Boron-doped diamond nanowires for CO gas sensing application

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Abstract:

Three groups of boron-doped ultrananocrystalline diamond (B-UNCD) nanowires (NWs) arrayed on a silicon substrate were prepared by the successive processes: microwave plasma chemical vapor deposition, electron-beam lithography and reactive ion etching. Au electrodes built on both ends of each group of B-UNCD NWs were combined with a basic electrical circuit to form high-performance gas sensor arrays for carbon monoxide (CO) sensing measurements. The B-UNCD with boundary grain size around few nanometers has been successfully synthesized, and three groups of reasonable straight diamond NWs with the same diameter and different lengths were built on one single substrate. The heavily boron doping of boron ions in the UNCD induced the ohmic contact between diamond and Au electrodes.

Typical transient response behaviors of the sensor exposure to 100 ppm CO gas at 200 °C show high response signal and response and recover time are about 200 s and 40 s, respectively. The sensing characterizations indicate the prototypical sensor arrays with high selectivity and fast response to CO gas as a promising candidate for gas sensor application. The sensing mechanism in the present case is attributed to the reaction between CO molecules and the oxygen anions on the surface of B-UNCD

NWs. Need to mention here is the design of the sensor arrays enables to utilize the four-point probe measurement of the sensing performance and would efficiently avoid the polarization effect caused by the water vapor originated from ambient gas.

1. Introduction

Detecting carbon monoxide (CO) as a poisonous and flammable gas has always been the subject of prime interest. Several types of CO sensors, based on metal-oxide semiconductor or pure metallic, have been proposed and fabricated [1–5]. In comparison to common sensitive materials, such as ZnO, SnO₂, α -Fe₂O₃, and TiO₂ [6–9], diamond is a very attractive material for this field due to the extraordinary mechanical and electrical properties as predicted by theory for quasi one-dimensional sp³ nanostructures [10–11], as well as high chemical/electrochemical stability [12], wear/corrosion resistance [13–14], optical transparency from deep ultraviolet to far infrared [15–16].

Up to today, the preliminary success on the diamond based gas sensor has been achieved. Kang's group employed multi-crystalline diamond [17] and the heterostructure of diamond/SnO_x [18], diamond/SnO₂ [19], diamond/Pd [20] to detect H₂, O₂, CO and hydrocarbon gases, respectively. But the real research on diamond nanomaterials based gas sensor didn't start until Joshi et al. [21] detected CO with boron-doped microcrystalline diamond (MCD) thin film at 2010 in which diamond was functioned as sensing layer to react with CO molecules. Then Davydova [22] et al. revealed that H-terminated nanocrystalline diamond (NCD) films response to toxic carbonyl chloride gas. From 2013 to 2016, several research groups [23–27] discovered that hydrogenated diamond nanostructures synthesized by different routines are sensitive to soluble and acid gases, such as H₂S, NO_x, HCl et al. Recently, Feng [28] synthesized well-arranged nitrogen-doped ultrananocrystalline diamond (UNCD) nanowires (NWs), which has excellent sensing performances to CH₄. UNCD differs from NCD and MCD in its small grain sizes ranging from 3 to 5 nm and a nanoscaled root mean square (RMS) roughness of 4–7 nm, which provides more adsorption sites for gas molecules resulting in optimized sensing performances.

It is expected that one dimensional nanostructures would have high response to gas owing to its high surface to volume ratio, and doping with boron atoms into diamond lattice offering high conductivity of the film suggest boron-doped UNCD NWs (B-UNCD NWs) a competitive candidate for nanoelectronic devices. Here it should be mentioned that progressive growth in the field of gas sensor technology requires minimal size and maximal integration involved in the fabrication technique. A large number of devices could be fabricated on a single wafer with enhanced functionality, which consumes less power and therefore would produce these single wafer devices more economically. In this work, we prepared and characterized three groups of one dimensional B-UNCD NWs in a single silicon wafer to build sensor arrays for CO sensor application. We are presenting routes for fabrication of B-UNCD NWs using microwave plasma chemical vapor deposition, electron-beam lithography and reactive ion etching (MPCVD-EBL-RIE) processes. Field emission scanning electron microscope (FESEM) and atomic force microscopy (AFM) were used to analyze the morphology of the sample. Energy dispersive X-ray spectroscopy (EDS) was characterized to detect the chemical contents, and Raman spectroscopy was employed to determine the molecular structure and sp^3/sp^2 Raman bands ratio. The gas sensing properties of the device were also examined. The influences of testing gas type, gas concentration and operating temperature on sensing performances were investigated.

2. Experimental details

2.1. Preparations of the B-UNCD NWs

Three processes were required by successful fabrication of the B-UNCD NWs in the Argonne national lab. The detailed experimental procedure was the following:

2.1.1. Growth of B-UNCD thin film via MPCVD process

A 915 MHz Lambda MPCVD system was used to deposit B-UNCD thin film. The plasma height and shape (donut vs. spherical) can be adjusted to provide uniform plasma energy delivery over the substrate the uniformity of diamond films on

substrates. An 18 inches quartz bell jar was used to eliminate the contact between bell jar and the plasma and therefore significantly diminish the Si contamination caused by plasma etching of the quartz. Two circular resistive heaters can independently heat different zone (inner or outer) to level the temperature with plasma heating effect. The heater stage was pumped separately to minimize contaminations from filaments. The system was computer driven with specific growth conditions configured as “recipes” to fully control the synthesis process.

The 2×2 inch Si substrate was used in our study. Prior to experiment, the substrate was boiled in a sulfuric peroxide mixture ($\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}_2\cdot\text{H}_2\text{O}=3:3:1$) at 300 °C for 15 min, followed by a hot $\text{HF}:\text{HNO}_3$ 1:1 V/V etching treatment. This treatment removed organic and metallic contamination from the surface. After the chemical treatment, the sample was rinsed by deionized water. The clean substrate was set on a diamond-coated molybdenum holder. Before deposition, the Si wafer was immersed into an ultrasonically agitated solution containing 4–50 nm ultra-dispersed diamond detonation-synthesized nanopowders for seeding. During the experiment, the chamber was fed with $\text{CH}_4/\text{Ar}/\text{trimethylborate}$ (TMB) mixture gas from the top, with flow rates of 4, 50, and 50 sccm, respectively, and kept a total pressure at 5 Torr. This mixture chemistry produces carbon dimers (C_2) in the plasma, derived either from collision-induced fragmentation of methane or by thermal conversion via the following reactions:

The C_2 dimers have been proposed to play a critical role in the diamond nucleation and growth process [29–30]. The substrate temperature was maintained at 1100 °C during the deposition process.

2.1.2. Au layer deposition as electrode

Then the prepared UNCD film was transferred to a rf magnetron sputtering

system (HUMMER TURBO sputtering system, ANATECH LTD.) to deposit Au electrodes with thickness of 10 nm. By using masks (bought from SoEase Semiconductor, Inc., China) during deposition, the four Au electrodes are well arranged abreast with three different gaps as 5, 10 and 20 μm , respectively.

2.1.3. EBL and RIE processes for fabricating the B-UNCD NWs

After the first two stages above were completed, the B-UNCD NWs were fabricated by using EBL patterning and RIE processing. The process schematic diagram is shown in figure 1. In order to form a negative-tone electron beam resist layer, hydrogen silsesquioxane (HSQ) was coated on the surface of B-UNCD film afterward the deposition. Flowable oxide (FOx-12) and methyl isobutyl ketone (MIBK) mixing with ratio of 1:1, was spun onto the sample at a speed of 5000 rpm to create a layer with thickness of 100 nm. NWs patterns were written onto the sample by a JEOL 9300FS 100 kV EBL system with dosages ranging from 1200 to 1350 $\mu\text{C cm}^{-2}$, depending on the demanded width.

Figure 1. Schematic diagram of B-UNCD NWs fabrication process by EBL/RIE.

A recipe of 10 sccm sulfur hexafluoride gas flow rate, 310 W ICP power, 10 W rf power, 10 mTorr chamber pressure was used for 6 min to etch the B-UNCD NWs. Then, the HSQ mask removal and the cleaning of the residual material thoroughly were all realized by ICP-RIE. The detailed experimental process can be found in Ref [31, 32].

2.2. Characterizations

The morphology and the chemical contents of the as-prepared sample were then

characterized by FESEM and EDS. Room temperature (RT, 25 °C) micro-Raman spectroscopy was performed using a Jobin–Yvon T64000 Triplemate system with the radiation of 514.5 nm from a coherent argon ion laser, and a liquid nitrogen cooled charge-coupled device system was used to collect and process the scattered data (made by HORIBA group in Japan).

2.3. Measurements of sensing properties

The sensing properties of the sensor arrays were characterized under CO/air gas mixture ambient. The CO concentration was from 25 to 100 parts per million (ppm) and operation temperature was from RT to 400 °C . First, the sensor arrays were placed into a closed chamber with a constant flow rate of clean air, and then the valve was switched to a CO/air mixture gas waiting for the resistance of the sensor reaching a stable value and then switched back to pure air at the same flow rate. The resistance measurements were performed by varying different pair of electrodes connecting to external circuit. The CO/air mixture gas was prepared by a gas supplier with various CO concentrations mixed in air. During measurements, the chamber was kept at an atmospheric pressure. In order to eliminate the influence of the humidity on the conductivity of the sample, relative humidity (RH) inside the chamber was controlled as 40%. The RH level was measured with a commercial humidity sensor (HUMIREL, HM1500LF).

3. Results and discussion

The low and high resolution FESEM and AFM images of the as-prepared B-UNCD thin film are shown in figure 2, from which we can see the flat film with boundary grain size around few manometers and RMS roughness about 4.5 nm obtained.

Figure 2. (a) Low resolution, (b) high resolution FESEM images of the UNCD film. (c) The AFM image of the UNCD film.

Figure 3 shows the photo, FESEM images and EDS spectrum of B-UNCD NWs produced by the EBL/RIE process. A prototype of the sensor arrays based on B-UNCD NWs is presented in figure 3(a). Four Au wires are silver painted on the Si wafer for connecting to external circuit. Figure 3(b) exhibits the FESEM image of the sample with four sputtered Au electrodes,. The high resolution FESEM image is shown in figure 3(c). It exhibits the gaps between two adjacent electrodes are 5, 10 and 20 μm , respectively. Three groups of NWs with different lengths were arranged between two adjacent electrodes.

Figure 3. (a) The photo of the prototypic sensor. (b) The low resolution FESEM image of the sample with four sputtered Au electrodes, labeled as 1, 2, 3, and 4 respectively. (c) The zoom FESEM image of Au electrodes. (d) The high resolution FESEM image of the B-UNCD NWs

between internal electrodes 2 and 3. (e) The zoom FESEM image of (d). (f) The EDS spectrum of the NWs.

Figure 3(d) shows the magnified FESEM image of the B-UNCD NWs between internal electrodes 2 and 3, i.e., second group of NWs with 10 μm in length. Highly-ordered NWs arrays are clearly visible. What's more, the diameters of all the NWs are the same, around 70 nm, which is further confirmed by another magnified FESEM image, as shown in figure 3(e). At the same time, the EDS spectrum in figure 3(f) from diamond NWs shows the heavily doping of boron was successfully achieved. The doping level of boron in the diamond NWs, expressed as B/C atom ratio, was about 0.227.

Table 1. The resistances of the NWs with different pairs of electrodes.

Electrodes	NWs measured	Resistance ($\text{k}\Omega$)
1-2	r_1 (5- μm -NWs)	3.2
2-3	r_2 (10- μm -NWs)	5.6
3-4	r_3 (20- μm -NWs)	8
1-3	r_1 and r_2	8.5
2-4	r_2 and r_3	14
1-4	r_1 , r_2 and r_3	17.5

The resistances of three groups of NWs at RT are exhibited in table 1. We donate the resistance of 5, 10 and 20 μm NWs as r_1 , r_2 and r_3 , respectively. It has been demonstrated by Bhattacharyya et al. that the conductivity of doped diamond nanowires has been increased up to $143 \text{ cm}^{-1}\Omega^{-1}$ [33], and hall effect measurement results shown by Williams et al. prove diamond as a clear conductivity with very low thermal activation energy [34]. In our work, the resistance values of the B-UNCD NWs are small, only around several kilo-ohms. This magnitude of the baseline resistance is desirable to extract a differential measurement between the baseline state and the chemically excited state. Too high or too low baseline resistance would affect precise measurements.

Figure 4. Raman spectra of three groups of B-UNCD NWs. The peak at 1556 cm^{-1} is attributed to Raman scattering due to the gas molecules from atmospheric oxygen.

Raman scattering experiments were performed to verify the insertion of boron ions into diamond lattice and the data are shown in figure 4. A sp^3 carbon peak at 1333 cm^{-1} is clearly observed in the Raman spectra, which proves that the NWs are indeed diamond. The half-width of this sp^3 peak is a little broader, which is ascribed to the small size of the crystalline diamond grains. It is clear that as the NWs length scales up, the intensity of diamond peak in the Raman spectra increases. This may be due to the fact that the longer NWs length is, the larger the exposed diamond area would be, and consequently stronger Raman signal would be generated. A peak at 1556 cm^{-1} is attributed to Raman scattering induced by the gas molecules from atmospheric oxygen [35].

Figure 5. Measured current-voltage characteristics of the NWs between different pairs of electrodes.

Figure 5 shows the typical I-V curves of the NWs between different pairs of electrodes at RT. The obtained I-V curves exhibit strictly linear behavior, indicating good ohm contacts between the B-UNCD NWs and the Au electrodes. This phenomenon is attributed to heavily doping of boron element in diamond. It is well-known that a high concentration of dopant in semiconductor will induce the narrow of the depletion region at the interface of metal and semiconductor. In this case, the tunneling effect happens and the tunneling current is dominated, leading to a very small contact resistance. Consequently, good ohmic contact is realized between diamond and Au. From experimental data shown in figure 5, it can also be found that the resistances of the B-UNCD NWs between different gaps are different, which is coincident with the results in table 1.

Figure 6. The response of the 10 μm B-UNCD NWs based sensor to CO, O₂, H₂, CO₂, CH₄, H₂O, C₂H₅OH, and CH₃OH gas with concentration of 100 ppm, at 400 °C .

The response was calculated by the ratio of the resistance change occurred in the sample under exposure of the CO/air mixture gas to the original resistance: $(R_0 - R_g) / R_0 \times 100\%$, where R_g refers to the resistance at CO/air mixture gas and R_0 represents the original resistance of the sensors at pure air. The response of the 10 μm B-UNCD NWs based sensor to different gases at 400 °C is shown in figure 6. The experimental results indicate the sensor has very low response to O₂, H₂, CO₂, CH₄, H₂O, C₂H₅OH, and CH₃OH at 100 ppm condition. The obtained response of the

fabricated sensor to CO is at least 4 times higher than that of the other selected gases with concentration of 100 ppm, at 400 °C . Therefore, we can conclude that the obtained sensor has high selectivity to CO at this experimental condition

Grain boundaries in the NWs are active sites for the CO molecules adsorption. The sensor was first exposed to a continuous flow of air, leading to the absorption of oxygen molecules in air on conductive diamond surface, and dissociating into O_2^- , O^- or O^{2-} . Takata et al. found that the stable oxygen ions are O_2^- below 100 °C, O^- between 100 and 300 °C, and O^{2-} above 300 °C [36], respectively. The dissociated species are adsorbed primarily on grain boundaries of the B-UNCD. After switching gas from pure air to CO/air mixture gas during resistance measurement, the CO molecules also get adsorbed onto the conductive diamond surface and interact with the pre-adsorbed oxygen anions via the oxidation reactions [37–38].

The CO oxidation during the continuous flow leads to the transfer of electrons from oxygen anions to the B-UNCD NWs and initiates charge neutrality. This process causes depletion in the total number of charge carriers and leads to a decrease in conductivity due to the unavailability of free carriers for conduction by B-UNCD NWs.

Figure 7. Comparisons of the responses of the three groups of NWs to CO as a function of (a) operating temperature, (b) CO concentration.

The comparisons on the responses of the each unit of the sensor arrays as a function of operating temperature and CO concentration were carried out, as shown in figure 7. A chamber with heater was employed to provide varying temperature or CO concentration in incremental steps, while other parameters were remained unchanged. The small size and the grain boundaries of UNCD crystal increase the surface area in the UNCD films and consequently provide more adsorption sites of the sensor surface. The responses of all the obtained sensors increase with temperature and the CO concentration. As we mentioned before, oxygen ions dissociates into O_2^- , O^- and O^{2-} , depending on the operation temperature. From the knowledge of catalytic activity, it is anticipated that reducing agents react rapidly with O^{2-} presented on the surface, but very slowly with O_2^- [39], resulting in an increase of response with temperature. It can also be observed that only the sensor with a pair of internal electrodes 2 and 3, i.e., the 10- μ m-NWs has strictly linear response curve with temperature over the range from 25 to 400 °C. Need to mention here, the resistance measurement for this linear curve is performed by using four-point probe, as shown in figure 8, which efficiently avoids the polarization effect caused by humid ambient gas.

Figure 8. Schematic illustration of four-point probe measurement of the resistance between internal electrodes 2 and 3.

In contrast when the traditional two-electrode technique is applied, some electrons would migrate from Au electrode into the diamond NWs. As a result, positive charges in the diamond immigrate towards the Au electrode creating a cation layer between the Au and diamond NWs, leading to inaccurate sensing signals. Utilizing four-point probe measurement would greatly reduce, or completely avoid this effect. The precise voltage drop across the pair of the internal electrodes could be measurable because of no more charge accumulation over there, whereas the charges would gather on the pair of external electrodes 1 and 4. Therefore in the following sensing characterizations, main focus would be on the 10- μm -NWs.

Figure 9. Transient response curves of the sensor under (a) 100 ppm CO gas ambient, (b) 40% RH, 200 °C.

Generally, transient behavior is an important characteristic to evaluate the performance of gas sensor. Typical transient response behaviors of the sensor

exposure to 100 ppm CO gas and 40% RH ambient at 200 °C are depicted in figure 9 (a). When the sensor was exposed to 100 ppm CO, the resistance of the sensor promptly increased and then reached a relatively stable value. When the ambient was switched to air again, the resistance abruptly decreased and gradually reached a relatively stable value. Further testing after three additional cycles indicates good reproducibility of the sensor. It is important to point out there is a drift in resistance after every exposure to CO gas, approximately 9%, 7%, and 2.5%, respectively, as shown in figure 9. Such a drift was responsible for change in electrical resistance of B-UNCD NWs, whereas no drift was observed with the varied ambient RH. It proves that the chemisorption of the CO gas on the surface of the B-UNCD NWs, since some CO molecules are adsorbed on B-UNCD NWs surface for conduction even after the ambient gas have been switched to air. The response time (defined as the time required reaching 90% of the total resistance change) is about 200 s, while the recovery time is about 40 s. Although further work is necessary to improve sensor performance, the above experimental results have indicated that the B-UNCD NWs is a promising candidate for a CO gas sensor.

4. Conclusions

In conclusion, the CO sensor arrays consist of three groups of well-defined B-UNCD NWs have been successfully prepared on a single Si wafer via MPCVD, followed by EBL/RIE processes. This method has several advantages in designing desired patterns. Raman spectroscopy confirms that the B-UNCD NWs maintain its intrinsic diamond structure without any graphitization. Good ohmic contacts between the Au electrodes and the diamond NWs have been achieved. The three groups of B-UNCD NWs all have high selectivity and responses to CO. The nanosizing and the grain boundaries of UNCD crystal are ascribed as the main reason for high response to CO. The sensing characterization indicates that the four-point probe measurement could efficiently avoid the polarization effect. The transient behavior of the sensor proves the fabricated sensor has a good reproducibility but the chemisorption of the CO gas on the surface of the B-UNCD NWs would result in a slight drift in the

baseline during every exposure.

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