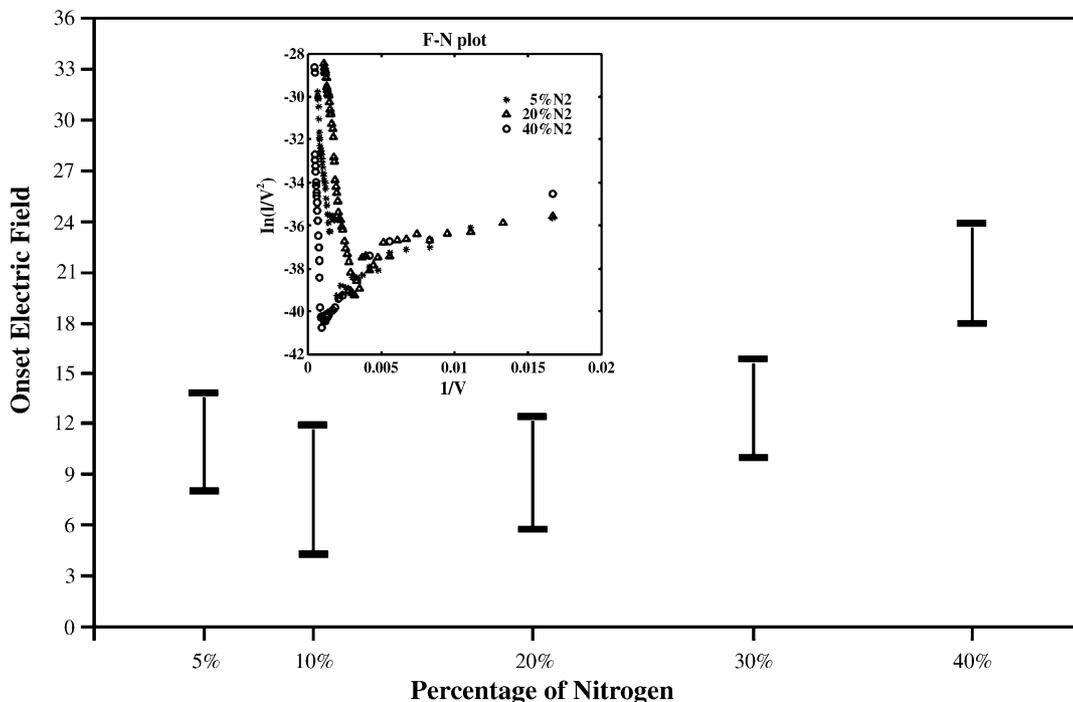


Fig. 4. Electron field emission properties of NCD films deposited by MPCVD with different percentages of N_2 addition measured using a diode test structure in vacuum.

References

- [1] K.M. McNamara, *Applied Physics Letters* 83 (7) (2003) 1325.
- [2] S. Bhattacharyya, O. Auciello, J. Birrell, J.A. Carlisle, L.A. Curtiss, A.N. Goyette, D.M. Gruen, A.R. Krauss, J. Schlueter, A. Sumant, P. Zapol, *Applied Physics Letters* 79 (10) (2001) 1441.
- [3] J. Birrell, J.A. Carlisle, O. Auciello, D.M. Gruen, J.M. Gibson, *Applied Physics Letters* 81 (12) (2002) 2235.
- [4] J.E. Gerbi, O. Auciello, J. Birrell, D.M. Gruen, B.W. Alphenaar, J.A. Carlisle, *Applied Physics Letters* 83 (10) (2003) 2001.
- [5] O.A. Williams, S. Curat, J.E. Gerbi, D.M. Gruen, R.B. Jackman, *Applied Physics Letters* 85 (10) (2004) 1680.
- [6] A.V. Karabutov, V.I. Konov, V.G. Pereverzev, I.I. Vlasov, E.V. Zavedeev, S.M. Pimenov, E.N. Loubnin, *Journal of Vacuum Science and Technology B* 22 (3) (2004) 1319.
- [7] T.D. Corrigan, D.M. Gruen, A.R. Krauss, P. Zapol, R.P.H. Chang, *Diamond and Related Materials* 11 (2002) 43.
- [8] A.V. Karabutov, V.D. Frolov, V.I. Konov, *Diamond and Related Materials* 10 (2001) 840.
- [9] J. Birrell, J.E. Gerbi, O. Auciello, J.M. Gibson, D.M. Gruen, J.A. Carlisle, *Journal of Applied Physics* 93 (9) (2003) 5606.
- [10] Y. Liu, C. Liu, Y. Chen, Y. Tzeng, P. Tso, I. Lin, *Diamond and Related Materials* 13 (2004) 671.
- [11] W. Zhu, A. Inspektor, A.R. Badzian, T. McKenna, R. Messier, *Journal of Applied Physics* 68 (4) (1990) 1489.
- [12] G. Herzberg, *Molecular Spectra and Molecular Structure I, Spectra of Diatomic Molecules*, D. Van Nostrand, New York, 1950.
- [13] R. Pfeiffer, H. Kauzmany, P. Knoll, S. Bokova, N. Salk, B. Gunther, *Diamond and Related Materials* 12 (2003) 268.
- [14] J.R. Rabeau, P. John, J.I.B. Wilson, Y. Fan, *Journal of Applied Physics* 96 (11) (2004).
- [15] S.M. Huang, Z. Sun, Y.F. Lu, M.H. Hong, *Surface and Coatings Technology* 151–152 (2002) 263.
- [16] P. Zapol, M. Sternberg, L.A. Curtiss, T. Frauenheim, D.M. Gruen, *Physics Review B* 65 (4) (2002) 045403.
- [17] J.X. Yang, H.D. Zhang, C.M. Li, G.C. Chen, F.X. Lu, W.Z. Tang, Y.M. Tong, *Diamond and Related Materials* 13 (2004) 139.
- [18] V.M. Ayres, M. Farhan, D. Spach, J. Bobbitt, J.A. Majeed, B.F. Wright, B.L. Wright, J. Asmussen, M.G. Kanatzidis, T.R. Bieler, *Journal of Applied Physics* 89 (11) (2001) 6062.