# Nitrogen-doped diamond nanowire gas sensor for detection of $CH_4$

**Andrew Zhou *1 Xinpeng Wang 2 and Peter Feng,*3**

[1]*Department of Physics, Indiana University of Pennsylvania, Indiana, PA 15705, USA*
[2]*Nanonex Corporation, Monmouth Junction, New Jersey 08852, USA*
[3]*Department of Physics, University of Puerto Rico, San Juan, Puerto Rico 00936, USA*

*Corresponding authors. E-mail: fzhou@iup.edu; peter.feng@upr.edu.

## Abstract

Diamond-based sensors have shown great potential in the past few years due to their unique physicochemical properties. We report the development of high-performance nitrogen doped ultrananocrystalline diamond (UNCD) nanowire based $CH_4$ gas sensors, taking the advantage of a large surface-to-volume ratio and a small active area offered by the 1D nanowire geometry. The morphologic surface and crystalline structures of UNCD are also characterized by using scanning electron microscopy (SEM) and Raman scattering, respectively. By using synthesized nanowires arrays combined with 4-pin electrical electrodes, prototypic highly sensitive $CH_4$ gas sensors have been designed, fabricated and tested. Various sensing parameters including the sensitivity, response time and recovery time, and thermal effect on the performance of the gas sensor have also been investigated in order to reveal the sensing ability. Enhanced by the small grain size and porosity of nanowire structure, the fabricated nanowire UNCD sensors demonstrated a high sensitivity to $CH_4$ gas at room temperature down to 2 ppm, , as well as a fast response and recovery times which are almost 10 times faster than that of regular nanodiamond thin film based sensors. 

**Keywords:** nitrogen doping, ultrananocrystalline diamond (UNCD), nanowire, gas sensor, $CH_4$

## Introduction

Various diamond based gas sensors have been demonstrated to detect hydrogen, oxygen, carbon monoxide, etc., based on the surface conductivity change with adsorbed gas molecules.[1–3] Diamond based gas sensors are expected to have high sensitivity, fast response, and tolerant to high temperatures. For example, X. Peng et al. reported boron-doped ultrananocrystalline diamond (UNCD) nanowire based carbon monoxide (CO) gas sensors.[4] Yasar Gurbuz et al. built boron-doped polycrystalline diamond (PCD) film based sensors for detection of benzene ($C_6H_6$) and toluene ($C_7H_8$).[5] Hydrogenated nanocrystalline diamond (NCD) films synthesized using chemical vapor deposition (CVD) technique have been demonstrated for detection of ammonia ($NH_3$).[6] The three-dimensional model of the current density distribution of the hydrogenated NCD was used to describe the transient flow of electrons between interdigitated electrodes and the hydrogenated NCD surface.[7]

The current studies have shown progress on the development of diamond film and nanowire based gas sensors. However, very few papers report the gas sensors based on nitrogen-doped (N-doped) diamond materials, especially with nanowire geometry. It will be interesting to see if a nanowire diamond based methane gas sensor could offer a better performance, although we observed the electrical property change of nitrogen doped ultrananocrystalline diamond caused by methane gas.[8]

In this paper we present experimental results on the fabrication of N-doped UNCD nanowire arrays for gas sensor applications. Both crystalline structures and electrical properties of UNCD nanowire arrays have been characterized. The focus of our experimental studies is on the basic properties of the nitrogen-doped UNCD nanowire $CH_4$ gas sensor, including the sensitivity, response time, recovery time, repeatability, and stability of newly designed $CH_4$ gas sensors.

## Experimental

### *Fabrications*

Fig. 1(a) shows a schematic diagram of platform with highly ordered nanowire arrays combined with a pair of external electrodes (labelled as “1” and “4”) and a pair of internal electrodes (labelled as “2” and “3”) for $CH_4$ gas sensors. As shown in Fig. 1(b), the spaces are 5 μm between the electrodes “1” and “2”, 10 μm between electrodes “2” and “3” and 20 μm between electrodes “3” and “4”. The conductive electrodes “1” and “4” (the external electrode pair) are connected to a switcher, a DC power supply with a step voltage $V_p$, and a high precision resistor R in series, respectively. One voltmeter ($V_{in}$) is connected to the electrodes “2 “ and “3” (the internal electrode pair) and the other voltmeter ($V_{ex}$) is connected in parallel with the resistor in the external electrode circuit. Both voltmeters monitor the voltage variations of the gas sensors formed between the internal electrode pair and external electrode pair simultaneously. In order to test the operation above room temperature, a thermocouple and tungsten filament are used to control the operating temperature of the sensor. At a given temperature ($T_o$), the sensor output voltage signal is measured as a function of gas concentration.

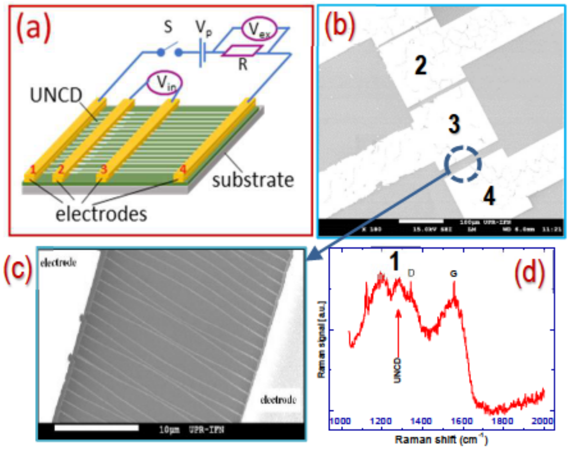


Fig. 1(a) Schematic diagram of platform. (b) SEM image of UNCD film (grey) with four Ti/Au (white) electrodes. (c) the magnified SEM image of UNCD nanowires between the two (white) electrodes. (d) Raman spectrum of UNCD recorded with 514 nm excitation wavelength.

The sensing material of N-doped UNCD film used in this study was synthesized by the MPCVD technique at Argonne National Laboratory.[9] The film round 50~100 nm thick was deposited on a Si substrate. The microwave frequency for the MPCVD system was 2.45 GHz and the power was around 2 kW. The gas mixture contained 95%-99% Ar, 0-3% of $H_2$, 1% of $CH_4$, and other dopant gas and the chamber pressure remained at around 100 Torr. During synthesis, the substrate temperature was kept around 600 °C.

Unlike polycrystalline diamond (PCD) film or nanocrystalline diamond (NCD) film, in general, the surface roughness of UNCD film is very small, around only a few nm (RMS), which doesn't change when the film thickness increases. This is important for the nanowire fabrication. In contract to UNCD growth in Ar-rich environment, for NCD growth in hydrogen-rich condition, the hydrogen abstraction take place to replace each C-H bonding of $CH_4$ with the C-C bonding individually. This process gives the chance for diamond crystal to grow, leading to a columnar crystal growth with a higher surface roughness.[9,10]

In order to enlarge the contact surface area of the sensor, top-down fabrication techniques were used for achieving UNCD nanowire arrays. The process typically involves design, lithographical patterning, etching, mask deposition and removal steps. Briefly, 10/100 nm titanium/gold (Ti/Au) or titanium/platinum (Ti/Pt) layer was deposited on the synthesized UNCD film through a mask to form the four electrodes separated by 5, 10 and 20 μm gaps between two adjacent electrodes. Then the hydrogen silsesquioxane (HSQ) resist was spin coated at top, and the nanowire pattern between the electrodes was defined using electron beam lithography, followed by reactive ion etching with the photo resist as an etch mask. After etching nanowires and removal of the photo mask, the sample was annealed at 150 °C for 5 min in the probe station chamber by LakeShore temperature controller. Very detailed description of MOCVD equipment, synthesis, crystalline structure characterization, and nanowire patterning and fabrication can be found from our previous reports.[11]

Fig. 1(c) shows the enlarged SEM image of UNCD nanowire arrays between the two (white) electrodes where the width and length of each diamond wire is around 150 nm and 20 μm, respectively. The UNCD sensing composite material was also analysed by Raman spectroscopy using triple monochromator with an excitation wavelength of 514 nm ($Ar^+$ ion Laser). The microscope focused the laser beam onto the surface of the UNCD. The broad band peaked at around 1332 cm$^{-1}$ confirms its nanodiamond crystallites from sp$^3$ carbon, while the sp$^2$-bonded carbon around 1340-1600 cm$^{-1}$ (in particular D-band at 1350 cm$^{-1}$ and G-band at 1580 cm$^{-1}$) are clearly shown in Fig.1(d). Typically, UNCD films contain the mixtures of sp2/sp3-bonded carbon (trans-polyacetylene (t-PA) like, and graphite-like sp$^2$-bonded CH groups and sp$^3$-bonded $CH_2$ groups), with C-H vibration characteristics at 1120 -1190 cm$^{-1}$. The peak lower than 1000 cm$^{-1}$ is not related to the UNCD. It could be from the Si substrate.[12]

### *Electrical properties*

To explore the possibility of using the N-doped UNCD nanowire devices, it is essential to understand their electrical characteristics. Fig. 2(a) shows the current–voltage (I-V) plots of the UNCD nanowires measured by using a pair of internal electrodes at different temperatures. A linear relationship between electrical current and the applied voltage is clearly visible in the low forward current range, indicating there is no more charge accumulation and very good ohmic contact in the interface between the electrode and the sensing material. However, it has not yet been fully understood the reasons why the increase of the temperature does not affect the conductivity of N-doped UNCD nanowires in this case. The estimated resistance $R = \Delta V/\Delta I \approx 33$ kΩ, showing a high conductivity of the N-doped UNCD nanowires. The I-V properties of the UNCD nanowires were also characterized by using a pair of external electrodes as shown in Fig. 2(b), which are almost linear, giving estimated resistances of 188 kΩ at 250 °C, 219 kΩ at 100 °C and 350 kΩ at room temperature, respectively. Using a simple wire mode for resistance $R = \rho l/A$ where $l$ is the length, and $A$ is its cross-sectional area, the different resistivities $\rho$ can be estimated. This is attributed to the high incorporation level of nitrogen that affects the original electron transport. The resistance of the UNCD decreases with the temperature.

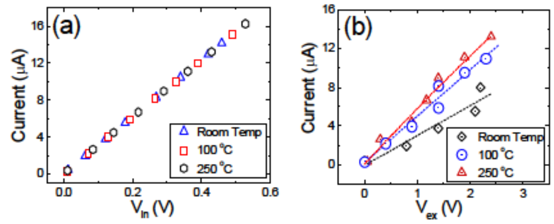


Fig. 2 Electrical properties of UNCD characterized in the low forward current range at different temperatures by using (a) an internal pair and (b) external pair of electrodes.

*Prototypic $CH_4$ gas sensors*

The circuit used for the prototypic gas sensor test is shown in Fig. 1(a). This simple but useful electrical circuit has been widely used for oxide semiconductor gas sensor and humidity sensors.[13-15] The variation of the voltage output of the fabricated sensor is caused by the reaction of incoming gaseous molecules or targeted gas with the chemisorbed oxygen at the UNCD grain boundaries that changes the nanowires' conductivity. The UNCD nanowire has the ideal structure with a large number of grains and boundary surfaces, as well as a large surface area to volume ratio. The electrical properties of the nanowire surface and grain boundaries are affected by the adsorption and desorption of the gaseous molecules. As a result, negative charge carriers are added to the material and hence the resistance decreases:[16]

$$CH_4 + 4O^-_{adsorption} \rightarrow CO_{2(air)} + 2H_2O + 4e^-$$

Therefore, we can detect the $CH_4$ gas concentration by measuring the conductivity change of the UNCD nanowires. From the measurement of variation of voltage ($V_m$) across the precision resistor $R$ =1.0 kΩ, the change of the conductivity of the sensor can be obtained by $R_s = (V_p - V_m)R/V_m$ where the power supply voltage $V_p$ = 12 V. Necessary calibrations of the sensor were conducted at the characterization chamber (see Fig. 3).[17] It includes a plasma beam source for the treatment of the surface of the sensor device, the gas flow meter and controller, a precision pressure gauge, and a mass spectrometer.

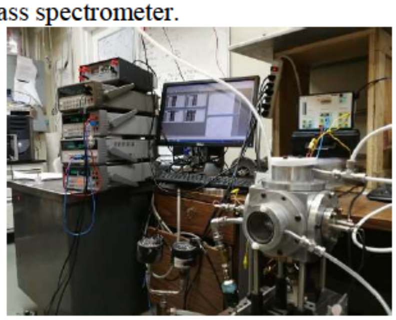

Fig. 3 Photograph of experimental set up for characterization of the newly fabricated gas sensors.

## Results and discussion

The characterizations of the fabricated sensors include the repeatability and stability, which are the most important parameters for a gas sensor, as well as sensitivity/resistance ($R_s$), the response time ($t_{resp}$), and the recovery time ($t_{rec}$). Fig. 4(a) shows the typical responsivity when the nanowire diamond gas sensor was cycled with a period of 120 seconds between "switch on" and "switch off" the inlet valve for the methane gas. The measurements are based on a pair of internal electrodes. The concentration of the gas molecule is 2 ppm for the results shown in Fig. 4(a) and 15 ppm for Fig.4(b). The sensor has much better features such as good repeatability and stability. The changes in the conductivity can be attributed to the adsorption of methane molecules. The response and recovery times of the sensors are only few seconds as shown in Fig.4(a).

Fig. 4(b) depicts the response of the fabricated gas sensor tested at the methane concentrations of 15 ppm, where the gas flow rate was controlled at 1.5 sccm. The measurements are performed at the room temperature. The period for the cycle is manually controlled at 120 seconds. The charge of the electrical resistance of the nanowires is found upon exposure to the methane gas. In general, at the high concentration of the methane gas, the output signal of the fabricated gas sensor is strong, around 1.25 units that is almost 6 times larger than that output of the sensor with a pair of internal electrodes. Furthermore, the external electrodes based sensor has well shaped edges in its output signal, indicating fast time response. In fact, the response-recovery time of the sensor depends on the many parameters such as the nature of samples, concentration, and operating temperature, electrode arrangement. In the case of the low concentration of the targeted gas, the time response and recovery are delayed, which can be explained by that there are not enough molecules participating in the reaction with the UNCD nanoparticles, yielding more time is needed for reaching the balance of the reaction between the sensing material and the targeted molecular gas. In contrast in the high concentration case, much short time is needed to reach the balance of the reaction. Consequently, the fast time response can be obtained.

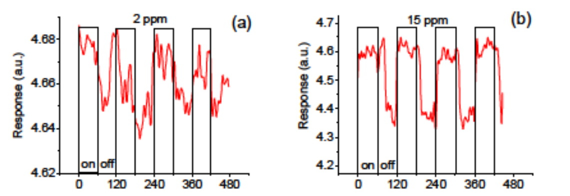


Fig. 4 Typical responsivities from the internal electrode pair of the nanowire N-doped UNCD gas sensor to the "on" and "off" of the methane gas at the concentration of (a) 2 ppm and (b) 15 ppm.

As a comparison, the fabricated sensor is also characterized by using a pair of external electrodes. Stability or repeatability features obtained from the cycled test are shown in Fig. 5(a) where the concentration of methane gas is 15 ppm. One can easily find that when the sensor is exposed to the methane gas, the resistance of the sensor promptly decreased and then reached a relatively stable value. When the targeted gas is removed out, the resistance abruptly increased and then gradually reached a relatively stable value.

As seen that good base line stability is always visible for the fabricated sensor operating at the room temperature, while the response of the fabricated sensor is not linearly related to the targeted gas concentrations as shown in Fig. 5(b). Normally, 2 ppm concentration of the methane gas causes the output of the sensor around 0.3 units, 12 ppm concentration yields 1 unit, and 40 ppm yields around 1.8 units of the output. If the methane gas concentration continuously increases from 40 to 70 ppm, and then to higher value, the saturation of the output of the sensor would occur as shown the insert in Fig. 5(b). Clearly the relative sensitivity of the fabricated sensor is high at the low concentration range.

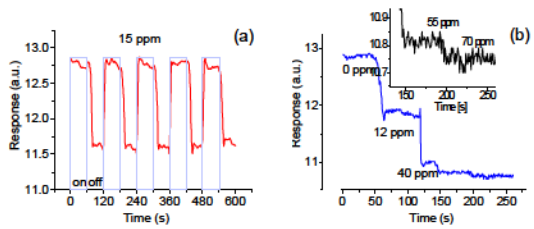

Fig. 5 Responsivities from the pair of the external electrodes to the methane gas with (a) a concentration of 15 ppm and (b) continuous increase of the concentration, measured at room temperature.

It is also noticed that each response profile from the fabricated sensor has a shape edge as shown in Fig. 5(a), which strongly suggests that the UNCD based gas sensor has very quick time responsivity. This is in good agreement with the data shown in Fig. 4(b). In order to obtain the precise values of the time responsivity, dynamic measurements are carried out as shown in Fig. 6(a), from which the response time of 3 s and the recovery time of 9 s are obtained. The definition is based on the time duration from 10% to 90% of the full response of the sensor. Clearly, the obtained time response value is much shorter than that of the regular sensors that are usually about 100 s for the response time and more than 200 s for the recovery time, respectively.[18]

It is expected that real sensing response time and recovery time for the present gas sensor might be shorter. This is because time delayed in tuning on or off the valves of the gas inlet and outlet, as well as low pumping capacity (7m$^3$/h) would affect the measured results.

The operating temperature has a great influence on the properties of the UNCD nanowire arrays based sensor. Fig. 6(b) shows temperature effect on the responses of the sensor when it exposes to the targeted gas. At room temperature (25 $^0$C) when the fabricated sensor is exposed to the 2 ppm methane gas, the output of the sensor is around 0.3 units. At operating temperature of 50 °C where the 2 ppm concentration of the methane gas remained unchanged, the output of the sensor increased up to 0.45~0.5 units then reached a stable value. However, no obvious improvement for the response time is observed. Similar phenomenon was also observed for the case at operating temperature of 75 °C as shown in Fig. 6(b) but the output of the sensor increased up to 0.6~0.65 units. The probable reason for no outstanding rise time is because of time delay during adjustment of the gas flow rate to a specific rate of 1.5 sccm.

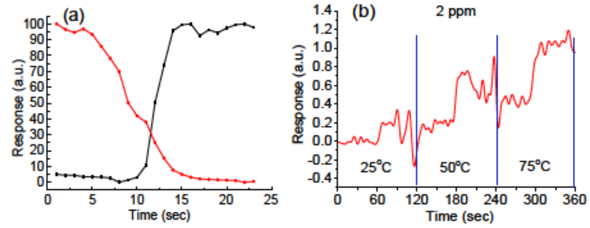

**Fig. 6.** Sensor response to methane gas at concentrations of (a) 15ppm at room temperature, and (b) 2 ppm at the operating temperature of 25, 50, and 75 $^0$C.

It is also found that operating UNCD nanowire arrays based sensor at high temperature would cause instability on its response and output, resulting in poor base line stability. This phenomenon is, in fact, related to the defect in the interface. In the case of Ti and Al, the carbide that formed during deposition and/or earlier stages of annealing limited the diffusion of these defects. As a result, these contacts on the diamond surface retained their ohmic character even after the annealing. If the defect is the dominant mechanism governing the electrical properties of metal-diamond interface, then ohmic contacts formed on the diamond surface with carbide forming reactions are accompanied by defect formation at the interface. The contacts suffer from high temperature stability problems since those defects are not thermally stable.[19] More studies are necessary in order to establish the reliability of metal contact for diamond based sensing device operating at high temperatures.

## Conclusions

High performance nanowire diamond gas sensor has been fabricated and tested. Both effects of the electrical electrodes and temperature on the electrical and sensing properties of the N-doped UNCD nanowire based $CH_4$ gas sensor have been investigated. Analyses of the experimental data clearly indicated the fabricated sensor has much better features such as good repeatability and stability at room temperature. When the sensor was exposed to the methane gas, the resistance of the sensor promptly decreased and then reached a relatively stable value. When the targeted gas was removed out, the resistance abruptly increased and then gradually reached a relatively stable value, from which the response time of 3 s and the recovery time of 9 s are obtained.

We conclude that the high concentration of the methane gas results in the strong signal output from the sensor but the output signal strength is not linearly related to the targeted gas concentrations. The relative sensitivity of the fabricated sensor is high at the low concentration down to 2 ppm. Too high concentration (more than 70 ppm) of the methane gas would cause the output saturation from the sensor. It is also found that the response or sensitivity of the sensor to the targeted gas would be enhanced at slightly high operating temperature. However, no obvious improvement for the response time is observed.

**Acknowledgements**

This work is financially supported by NSF-CREST Center for Innovation, Research and Education in Environmental Nanotechnology (CIRE2N) Grant Number HRD-1736093. Authors also would like to thank Drs. Anirudha Sumant, Ralu Divan, Leo Ocola and Daniel Rosemann from Argonne National Lab for help of UNCD nanowire fabrication. Use of the Center for Nanoscale Materials was supported by the US Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357. AFZ acknowledges the receipt of the 2017-2018 IUP Senate Fellowship grant and the partial support of this work by the NSF CMS-1725557.

**References**

1. Wang, Q.; Qu, S. L.; Fu, S. Y.; Liu, W. J.; Li, J. J.; Gu, C. Z.; *J. Appl. Phys.* **2007**, 102, 103714.
2. Helwig, A.; Muller, G.; Garrido, J. A.; Eickhoff, M. *Sens. Actuators, B: Chemical* **2008**, 133, 156.
3. Gurbuz, Y.; Kang, W. P.; Devidson, J. L.; Kerns, D. V.; *Sens. Actuators, B: Chemical,* **2004**, 99, 207.
4. Peng, X.; Chu, J.; Wang, L.; Duan, S.; Feng, P. *Sens. Actuators, B: Chemical*, **2017**, 241 , 383.
5. Gurbuza, Y.; Kang, W. P.; Davidson, J. L.; Kerns, D. V. *Sens. Actuators, B: Chemical*, **2004**, 99, 207.
6. Das, S.; Jana, S.; De, D.; Gangopadhyay, U.; Garain, S.; Ray, S.; Mondal, A.; Ghosh, P. "A Novel Room Temperature Ammonia Gas Sensor Based on Diamond-Like Nanocomposite/ c-Silicon Heterojunction" In: Jain V., Verma A. (eds) *Physics of Semiconductor Devices. Environmental Science and Engineering*. Springer, Cham, **2014**, pp 479-482. doi:10.1007/ 978-3-319-03002-9_120. NH3
7. Davydova, M.; Kulha, P.; Laposa, A.; Hruska, K.; Demo, P.; Kromka, A. *Beilstein J. Nanotechnol.* **2014,** 5, 2339. doi: 10.3762/bjnano.5.243
8. Feng, P.; Wang, X.; Aldalbahi, A.; Zhou, A. F. *Appl. Phys. Lett.* **2015**, 107, 233103.
9. Auciello, O.; Sumant, A. V. *Diamond. Relat. Mater.* **2010**, 19, 699.
10. Wang, X. Synthesis, Fabrication, Characterization and Application of Ultrananocrystalline Diamond Micro- and Nanostructures. Doctoral dissertation, University of Puerto Rico: San Juan, Puerto Rico, 2012.
11. Wang, X.; Ocola, L. E.; Divan, R. S.; Sumant, A. V. *Nanotechnology*, **2012**, 23, 075301.
12. Teng, C.; Song, S.; Sung, C.; Lin, C. *Journal of Nanomaterials*, **2009**, 2009, 621208. doi: 10.1155/2009/621208
13. Mandal, S.; Naud, C.; Williams, O. A.; Bustarret, E.; Omnes, F.; Rodiere, P.; Meunier, T.; Saminadayar, L.; Christopher, B. *Nanotechnology* **2010**, 21, 195303.
14. Peng, X.; Yang, B.; Chu, J.; Feng, P. *Sens. Actuators, B: Chemical*. **2012**, 174, 258.
15. Chu, J.; Peng, X.; Feng, P.; Sheng, Y.; Zhang, J. *Sens. Actuators, B: Chemical*, **2013**, 178, 508.
16. Basu, S.; Basu, P. K. *Journal of Sensors* **2009**, 2009, 861968.
17. Chu, J.; Peng, X.; Sajjad, M.; Yang, B.; Feng, P. *Thin Solid Films*, **2012** 520, 3493.
18. Feng, P.; Zhang, H.; Peng, X.; Sajjad, M.; Chu, J. *Review of Scientific Instruments* **2011**, 82, 043303.
19. Tachibana T.; Glass J.T. (1995) Electrical Contacts to Diamond. In: Pan L.S., Kania D.R. (eds) Diamond: Electronic Properties and Applications. The Kluwer International Series in Engineering and Computer Science (Electronic Materials: Science and Technology). Springer, Boston, MA. doi: 10.1007/978-1-4615-2257-7_8