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Room Temperature Gas Sensor Based on Helical Carbon Coils

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Abstract. Growth of helical carbon coils can be achieved by sputtered Inconel® 600 films on silicon (Si) substrates followed by thermal chemical vapor deposition (CVD) using acetylene as a carbon source along with the injection of sulfur hexafluoride (SF_6). The coils were used to prepare electronic ink for fabrication of flexible room temperature gas sensors. The ink as a sensing film was deposited onto silver-screen printed plastic substrates by drop casting. Before dripping the sensing film, the coils were purified using oxidation and acid treatments. The purified coils were then dispersed in different solvents such as deionized water (DI water), ethanol and dimethyl sulfoxide (DMSO) for comparisons. The performance of sensors was investigated for its response to ammonia (NH_3) and volatile organic compounds (VOCs) including ethanol, methanol, and dimethylformamide (DMF) in concentration of 1000 ppm at room temperature. Because the baseline resistance of sensor falls within the working range (i.e. kΩ), the coils dispersed in DI water are performed to show the highest selectivity and sensitivity to NH_3. The sensing mechanism of helically coiled carbon gas sensors has been also discussed based on the reducing reaction process between NH_3 and chemisorbed oxygen on the surface of purified carbon coils.

Introduction

Ammonia (NH_3) and other volatile organic compounds (VOCs) have been thought to the high toxicity. The monitor of them is very important in medical treatment, industrial process and environmental applications. Recently, the development of feature for gas sensor has been focused on low-cost, flexible, selective and sensitive detections at room temperature [1]. Moreover, carbon nanostructures such as multi-walled carbon nanotubes (MWCNTs), single-walled carbon nanotubes (SWCNTs) can be also considered as good candidates to design the high performance of NH_3 and VOC gas sensors [2-3]. Good dispersion and good solubility between active carbon materials and the solvent are significant to enhance the properties of carbon-based ink used for the preparation in printable gas sensor. Although the water was reported as a cost-effective solvent used in the fabrication of carbon-based gas sensor by printing technique, the nature of carbon in poor dispersion has limited in less selectivity and low sensitivity for gas sensor works [4]. The performance of carbon-based gas sensor has been reported to be dependent on the number of hybridized sp^2 networks and specific surface area [5]. Helical carbon coils as a fiber structure of carbon have attracted increasing attentions due to its high specific surface area and large number of sp^2 networks. The injection of sulfur hexafluoride (SF_6) was presented as a main cause for the formation of helical carbon coils using a thermal chemical vapor deposition (CVD) technique [6]. However, the poor dispersion of helical carbon coils within various solvents is still a big problem for the preparation of sensing films in gas sensor applications.

In this work, helical carbon coils were grown on sputtered Inconel films by using acetylene (C_2H_2) as a carbon source along with the injection of SF_6 during thermal CVD process. The coils were prepared to electronic ink as a sensing film for flexible room temperature gas sensor. The main problem such as the poor dispersion of helical carbon coils within the solvents was solved together with an enhancement of gas sensitivity by using oxidation and acid treatment procedures. Moreover, the sensitivity of gas sensor obtained from different solvents was compared for finding the optimum condition in the highest gas sensing performance.

Experimental Procedure

The 3.0 × 3.0 cm^2 silicon wafers with a thickness of 0.3 mm were used as substrates. Firstly, aluminium oxide (Al_2O_3) films with a thickness of approximately 100 nm as buffer layers were coated onto the substrates using reactive magnetron sputtering. The Al_2O_3 films were used as a buffer layer for preventing the diffusion of catalysts into the oxide layer of substrate during the CVD process [7]. Thin Inconel® 600 films with a thickness of 80 nm were then sputtered onto the buffer films as an effective catalyst [8]. After coating the films, the substrates were placed in a quartz tube of a home-made thermal CVD system. The details of this system were reported in a previous work of first author [9]. The chamber was heated up to the temperature of 770 ºC under an inert gas of argon (Ar). Hydrogen (H_2) as a reductive gas was injected into the chamber with a flow rate of 200 sccm. The catalytic Inconel nanoparticles were formed in this step. Then, C_2H_2 as a carbon source was fed into the chamber with a flow rate of 60 sccm for 60 min. During the injection of gases, the additional gas of SF_6 was employed for the formation of the helical carbon coils. The flow rate of SF_6 was constantly fixed at 40 sccm for 60 min. All settings were chosen from the repeatedly previous work of us as a suitable flow rate for the optimum result. After the thermal CVD process, the morphology of as-grown helical carbon coils was examined with a scanning electron microscope (SEM, Quanta 450 FEI) and a transmission electron microscope (TEM, Hitachi HT 7700). Furthermore, the coils were used to fabricate the flexible room temperature gas sensors. Before fabricating the sensors, the as-received black coiled powder was heated at 400 ºC for 5 h in air to remove carbonaceous impurities. And then, the 0.5 g of coiled powder was immersed in 80 ml mixture of sulfuric acid and nitric acid (3:1 H_2SO_4/HNO_3) under continuous sonication for 2 h. The purified coils were then washed several times with distilled water, and dried at 80 ºC in an oven. After that, the purified coils were investigated using Fourier transform infrared spectroscopy (FTIR, Perkin Elmer Spectrum 400) to confirm the formation of carboxylic (COOH) groups on the surface of helical carbon coils. The dried powders as the sensing materials were then dispersed ultrasonically in different solvents such as deionized water (DI water), ethanol and dimethyl sulfoxide (DMSO) for comparisons. Finally, the electronic ink as a sensing film was deposited onto silver-screen printed plastic substrates by drop casting. A standard flow-through system was conducted to study the sensitivity of all fabricated sensors to NH_3 and VOCs including ethanol, methanol, and dimethylformamide (DMF) for the concentration of 1000 ppm at room temperature.

Results and Discussion

The morphology of as-grown helical carbon coils is shown by SEM (Fig. 1a) and TEM (Fig. 1b) images. The size distribution of helical carbon coils was measured on 200 coils taken in various SEM images. Using the analysis image software program (i.e. ImageJ), the calculation of mean values for coiled diameters and coiled pitches are found to be 114 ± 16 nm and 93 ± 23 nm, respectively. The details of size distribution for helical carbon coils analyzed by using ImageJ can be seen in Fig. 1(c). After purifying the coiled surface, the coils were characterized using FTIR spectroscopy to confirm the formation of COOH groups on their sidewalls. The schematic illustration of modification for a helical carbon coil with COOH groups is shown in Fig. 2(a). By using the FTIR spectrum, the as-grown helical carbon coils exhibit very weak peak of C=C bonding shown in Fig. 2(b). After the acid treatment process, the appearance of a strong peak was observed within the wavenumber range of 3400-3500 cm^{-1}. This peak represents the vibration of O-H groups.

As can be seen in Fig. 2(c), the other peaks of FTIR spectrum at around 1000-1200 cm^{-1} were assigned to C=O bonding. Therefore, it can be confirmed that the COOH groups are successfully attached on the surface of helical carbon coils after purification with acid treatment.

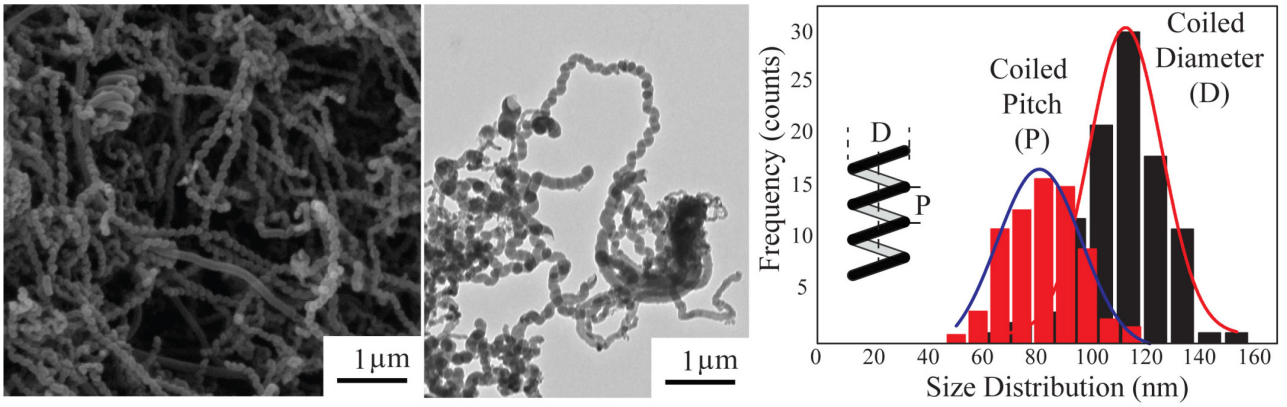

Fig. 1 (a) SEM, (b) TEM images and (c) size distribution of as-grown helical carbon coils.

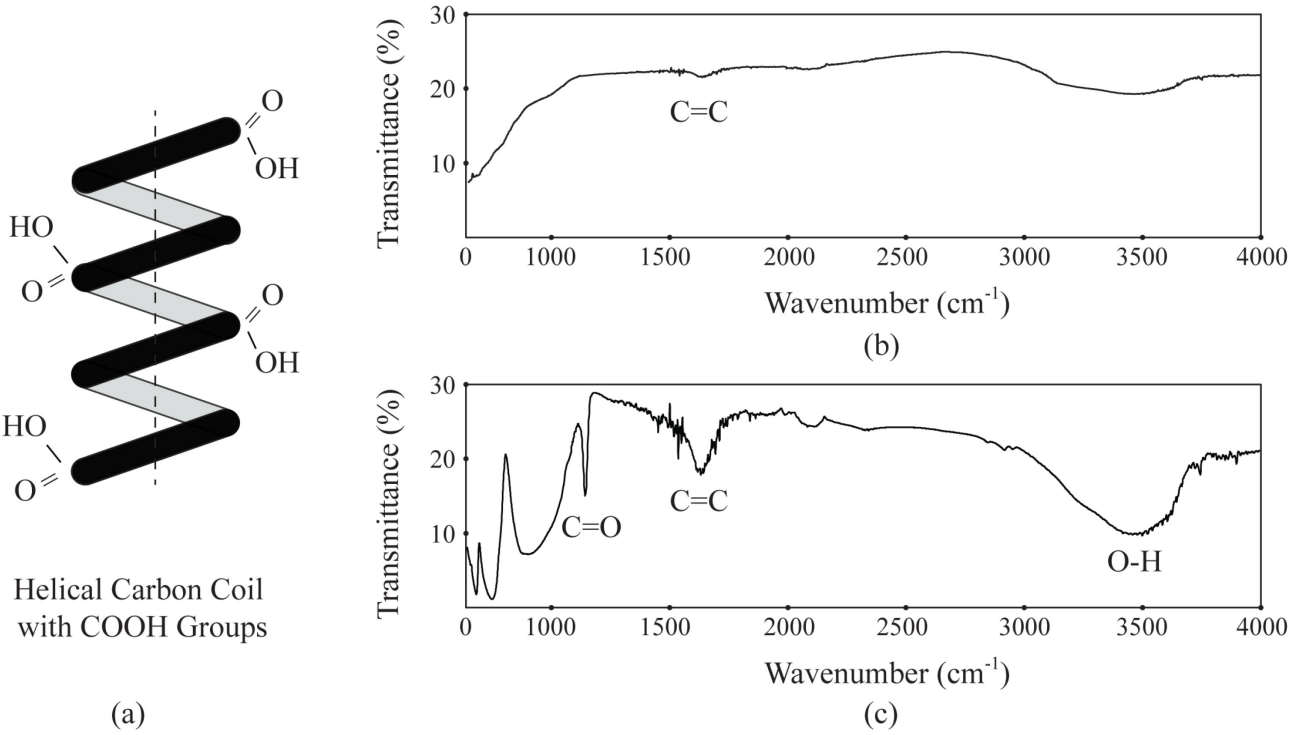

Fig. 2 (a) Schematic illustration of modification for helical carbon coil with COOH groups, FTIR spectra of (b) as-grown helical carbon coils and (c) purified helical carbon coils.

The coils were then dispersed in different solvents to prepare the sensing film in form of electronic ink. The ink had a strong effect on the dispersion of purified helical carbon coils in all aqueous solvents even after storage in 30 days. The ink was carefully dropped onto a plastic substrate by a micropipette with a volume of 20 µl. Schematic illustration and photograph of sensor structure is displayed in Fig. 3(a) and Fig. 3(b), respectively. A standard flow-through system as shown in Fig. 4 was conducted to measure the gas response for all our sensors. To allow measurement, the sensor was inserted into a test chamber connected to a designed circuit board. Pure air and test gas were introduced through two flow meter controllers. The ball valves (Swagelok, B-42S4) were used to open/close all test gases. The resistance of sensor was measured every second using a LabVIEW software program together with a USB DAQ device. Fig. 5(a)

shows the dynamic resistance of room temperature gas sensor exposed to 1000 ppm NH_3 with the different solvent conditions. The gas response was then calculated from the change of the sensor resistance defined as S (%) = $[(R_{gas}-R_{air}) \times 100]/R_{air}$, where R_{air} and R_{gas} represent the sensor resistance in pure air and in test gas, respectively. For the solvent conditions of DI water, DMSO and ethanol, the calculated sensor responses exposed to NH_3 are found to be 33.3%, 2.8% and 0.6%, respectively. In order to investigate the sensivity and selectivity of helically coiled carbon gas sensors, they were also exposed to various VOC vapors including ethanol, methanol and DMF as shown in Fig. 5(b). It indicates that the optimized gas sensor obtained from DI water sovent exhibits a remarkably high response to NH_3 (33.3%) while those fabricated sensors show low response ($\leq$ 5 %) to NH_3 and other VOC vapors at room temperature. However, the sensors obtained from all solvents were found to be more sensitive to NH_3 while comparing the other gas vapors.

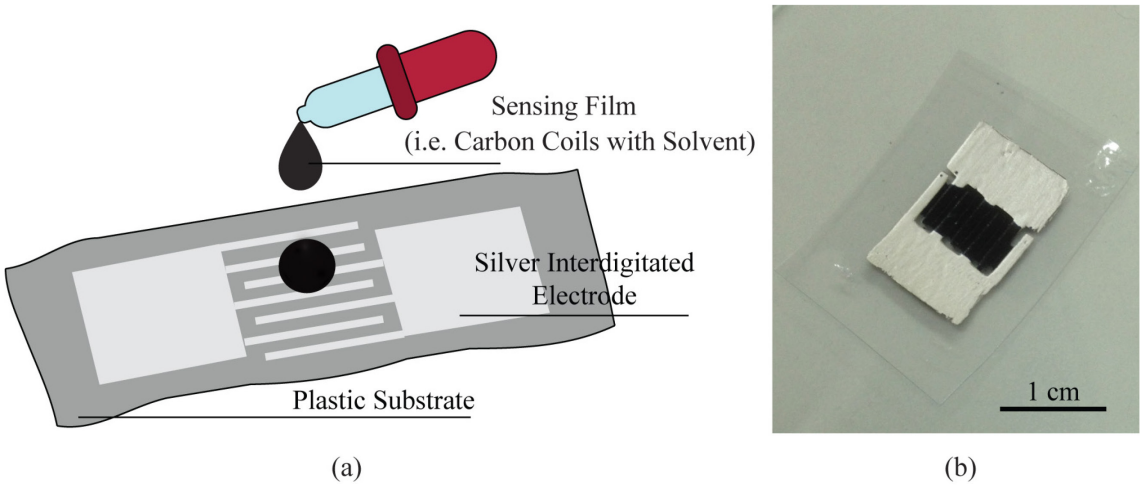

Fig. 3 (a) Schematic illustration and (b) photograph of helically coiled carbon gas sensor.

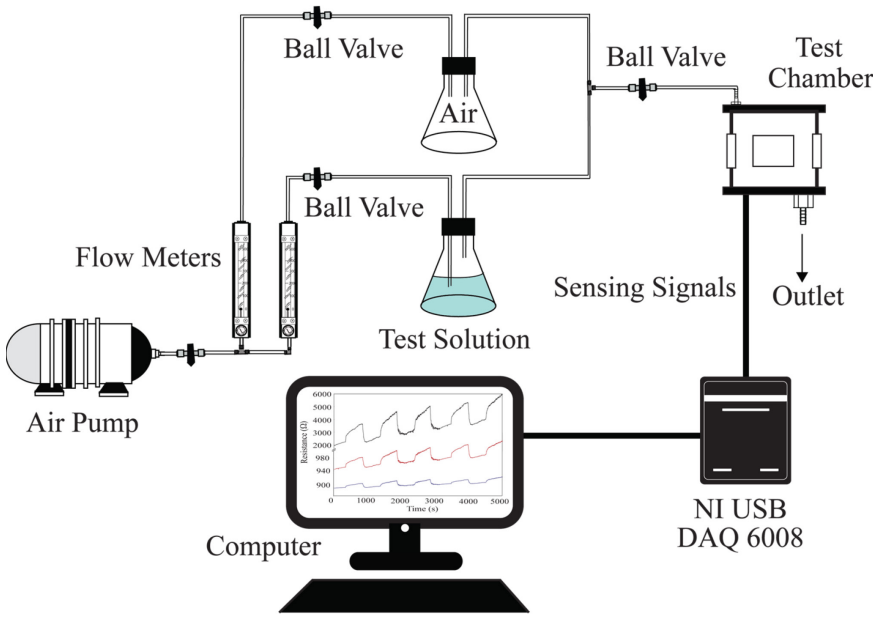

Fig. 4 Schematic illustration of standard flow-through system for gas sensing measurements at room temperature.

After the acid treatment process, the formation of COOH groups onto the hybridized sp^2 networks of MWCNTs was claimed as the main cause for the selectivity to NH_3 at room temperature [10]. In case of purified helical carbon coils, the presence of COOH groups on their sp^2 networks was also found to be more sensitive to NH_3. The sensing mechanism of helically coiled carbon gas sensor has been discussed based on the reducing reaction process between NH_3 and

chemisorbed oxygen on the surface of purified carbon coils. When the coils adsorb NH_3 molecules on their surfaces, the NH_3 molecules will donate electrons to the oxygen groups on the coiled surface since the concentration of oxygen species is very high after the purification. The depletion of holes from the valence band for helical carbon coils leads to the increase of the sensor resistance when NH_3 molecules are adsorbed on the carbon coiled sidewalls.

For the carbon-based gas sensor, the sensitivity was reported to depend on the size of carbon structures. In case of small carbon structure such as SWCNTs (0.6-3 nm in diameter), the working range of baseline resistance for the SWCNT-based gas sensor in response to NH_3 was found to be in the range of 20-200 Ω [4]. For the larger size of MWCNTs and carbon nanofibers (50-200 nm in diameter), it was also reported to be in the order of kΩ (≥1 kΩ) [4,11]. The baseline resistance of carbon-based gas sensor can be modulated by the filling of oxygen vacancies onto the carbon sidewalls using a solvent dispersion [12]. Again, it can be seen in Fig. 5(a) that the baseline resistances for the helically coiled carbon gas sensors obtained from ethanol, DMSO and DI water are found to be 0.80, 0.95, and 1.99 kΩ, respectively. Therefore, the coils (60-160 nm in coiled diameter) dispersed in DI water are performed to show the highest selectivity and sensitivity to NH_3 because the baseline resistance of gas sensor falls within the working range (i.e. kΩ) unlike in the case of ethanol and DMSO. It is believed that the oxygen vacancies on the coiled surface obtained from the dispersion in DI water lead to the increase in resistance and higher sensor signals to target gas. The response time of our gas sensors is defined as the time to reach 90% of the maximum change for total resistance. In case of purified coils exposed to NH_3, it is estimated to be ~8 min. However, the non-recovery of all fabricated sensors was further observed because of the highly strong bonding between NH_3 molecules and oxygen containing groups on helical carbon coiled surface at room temperature.

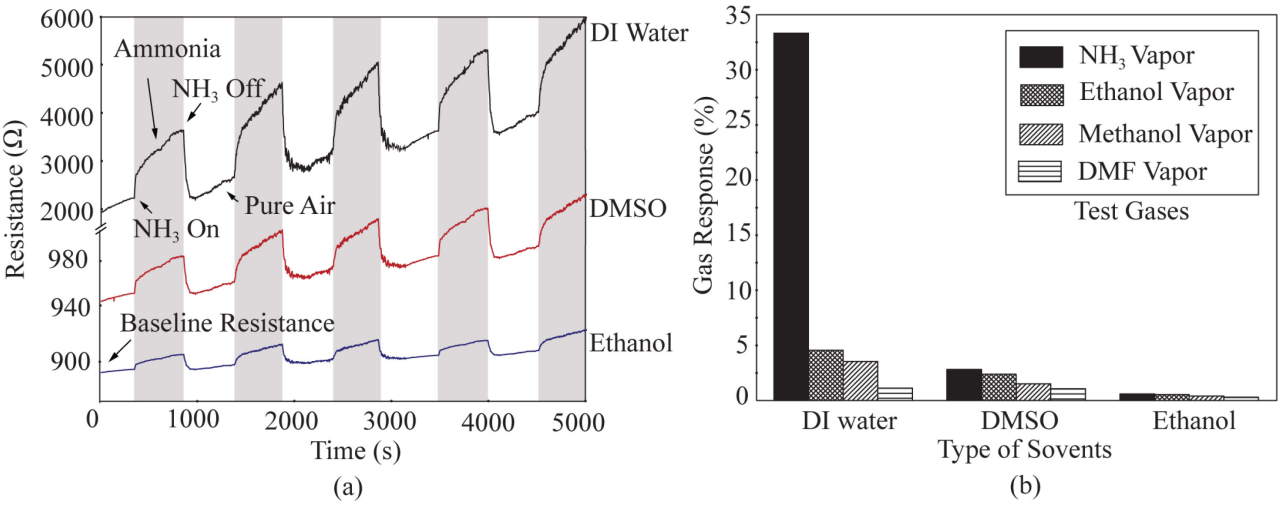

Fig. 5 (a) NH_3 sensing behavior and (b) gas response of fabricated as sensor at room temperature.

Summary

In this work, helical carbon coils were successfully grown on Inconel films by the injections of C_2H_2 and SF_6 during thermal CVD process. The mean coiled diameters and coiled pitches are found to be 114 ± 16 nm and 93 ± 23 nm, respectively. The coils were purified using oxidation and acid treatments. The purified coils were used to fabricate flexible gas sensors for testing the sensitivity and selectivity to NH_3 and VOCs at room temperature. The sensor exhibits high sensing performance to NH_3 with a concentration of 1000 ppm. The formation of COOH groups onto the sp^2 networks for purified coils leads to considerable enhancement of NH_3 adsorption. The working range of baseline resistance for helically coiled carbon gas sensors in response to NH_3 is found to be in the order of kΩ. Moreover, the gas response of all fabricated gas sensors obviously increases when using DI water as the solvent. Finally, this finding may lead to a good selection of highly sensitive gas sensing materials applied to printable, flexible and wearable electronic gas detections.

Acknowledgements

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